A Silicon-Containing Polytriazole Resin with Long Storage Time

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Abstract— *A novel silicon-containing polytriazole resin with long storage time was prepared from DMSEPE (internal alkynes) and BPDBA (diazide) through thermal 1, 3-dipolar cycloaddition polymerization. The resin was soluble in common solvents such as tetrahydrofuran (THF), chloroform and so on. It was easy to be molded due to the low viscosity of the resin at low temperature. The value of apparent activation energy (E_a) of the curing reaction obtained by Kissinger's method was 105.0 kJ/mol. The non-isothermal DSC tests showed that this kind of polytriazole resin could be cured at around 100 ^oC. The glass transition temperature and the temperature of 5% weight loss of the cured resin were 289 and 350 ^oC, respectively. The storage time of this polytriazole resin was more than 40 days at 35 ^oC.*

Keywords— ***polytriazole resin, 1,3-dipolar cycloaddition polymerization, internal alkynes, diazide.***

I. INTRODUCTION

Cyclo addition reactions have been employed in polymer synthesis since the mid-1960s, these reactions can be used for linear, hyper branched and dendritic architectures that feature special heterocyclic or strained multicyclic units within the polymer backbone. Cyclo addition reactions are very efficient, highly selective and allow even stereo selectivity. Polymers obtained via cycloaddition chemistries have found use in several advanced applications such as liquid crystal displays, semiconductors, electrolyte membranes, and high-temperature performance polymers.[1,2]

Micheal discovered 1,3-dipolar cycloaddition of phenyl azide and dimethyl acelene dicarboxylate in 1893. As one of a classical cycloaddition reactions, this reaction formed a mixture of 1,4-and 1,5-disubstitued1,2,3-triazole.[3] Since then, the 1,3-dipolar cycloaddition between alkyne and azide groups has become an important rule to synthesize 1,2,3-triazole products and their derivatives.[4,5] In 1960s, the Johson groups synthesized a series of linear polytriazoles (PTAs) from self-polymerizations of monomers containing both azide and alkyne groups. The obtained PTAs were thermally stable but hardly processable polymers due to the rigid molecular chains, [6,7] thus the PTAs did not cause enough attentions for scientists.

Until 2002, the Sharpless and Meldal groups independently discovered the copper-catalyzed azide-alkyne cycloaddition (CuAAC reaction), which effectively formed 1,4-disubstitued 1,2,3-triazole.[8,9] CuAAC reaction has remarkable features such as high yield, mild reaction conditions, functional tolerance and simple product isolation. These appealing features enable CuAAC reaction to be a powerful synthetic tool and applied in diverse areas. In particular, it gains popularity in materials science. [10-16]

Our laboratory has engaged in developing a series of novel polytriazole resins with good processing property and thermal stability by 1,3-dipolar cycloaddition of azide with alkyne groups since 2002. These resins can be cured at 80℃ without Cu (I).[17-21] After that, a series of novel polytriazoleimides (PTAIs) containing 1,2,3-triazole has been reported by thermal or chemical imidization methods. These PTAIs have good mechanical properties and chemical stabilities, and are expected to be used as resins for advanced composites.[22,23]Although these resins have good properties, the storage time of these resins is short due to high reaction activity of terminal alkynes and azide, which limits their applications. Therefore, in order to meet higher requirement of performances, such as higher glass transition temperatures (T_g) and longer storage time, a silicon-containing polytriazole resin with good processing propertyis prepared and characterized.

II. EXPERIMENTAL

2.1 Raw materials

Magnesium powder (AR), acetic acid (AR), tetrahydrofuran (AR), bromoethane (AR), toluene (AR), hydrochloric acid (AR), and magnesium sulfateanhydrous (AR)were purchased from ShanghaiNo.1 Reagent Company(Shanghai, China). Dimethyldichlorosilane was obtained from Aladdin Reagent (Shanghai, China).Phenylacetylene was obtained from Tokyo Chemical Industry (Shanghai,China). 1,3-diethynylbenzene and 1,4-diethynylbenzene were purchased from Shanghai Record

Pharemaceuticals Co., Ltd(Shanghai,China). THF was refluxed over sodium with benzophenone and freshly distilled in nitrogen gas before use. Other chemicals were purchased and used as received without further purification.

2.2 Instrument

^{1}H-NMR and ^{29}Si-NMR spectra were recorded on a Bruker Avance 500 (500 MHz) nuclear magnetic resonance spectrometer. $CDCl_3$ was used as the solvent and chemical shifts were reported in ppm and tetramethylsilane (TMS) was used as an internal standard. Fourier transform infrared spectroscopy (FT-IR) was performed on a Nicolet 5700 and viscous sample was spread over KBr pellet. Gel permeation chromatography (GPC) was performed with a waters 1515 at 30 ^{o}C. THF was used as an eluent at a flow rate 4.0 mL/min, the result was relative to known standards of polystyrene. Differential scanning calorimeter (DSC) was performed on a Q2000 (TA) with the heating rate of 5, 10, 15, 20 ^{o}C /min. Thermogravimetric analysis (TGA) was conducted on a TGA/DSC 1 (Mettler Toledo) in nitrogen gas with the heating rate of 10 ^{o}C /min. Rheological behavior was traced on a MARS 3 (Thermo Fisher Scientific) with the heating rate of 3 ^{o}C /min, and the shear rate of 0.1 s-1. Dynamic mechanical thermal analysis (DMTA) was carried out on a DMA 1(Mettler Toledo) in the dual cantilever clamp mode in the range of temperatures from 30 to 300 ^{o}C at the frequency of 1 Hz with a programmed heating rate of5 ^{o}C /min. Gel time of the resin was determined according to ASTM D3552. The test temperature was 80 ^{o}C.

2.3 Synthesis of poly (dimethylsilylene-ethynylenephenyleneethynylene) terminated with phenylacetylene (DMSEPE: internal alkynes)

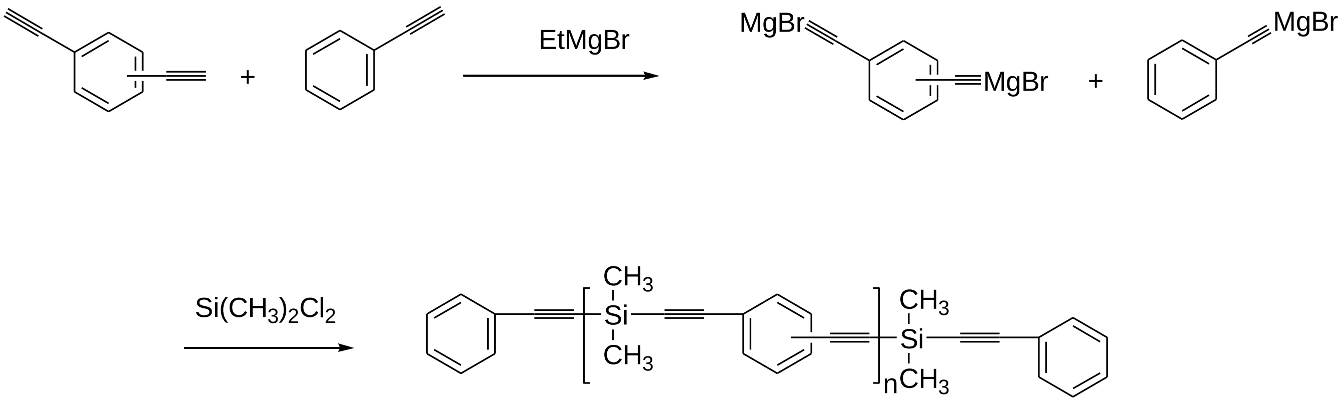

FIGURE 1: THE SYNTHESIS ROUTE OF DMSEPE

Magnesium powder (4.88 g, 0.20 mol) and dry THF (30 mL) were added to a round-bottom flask with a mechanical stirring and a condenser pipe. Bromoethane (17.10 g, 0.16 mol) dissolved in dry THF (30 mL) was added drop wise over 1 hour to the magnesium suspension under room temperature. Then, the solution was refluxed for 1 hour, after that phenylacetylene(5.60 g, 0.055mol) and diethynylbenzene (1,3-/1,4- molar ratio was about 65/35) (5.67 g, 0.045 mol) dissolved in dry THF (40 mL) were added slowly over 1 hour under room temperature, the solution was refluxed for 2 hours. After that, dimethyldichlorosilane(9.50 g, 0.074mol) dissolved in dry THF (30 mL) was added in three portions at room temperature, then the solution was refluxed for 3 hours. Thereafter, THF was distilled with anevaporator and the reaction was quenched with acetic acid (50 mL) and 10 wt% dilute hydrochloricacid (50 mL) in an ice bath. The solution was extracted with100 mL toluene and the organic phase was washed with deionized water until the washed water was neutral. Then toluene was distilled off and the brown viscous product was obtained. The yield was 70%.FT-IR: 2156 cm^{-1} -CΞC-, 1253 cm^{-1} (-Si-CH_3-); ^{1}H-NMR ($CDCl_3$, ppm): 7.21-7.51 (Ar-H), 0.37 (-$Si(CH_3)_2$-); ^{29}Si-NMR ($CDCl_3$, ppm): -40 (-$Si(CH_3)_2$-). GPC (polystyrene standard): Mn=1707, polydispersity=2.32.

4, 4'-biphenyl dibenzylazide (BPDBA: diazide) was prepared following the reported procedures [17].

2.4 Synthesis of silicon-containing polytriazole resin

The monomers, DMSEPA and BPDBA, well-proportioned with the functional group molar ratio of 1.1:1.0-1.5:1.0 ([alkyne]:[azide]) in THF (50 wt%), were mixed in a round-bottom flask with a magnetic stirring, a cooling condenser and a thermometer. The mixture was heated to 65 ^{o}C, and stirred for 2 hours. After evaporating the solvent, a transparent and viscous liquid silicon-containing polytriazole resin was achieved.

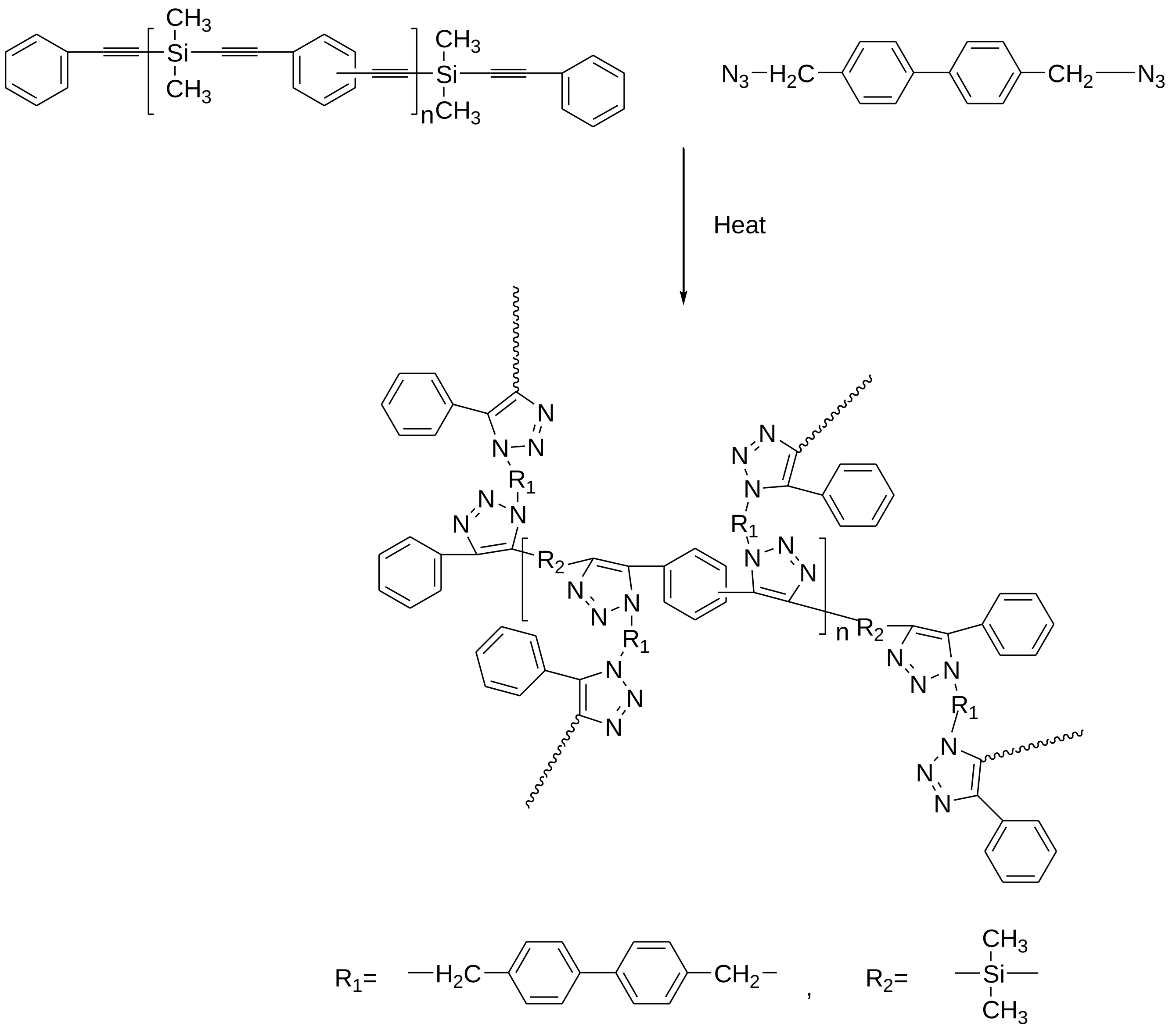

FIGURE 2: POLYMERIZATION OF DMSEPA AND BPDBA

III. RESULTS AND DISCUSSION

3.1 Solubility

The solubility of the silicon-containing polytriazole resin is shown in Table 1. The resin can be dissolved in common solvents, such as tetrahydrofuran, chloroform, etc.

TABLE 1
SOLUBILITY OF SILICON-CONTAINING POLYTRIAZOLE RESIN IN COMMON ORGANIC SOLVENTS

Solvent	Solubility		Solvent	Solubility
Tetrahydrofuran	+		Dimethylformamide	+
Dimethyl Sulphoxide	+		Chloroform	+
Hexane	−		Toluene	+
Acetone	−		Ethanol	−

+: soluble; −: insoluble

3.2 Rheological property

The silicon-containing polytriazole resin from DMSEPA and BPDBA is a transparent brown homogenous viscous liquid at low temperature. Rheological property of this resin is measured by a rheometer. The relationship between the viscosity and the temperature is shown in Fig. 3 for the resin ([alkyne]:[azide]=1.1:1.0). The result indicates that the viscosity of the resin is low as the temperature range is between 40 ^{o}C and 110 ^{o}C (about 500 mPa·s). The low viscosity of the resin is suitable for materials fabrications. On the other hand, the viscosity of the resin starts to dramatically increase over 110 ^{o}C, indicating that the 1,3-dipolar cycloaddition polymerization can take place over 110 ^{o}C and the initial curing temperature should be below 110 ^{o}C.

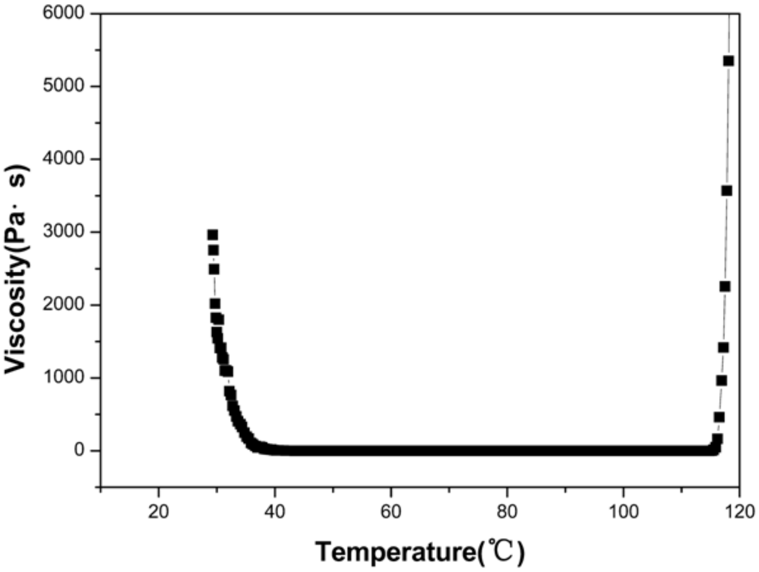

FIGURE 3 THE RELATIONSHIP BETWEEN THE VISCOSITY AND TEMPERATURE FOR SILICON-CONTAINING POLYTRIAZOLERESIN ([ALKYNE]:[AZIDE]=1.1:1.0)

3.3 Curing behavior

1,3-dipolar cycloaddition reaction of DMSEPA and BPDBA was traced by DSC ([alkyne]:[azide]=1.1:1.0). As shown in Fig. 4, the exothermic peaks are observed in the temperature ranging from 100 to 200 ℃, which are ascribed to the 1,3-dipolar cycloaddition. The results are summarized in Table 2.

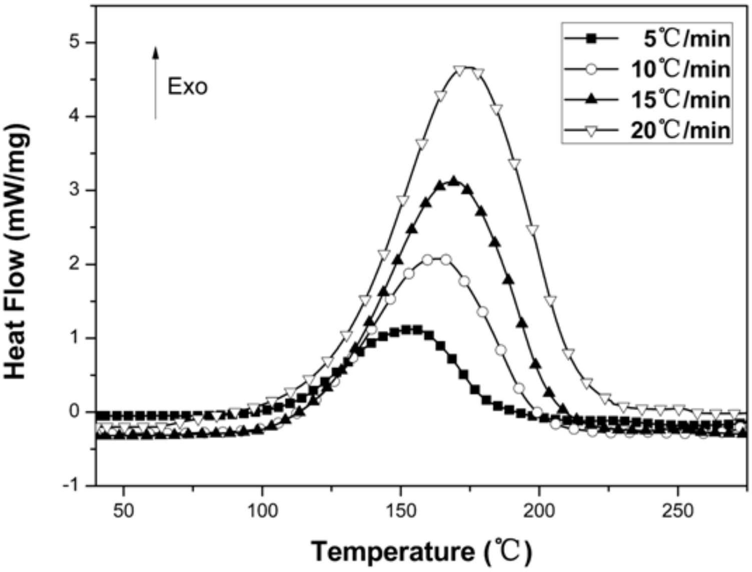

FIGURE 4: DSC THERMOGRAMS OF DMSEPA AND BPDBA AT DIFFERENT HEATING HATES

TABLE 2
DSC RESULTS OF THE SILICON-CONTAINING POLYTRIAZOLE RESIN

β(K/min)	T_p(K)	$1/T_p(10^3)$	ln (β/T_p^2)	ΔH(J/g)
5	427.6	2.339	-10.51	714.1
10	437.8	2.284	-9.86	741.6
15	441.4	2.266	-9.47	721.7
20	446.8	2.238	-9.21	752.0

Kissinger's method is usually used to calculate the activation energy as the following equation described [24].

$$\ln(\frac{\beta}{T_P{}^2}) = \ln(\frac{AR}{E}) - \frac{E_\alpha}{RT_P} \tag{1}$$

In equation 1, where R is the universal gas constant, A is the pre-exponential factor, β is the heating rate, α is the extent of conversion, T_p is the peak temperature, E_a is the apparent activation energy. A plot of ln (β/T_p^2) against $1/T_p$ yields values for E_a/R from the slope of the linear fit.

The plot of ln (β/T_p^2) against $1/T_p$by Kissinger's method is drawn in Fig. 5. The apparent activation energy (E_a) can be calculated from the slop of the line and E_a values obtained is 105.0 kJ/mol. The value is much higher than that of the reaction from terminal alkynes and diazide previous reported by our laboratory (80.7 kJ/mol). The reason of the higher apparent activation energy for the reaction of DMSEPA and BPDBA is due to the larger steric hindrance of internal alkynes, thus higher temperature is needed to complete the cycloaddition polymerization.

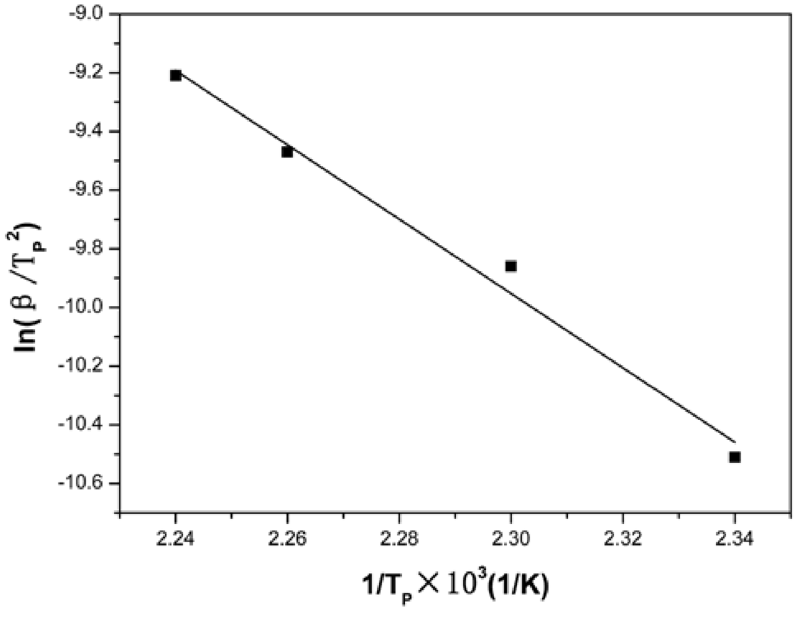

FIGURE 5: KISSINGER'S ANALYSIS FOR INTERNAL ALKYNESANDDIAZIDE

As shown in Fig. 4, the exothermic heat of the reaction is about 700 J/g. The result shows that the cycloaddition polymerization is a highly exothermic reaction. Thereby, the curing process should be strictly controlled to avoid the violent polymerization. For this reason, the initial curing temperature of the resin is implemented at 100°C, which is much higher than that of the previously reported polytriazole resin (70°C).Then the curing process is as follows: 100°C/2h, 120°C/2h,140°C/4h, 180 °C/2h. After the process, there is not exothermal peak for the cured resin as shown in Fig. 6, which means the 1,3-dipolar cycloaddition is complete.

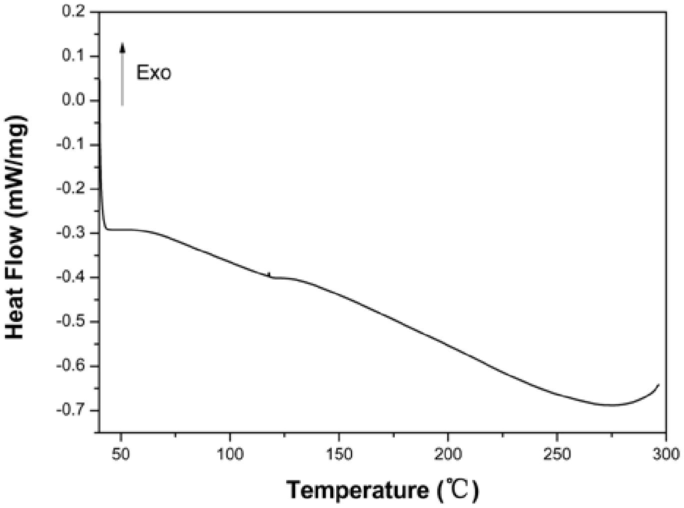

FIGURE 6 DSC THERMOGRAM OF CURED SILICON-CONTAINING POLYTRIAZOLE RESIN (HEATING RATE: 10 K/MIN)

3.4 Properties of the cured polytriazole resin

3.4.1 Glass transition temperature (T_g)

Dynamic mechanical thermal analysis (DMTA) was used to measure T_g of the cured polytriazole resin for different functional group molar ratios ([alkyne]:[azide]=1.5:1.0-1.1:1.0). As shown in Fig.7, T_g of the thermoset move to higher temperatures as the ratio is increasingly close to 1.0:1.0. The value achieved up to 289 ^{o}C after curing at 180^{o}C for 2 hours when the ratio is 1.1:1.0([alkyne]:[azide]). The material described here has a T_g that is up to 100^{o}C higher than the curing temperature. Other research groups found the same phenomenon for the alkyne-azideclycoaddition reaction. It has to be pointed out that the total enthalpy of the reaction is over 200 kJ/mol, the value is much higher than those observed for other chain growth polymerizations such as epoxies, cyanate-esters or bismaleimides (100-110 kJ/mol)[25,26]. The highly exothermic nature of the alkyne-azide cycloaddition reaction may induce increased local motion of polymer chains in the vicinity of the matrix, which forms more cross linked network structure even at low curing temperatures. The large difference between curing temperature and T_g justifies the application of such reaction in low temperature curing composites.

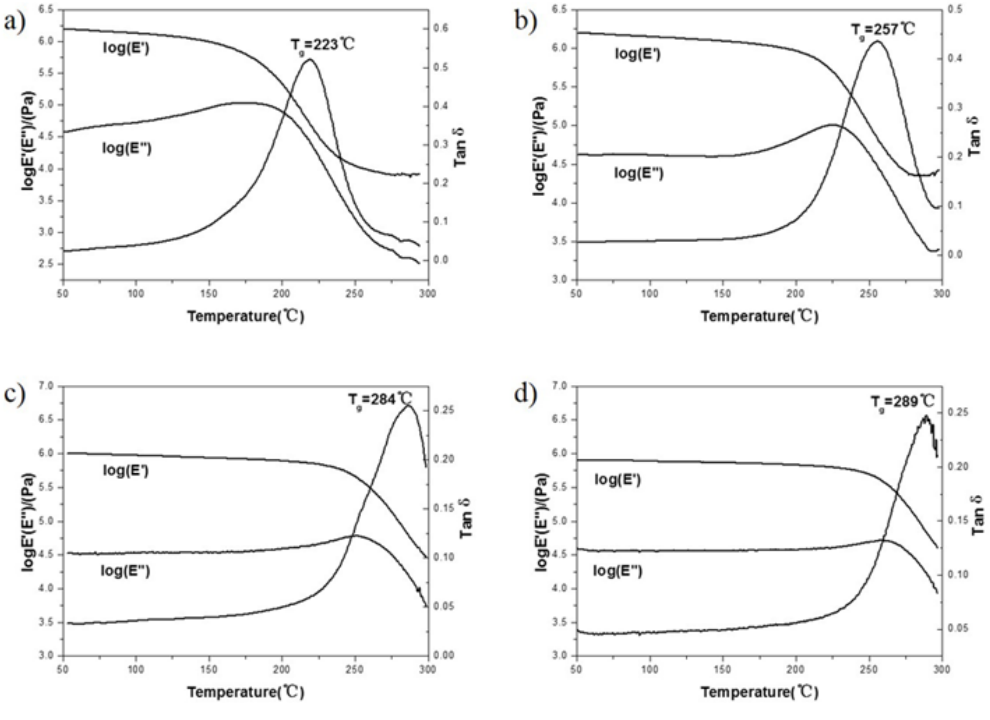

FIGURE 7 DMTA CURES OF CURED SILICON-CONTAINING POLYTRIAZOLE RESIN FROM DIFFERENT [ALKYNE]/[AZIDE] RATIOS. (A) 1.5:1.0, (B) 1.3:1.0, (C) 1.2:1.0, (D) 1.1:1.0

3.4.2 Thermal stability

The thermal stability of the cured silicon-containing polytriazole resin was measured with TGA for different functional group molar ratios ([alkyne]:[azide]=1.5:1.0-1.1:1.0). As shown in Fig. 8, the temperatures of 5% weight loss (T_{d5}) of the cured thermoset achieved to 350 °C. The result shows that the cured resin has good thermal stability, which is higher than that of common epoxy resins and equivalent to that of modified bismaleimide resins.

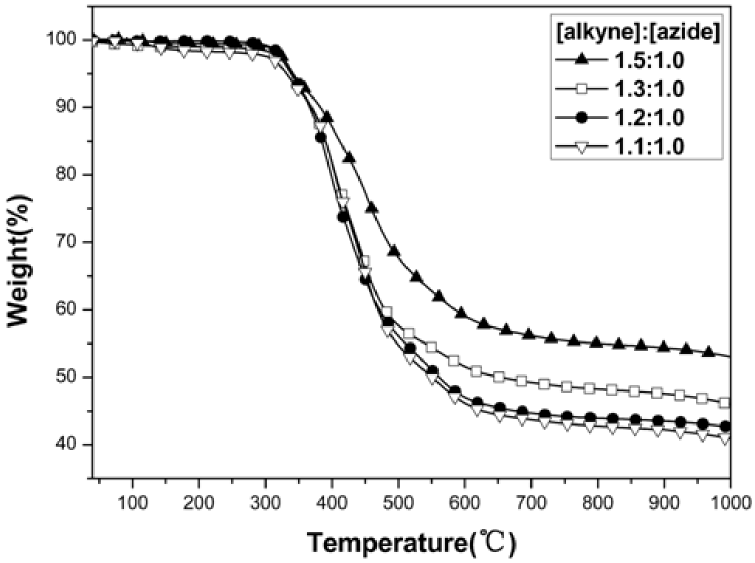

FIGURE 8: TGA CURVES OF THE CURED SILICON-CONTAINING POLYTRIAZOLE RESIN IN NITROGEN GAS

3.4.3 Storage time

The transparent and viscous liquid silicon-containing polytriazole resin was soluble in THF (50 wt%). After that, the solution was stored at 35 °C. The gel time was determined at regular intervals after eliminating the solvent, and the result was listed in Table 3.

TABLE 3
GEL TIME OF THE SILICON-CONTAINING POLYTRIAZOLE RESIN WITH VARIOUS STORAGE TIME AT 35°C

Storage time (day)	0	4	8	12	16	20	30	40
Gel time (minute)	180.3 ±0.7	168.2 ±0.9	154.2 ±0.4	138.1 ±0.6	120.8 ±0.6	110.3 ±0.8	105.4 ±0.7	97.5 ±0.8

Test temperature: 80°C

The gel time of this resin is more than 90 minutes after storing for 40 days at 35°C. The previous polytriazole resin from terminal alkyne and diazideprepared in our lab could only be stored for 7 days at 35°C (gel formation), due to the higher activity of terminal alkyne with azide. In comparison with terminal alkyne, the reaction of internal alkyne with azide should overcome higher activation energy because of larger steric hindranceas mentioned previously [27]. Therefore, this novel silicon-containing polytriazole resin from DMSEPA and BPDBA has much longer storage time. This new type of polytriazolereisn could be used as advanced composite resin matrix for carbon-fiber reinforced prepregmaterial of large devices.

IV. CONCLUSIONS

A novel silicon-containing polytriazole resin was obtained by the 1,3-dipolar cycloaddition polymerization between internal alkynes and diazide. The viscosity of the resin was 500 mPa·sand the resin had good solubility in common solvents. DSC and rheological studies showed that the curing reaction of this kind of polytriazole resin could occur at around 100°C. The apparent activation energy E_a obtained by non-isothermal DSC analysis was 105.0 kJ/mol. The T_g and the T_{d5} of the cured thermoset were 289 and 350^{o}C when the functional group molar ratio was 1.1:1.0 ([alkyne]:[azide]),respectively. The storage time of this polytriazole resin was extended to more than 40 days at 35 ^{o}C. The developed silicon-containing polytrizaole resin is potential for low-temperature molding and high-temperature use composite applications.

ACKNOWLEDGEMENTS

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