

Synthesis, characterization, and non-isothermal curing kinetics of two silicon-containing arylacetylenic monomers

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Received: 15 October 2010 / Accepted: 20 January 2011 / Published online: 6 February 2011
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Abstract Vinyltri(phenylethynyl)silane ((ph-C≡C)₃-Si-C=CH₂; VTPES) and phenyltri(phenylethynyl)silane ((ph-C≡C)₃-Si-ph; PTPES) were synthesized by Grignard reaction. Their molecular structures were characterized by means of ¹H NMR, ¹³C NMR, ²⁹Si NMR, and FT-IR spectroscopy. Their nonisothermal thermal curing processes were characterized by DSC, and the corresponding kinetic data, for example activation energy (*E*), pre-exponential factor (*A*), and the order of the reaction (*n*), were obtained by the Kissinger method. The results showed that the melting points of VTPES and PTPES were 84 and 116 °C, respectively. Their curing reaction rates were consistent with first-order kinetic equations. VTPES monomer had a lower activation energy and curing temperature as a result of coordination between reactive groups.

Keywords Vinyltri(phenylethynyl)silane · Phenyltri(phenylethynyl)silane · Grignard reaction · Structural characterization · Curing kinetics

Introduction

In 1968, Luneva first reported the synthesis of diethynyldiphenylsilane in a nitrogen atmosphere [1]. This kind of silicon-containing arylacetylenic monomer can be cured thermally without formation of volatiles. The polymers' high-temperature properties and high char yield resulted in their rapid development, because of their

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potential applications in biomaterials, optoelectronics, and ceramics precursors, etc. [2–8].

Synthesis of different alkynylsilane monomers has been reported in recent years [9, 10]. The main synthetic routes were dehydrogenation coupling reactions between hydrosilanes and alkynic compounds using metal compounds as catalysts. $\text{H}_2\text{PtCl}_6/\text{LiI}$, I_2 , $\text{I}_r\text{H}_2(\text{SiEt}_3)(\text{COD})(\text{AsPh}_3)$, $[\text{IrH}(\text{H}_2\text{O})(\text{bp})\text{L}_2]\text{SbF}_6$, and RhClL_3 ($\text{L} = \text{PPh}$, $\text{bp} = 7,8\text{-benzoquinolinato}$) have been used as catalysts [11]. In these cases, dehydrogenating cross-coupling reactions were found to accompany the significant hydrosilylation reactions to produce the corresponding alkenylsilanes, and dehydrocoupling in low yield was also found to accompany hydrosilylation and hydrogen-transfer reactions [12, 13]. Calas and Bourgeois obtained alkynylsilane ($n\text{-Bu-C}\equiv\text{C-SiEt}_3$) from Et_3SiH and 1-hexyne using Na or NaH as a catalyst [11]. Liu and Harrod reported that the CuCl/amine catalyst led to highly selective dehydrogenative cross-coupling reactions of hydrosilanes with alkynes [14]. Itoh et al. also found that solid bases (MgO) and metal hydrides (LiAlH_4 , NaAlH_4 , LiBH_4 , and $\text{LiAlH}(\text{Ot-Bu})_3$) catalyze the same selective dehydrogenating cross-coupling reactions [15]. However, these synthetic methods were carried out under moisture-free and oxygen-free conditions, the catalysts and raw materials (e.g. LiAlH_4 and phenylsilane) used were dangerous, and the products were rather expensive. Further, the hydrosilanes were mainly synthesized from chlorosilanes and lithium aluminum hydride in anhydrous diethyl ether or dioxane [16–18]. As a result, those methods were mainly limited to laboratory preparations, and the synthesized monomers were only characterized in the structures. However, the Grignard reaction is a common reaction method and the reaction conditions are mild [19]. Methyl-di(phenylethynyl)silane and $[-\text{SiH}(\text{R})-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{C}\equiv\text{C}-]$ ($\text{R} = \text{Ph}$, CH_3 , H) were synthesized by use of the Grignard reaction and yields were better than 75% [20, 21], but the synthesis of vinyltri(phenylethynyl)silane and phenyltri(phenylethynyl)silane by use of Grignard reactions has not been reported.

The main objectives in this work were to prepare vinyltri(phenylethynyl)silane and phenyltri(phenylethynyl)silane monomers by the Grignard reaction, using the relatively inexpensive vinyltrichlorosilane or phenyltrichlorosilane as raw materials, and to characterize the monomers' structures by use of FT-IR and NMR, and the non-isothermal curing process by use of DSC.

Experimental

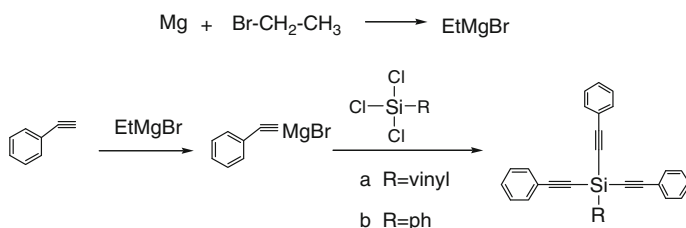
Materials and methods

Phenylacetylene was purchased from Hanwang Reagent Company, China. Vinyltrichlorosilane and phenyltrichlorosilane were purchased from Huarong Chemical Materials Company, China. Solvents were bought from Shanghai Reagent Company, and all chemicals and solvents were distilled or dried if necessary according to standard procedures.

Preparation of vinyltriphenylethynylsilane (VTPES) (monomer **a**)

An organic magnesium Grignard reagent was prepared as follows: Magnesium turnings (6.72 g, 0.28 mol) were introduced into a 500-mL four-necked flask and the atmosphere of the flask was replaced with dry nitrogen gas. THF (80 mL) which had been dried over sodium was subjected to simple distillation and introduced into the flask. A small piece of iodine was then added and the mixture was stirred to activate the magnesium. To the activated magnesium was added dropwise a solution of 20 mL (0.268 mol) ethyl bromide in THF (100 mL) at room temperature over approximately 1 h. The resulting mixture was reacted while being heated under reflux for 3 h to produce ethylmagnesium bromide. The reaction system was then added dropwise to a solution of 29 mL (0.264 mol) phenylacetylene in THF (100 mL) in a ice-bath over 2 h, with stirring, and the reaction was continued for an additional 3 h while being heated under reflux to produce the intended phenylethynylene Grignard reagent (0.264 mol).

Monomer **a** was then prepared by the following procedure. The reaction was performed subsequent to the foregoing preparation of the phenylethynylene reagent. A solution of 11 mL (0.086 mol) vinyltrichlorosilane in THF (100 mL) was added dropwise to the flask in a ice-bath over 1 h, with stirring, and the reaction system was further reacted for 3 h while being heated under reflux, following by the color variation from green to yellow. The reaction system was then post-treated as follows. An aqueous solution of hydrochloric acid (1 mol/L, 300 mL) was placed in another 500-mL flask and the reaction solution prepared in the 500-mL flask was transferred to a dropping funnel. The aqueous hydrochloric acid solution was gently stirred while the reaction solution was slowly added dropwise by use of the dropping funnel (over 30 min) in a ice-bath. Benzene (50 mL) was added to the reaction solution and the resulting oil phase was separated by use of a separatory funnel, washed with distilled water until no acid was present, then dried by adding anhydrous calcium chloride while standing overnight. The solution was filtered through a ceramic filter to remove the dehydrating agent. The solvent was removed from the solution by distillation under vacuum, eventually giving a viscous, oily, crude product. The crude product was repeatedly recrystallized in methanol to cause precipitation. The resulting precipitates were isolated by filtration and dried to give pin-like crystals (approx. 23 g, 74.7% yield) of the intended monomer **a** (Scheme 1).



Scheme 1 Synthetic routes to the two monomers

Preparation of phenyltriphenylethynylsilane (PTPES) (monomer **b**)

The same procedures used for preparation of monomer **a** were repeated, except that phenyltrichlorosilane was substituted for vinyltrichlorosilane to give columnar crystals of monomer **b** (70% yield).

Characterization

FT-IR spectroscopic characterization was carried out with a Nicolet 8700 FT-IR spectrometer and use of potassium bromide (KBr) pellets. ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on an Avance AV-400 superconducting Fourier digital NMR spectrometer (400 MHz for ^1H NMR, 100.61 MHz for ^{13}C NMR and 79.49 MHz for ^{29}Si NMR). The chemical shifts were recorded relative to tetramethylsilane (δ , 0.0 ppm) for ^1H NMR and ^{29}Si NMR, and CDCl_3 (δ , 77.7 ppm) for ^{13}C NMR. The differential scanning calorimetry (DSC) study was performed with a Mettler-Toledo-DSC 821e/400 under nitrogen atmosphere.

Results and discussion

Structural characterization of the monomers

Typical proton NMR spectra of the two monomers are shown in Fig. 1. The aromatic hydrogen resonated at 7.35–7.59 ppm and silicon vinyl protons resonated at 6.33 ppm. In a precise study of NMR peak integration, vinyl protons (m, 3H, $\text{CH}=\text{CH}_2$), aromatic hydrogen bonded to ethynyl (m, 6H, $\text{PhH}-\text{C}\equiv\text{C}$), and aromatic hydrogen (m, 9H, PhH) were in the ratio 3:6:9 for VTPES (Fig. 1a). For PTPES, aromatic hydrogen bonded to silicon (m, 2H, $\text{PhH}-\text{Si}$), aromatic hydrogen (m, 3H, $\text{PhH}-\text{Si}$), aromatic hydrogen bonded to ethynyl (m, 6H, $\text{PhH}-\text{C}\equiv\text{C}$), and aromatic hydrogen (m, 9H, $\text{PhH}-\text{C}\equiv\text{C}$) were in the ratio 2:3:6:9 (Fig. 1b). These results were in agreement with the structures of the silicon-containing arylacetylenic monomers [20–23].

The carbon spectra of the two monomers, with band assignments are shown in Fig. 2. The acetylenic carbons appeared as a pair of resonances at 86 and 107 ppm as they were bonded to the silicon and phenyl units of the two monomers. The phenyl carbon bonded to $\text{C}\equiv\text{C}$ and the side-chain phenyl carbon bonded to Si were observed at 128–134 ppm. For VTPES (Fig. 2a), 137 ppm corresponded to carbon attached to $\text{C}=\text{C}$. The aromatic carbons bonded to $\text{C}\equiv\text{C}$ and vinyl carbons bonded to Si were similar and difficult to separate between 128 and 134 ppm, because of similar chemical environments. Accurate chemical shift information will be investigated in the future.

^{29}Si NMR spectra of two monomers are shown in Fig. 3. The two signal peaks assigned to the silicon were observed at -71.34 ppm (VTPES) (Fig. 3a) and -69.15 ppm (PTPES) (Fig. 3b) because of the different chemical environments [18]. On the basis of the ^1H NMR, ^{13}C NMR and ^{29}Si NMR spectra we can see that

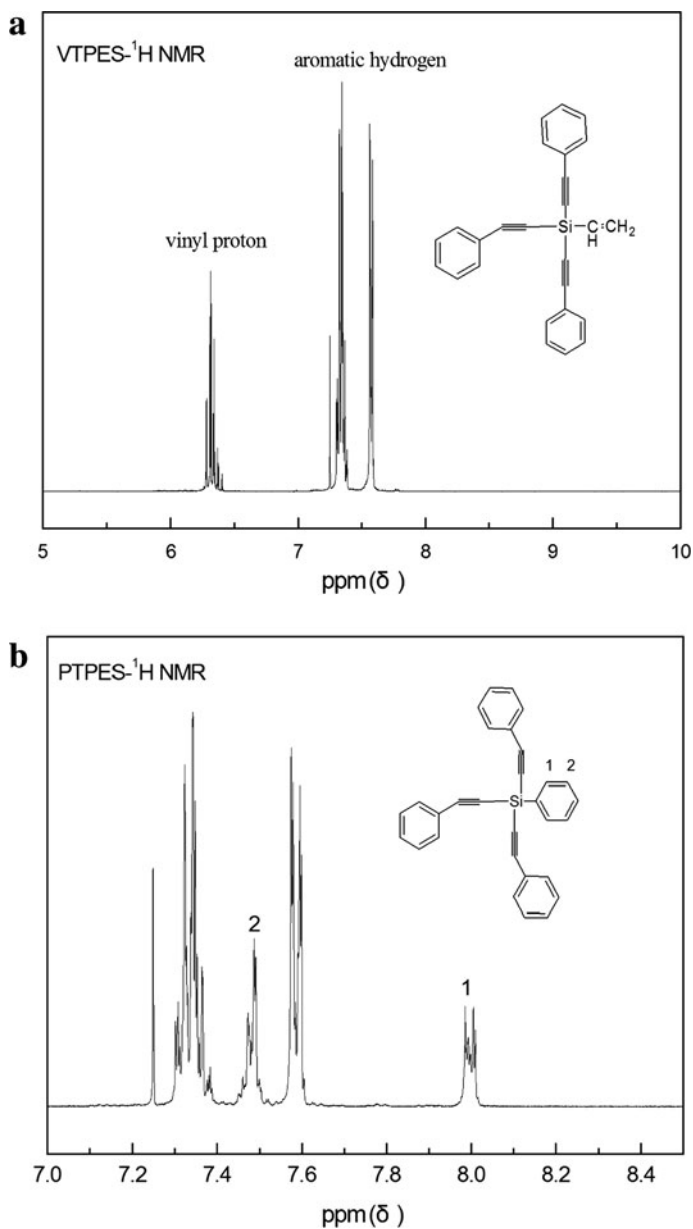


Fig. 1 ^1H NMR spectra of VTPES (a) and PTPES (b)

the chemical shift of phenylethynyl bonded to Si has not been affected dramatically by vinyl and phenyl, probably because of small steric and inductive effects in the silicon-containing monomers [22].

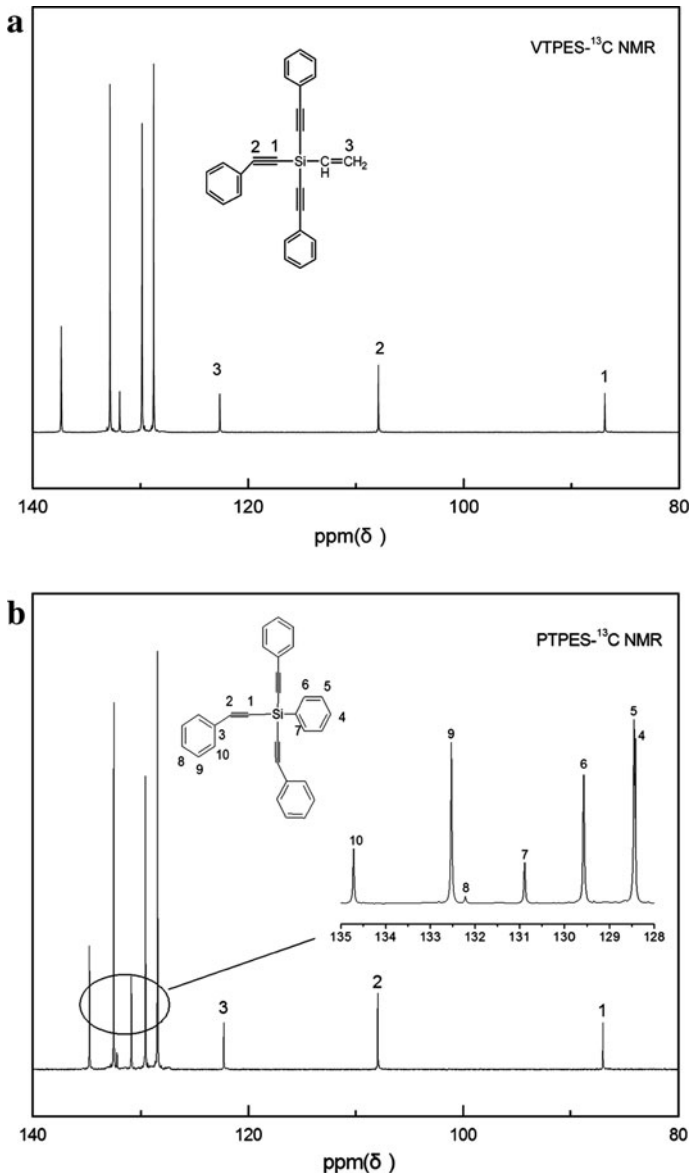


Fig. 2 ^{13}C NMR spectra of VTPES (a) and PTPES (b)

Non-isothermal curing kinetics of the two monomers

Cure reactivity of the two monomers

The heat curing behavior of VTPES and PTPES was examined by DSC (Fig. 4). The monomers gave distinct endothermic peaks at 84 and 116 °C corresponding to

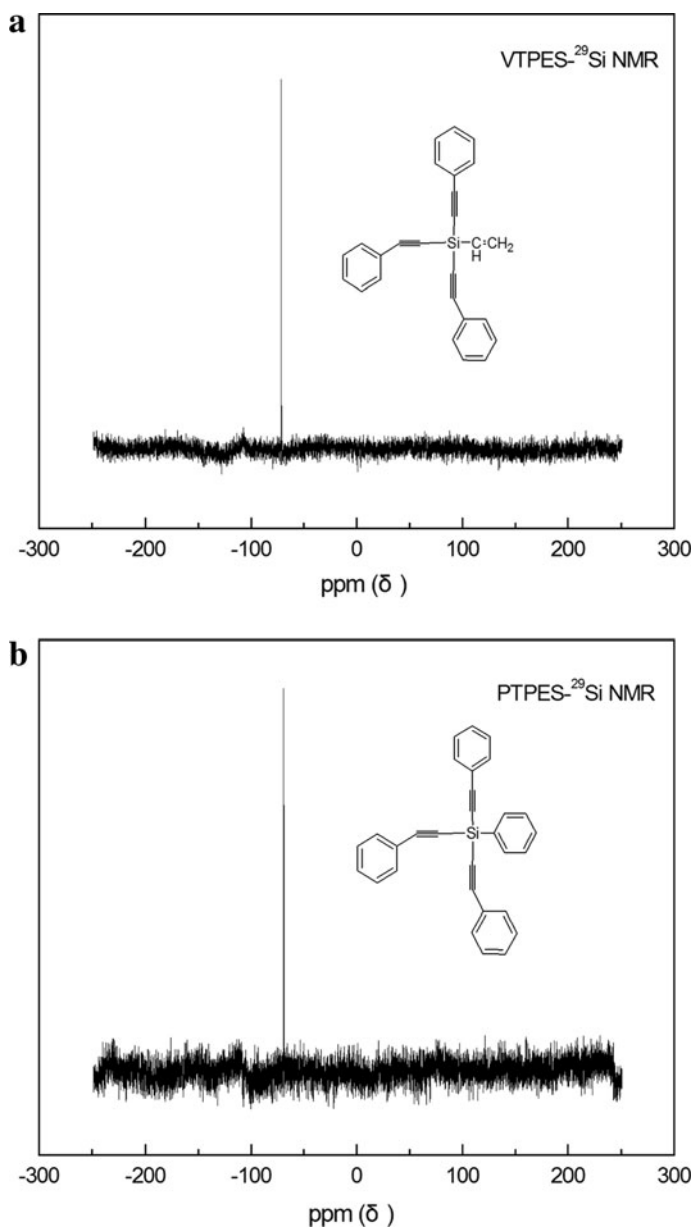


Fig. 3 ²⁹Si NMR spectra of VTPES (a) and PTPES (b)

their melting points. The curing temperatures of the two monomers were also shown in Table 1. It was noticed that with increasing heating rate, the curing time decreased, the peak became sharp, and the thermal curing temperature moved to the high-temperature region (Fig. 5). This is because with increasing heating rate, the

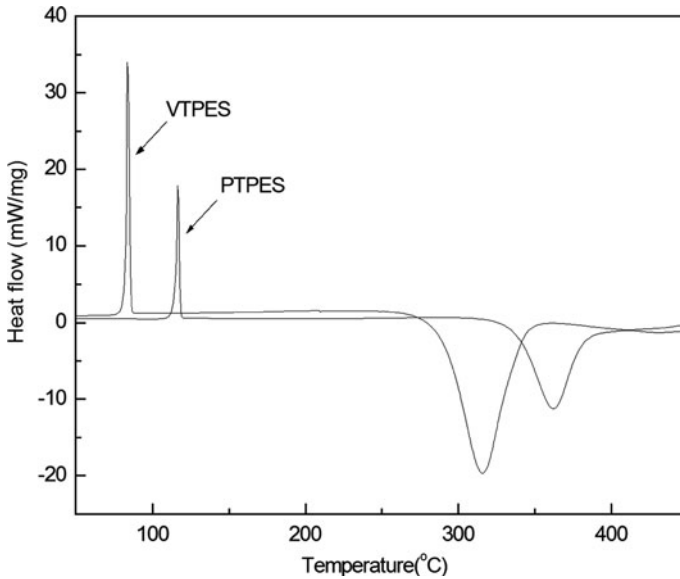


Fig. 4 DSC scans of VTPES and PTPES at a heating rate of 5 °/min

thermal effect per unit time increased, and a larger temperature difference was generated. As a result, the endothermic peak was shifted to higher temperature region. At the same time, we could see that the peak temperature of polymerization (T_p) of VTPES was 316 °C, which was 47 °C lower than that of PTPES (Table 1), and the reactive activation energy of VTPES (114.25 kJ/mol) was also 40 kJ/mol lower than that of PTPES. It is well known that thermal polymerization of phenylethylene monomers is a radical mechanism [24, 25]. Thus, it was theoretically possible to deduce that radicals formed by VTPES would be stabilized to a greater extent and more active than those formed by PTPES, and the coordination role reduced the reactive energy barrier at the unitary level between double bonds and acetylenic bonds.

Non-isothermal curing kinetics analysis of the two monomers by DSC

The generation of accurate time–temperature–degree of conversion curves is of great practical importance for establishing optimum cure schedules. Mechanistically, evaluation of the activation energy of the cure reaction could give valuable information about barriers to reaction and about mechanisms. The dynamic DSC method was used in this study to obtain kinetic data on the basis of the variation in the peak exotherm temperature (T_p) with heating rate (ϕ). A simple relationship between activation energy, heating rate, and peak exotherm temperature was based on the work of Kissinger, which had been shown to be effective in calculation of cure kinetics data [26]. The general rate equation is:

Table 1 Characteristics of non-isothermal DSC scans for the two monomers (N₂, 100 mL/min)

| Characteristic information | Monomers | |
|--|-----------------------|-----------------------|
| | VTPEs | PTPEs |
| 5 °C (min) | | |
| T_i^a | 289 | 336 |
| T_p | 316.4 | 362.9 |
| T_e | 341.9 | 381.9 |
| Δt (min) ^b | 10.6 | 9.2 |
| ΔH (kJ/mol) ^c | 346.5 | 285.6 |
| 15 °C (min) | | |
| T_i | 311 | 350 |
| T_p | 340.8 | 376.7 |
| T_e | 364 | 397.1 |
| Δt (min) | 3.5 | 3.1 |
| ΔH (kJ/mol) | 338 | 288 |
| 20 °C (min) | | |
| T_i | 315 | 362.6 |
| T_p | 347.8 | 392 |
| T_e | 369.4 | 412 |
| Δt (min) | 2.7 | 2.5 |
| ΔH (kJ/mol) | 337.2 | 297.4 |
| 25 °C (min) | | |
| T_i | 322.9 | 366.6 |
| T_p | 354.7 | 397.5 |
| T_e | 374.9 | 417.6 |
| Δt (min) | 2.1 | 2 |
| ΔH (J/g) | 393.8 | 313.3 |
| Linear-fitting equation of $\ln(\beta/T_p^2) \sim 1/T_p$ | $Y = -13.75x + 12.23$ | $Y = -18.51x + 17.75$ |
| Correlation coefficient (R) | 0.9978 | 0.9977 |
| Linear-fitting equation of $\ln\beta \sim 1/T_p$ | $Y = -14.9x + 26.96$ | $Y = -19.83x + 32.73$ |
| Correlation coefficient (R) | 0.9984 | 0.9975 |
| Activation energy, E (kJ/mol) | 114.25 | 153.89 |
| Frequency factor, A (1/s) | 2.82×10^9 | 9.42×10^{11} |
| Reaction order (n) | 0.92 | 0.93 |

^a T_i initial reaction temperature; T_p peak temperature; T_e eliminated reaction temperature

^b Δt curing time

^c ΔH enthalpy of reaction

$$\frac{da}{dt} = k(1 - \alpha)^n \quad (1)$$

$$k = A \exp(-E/RT) \quad (2)$$

Where α is the degree of cure, t the reaction time, k the rate constant defined by the Arrhenius relationship, n the order of the cure reaction, A the frequency factor, E the

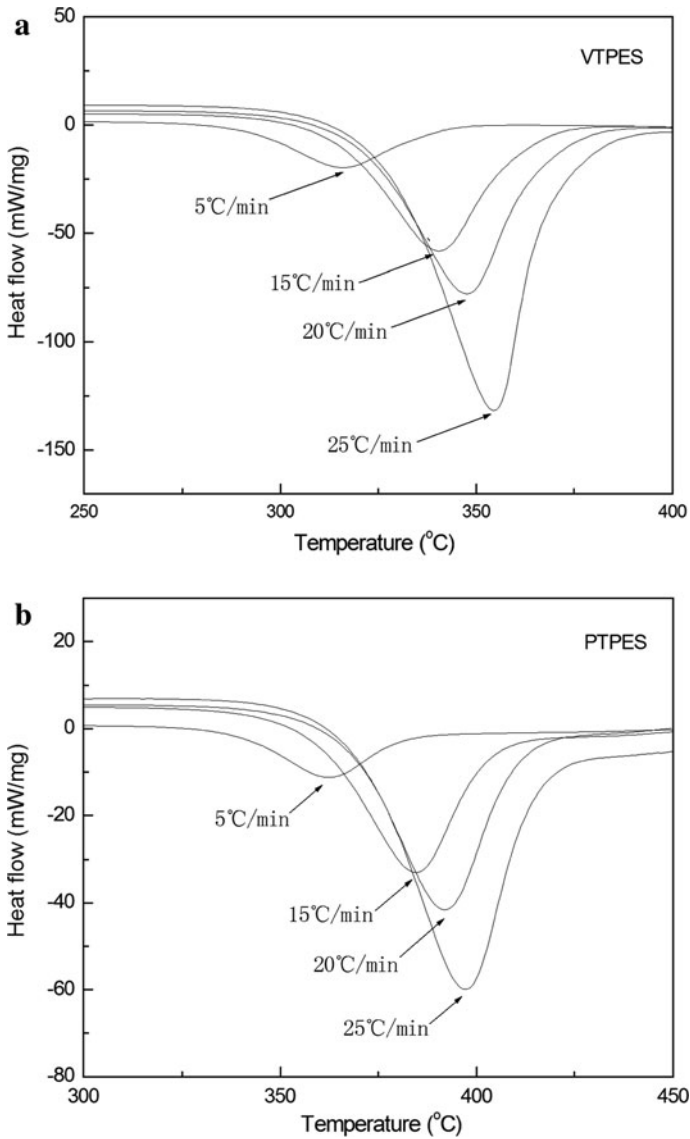


Fig. 5 DSC scans of VTPES (a) and PTPES (b) at a heating rates of 5, 15, 20, and 25 °/min

activation energy, R the universal gas constant, and T the temperature in Kelvin. Combining Eqs. (1) and (2):

$$\frac{da}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-a)^n \quad (3)$$

$$-\frac{E}{R} = \frac{d \ln(\varphi/T_p^2)}{d(1/T_p)} \quad (4)$$

A was found from the relationship:

$$A = \frac{\varphi E \exp(E/(RT_p))}{RT_p^2} \quad (5)$$

and n was determined by use of the Crane equation:

$$\frac{d \ln \varphi}{d(1/T_p)} = -(E/nR + 2T_p) \quad (6)$$

A plot of $\ln \varphi$ versus $1/T_p$ from several DSC curves would give a straight line with slope $(-E/nR)$, when $E/nR \gg 2T_p$.

In our study, the cure reactions of the above-mentioned monomers were investigated by use of the non-isothermal DSC technique at different heating rates of 5, 15, 20, and 25 °/min under a nitrogen atmosphere with a flow rate of 100 mL/min (Fig. 5). Table 1 shows the relationship between $\ln(\beta/T_p^2)$ and $(1/T_p)$ or $\ln\beta$ and $(1/T_p)$, obtained by use of the Kissinger method. The numerical values were fitted to a linear equation and the correlation coefficients were almost unity. The corresponding activation energy, frequency factor, and reaction order were also obtained. The results of calculation showed that the curing reactions of VTPES and PTPES approached first-order kinetics, with reaction orders of 0.92 and 0.93, respectively. Similar studies have been conducted on methyl-di(phenylethynyl)silane and multisubstituted acetylenic monomers; a first-order cure reaction was reported for both, suggesting that the order n might not be a function of the substituted groups on the resin and was probably only correlated with acetylenic bonds [27, 28]. However, the exact cure mechanism to account for the observed value of $n = 1$ in these thermal polymerizations was unclear. The theoretically predicted value for cyclotrimerization was 189 ± 10 kJ/mol based on bond energy calculations for the thermal polymerization of the acetylenic group [29], and the experimentally determined heats of polymerization for the phenyl and vinyl-substituted acetylenic monomers were 338 and 288 kJ/mol, respectively, which were higher than the predicted enthalpy of cyclotrimerization, suggesting that trimerization of the acetylenic groups might be the preferred reaction pathway, although trimerization of these secondary acetylenic groups to form hexasubstituted benzene rings seemed to be a sterically unfavorable process. Surprisingly, the frequency factor for PTPES was two orders of magnitude larger than that for VTPES. The differences between the activation energies and frequency factors were probably because of the existence of relatively stable radicals and lower steric factors [30], which caused the VTPES to react more easily. The analyzed results were in accordance with cure reactivity of the two monomers.

At the same time, a precursor monomer suitable for preparing heat-resistant polymer must have an adequately large processing window, i.e. a temperature range above the melting point of the monomer and below the onset of appreciable cure where the monomer can be held in a state of liquid flow. The ideal processing

window should be as broad as possible. Therefore practically, a processing window of at least 5–10 °C is necessary to ensure adequate flow behavior within processing temperature fluctuations. From Table 1, we can see that both monomers had a wide processing window above 200 °C, and that for the PTPES monomer was approximately 20 °C higher than that for VTPES. These broad processing windows mean the monomers have adequate time to impregnate other materials for preparing high-temperature polymers. Thus, the two monomers should be easily processed and are excellent candidates for further study as high-temperature-resistant polymers.

Non-isothermal curing analysis of the two monomers by FT-IR

In order to better understand the curing process of two monomers, FT-IR spectra were used to monitor the precise extent of the cure process and the chemistry of various reactions taking place. Spectra were taken every 5 min by means of four scans with a resolution of 4 cm^{-1} . Figure 6 shows the FT-IR spectra obtained as the two monomers were cured at different temperatures. The strong peaks at approximately 2160 cm^{-1} indicate the presence of acetylenic functionality; the absence of primary acetylenes is also apparent from the lack of absorption at 3295 cm^{-1} ($\text{C}\equiv\text{C}-\text{H}$). Other functionality was as follows: 1486–1629 cm^{-1} (aromatic, $\text{C}=\text{C}$), 1009–1220 cm^{-1} (CH_2-H), 756 cm^{-1} and 838 cm^{-1} ($\text{Si}-\text{C}$) from curve 1. The peak at 2160 cm^{-1} broadened with increasing curing temperature and vanished when the curing temperature reached 450 °C. This decrease in peak intensity was caused by conformational distribution of the products by a crosslinking reaction and was accompanied by an increase in intensity at 3056 cm^{-1} assigned to absorption of $\text{C}-\text{H}$ bonds in the benzene ring with curing. No new absorption peaks were observed in spectra except for the increased intensity of the absorption peak of the benzene ring, which indicated the occurrence of a trimerization reaction [31]. The results were in agreement with the DSC analysis, and a small red shift in the position of the triple bonds peak occurred from 2160 to 2139 cm^{-1} , which further confirmed occurrence of the trimerization reaction. It is worth mentioning that the peak of VTPES at 1392 cm^{-1} attributed to absorption of vinyl $\text{C}-\text{H}$ bonds bonded to silicon showed changes and vanished eventually, accompanied by an increase in the intensity of the 2928 cm^{-1} peak assigned to absorption of methylene $\text{C}-\text{H}$ bonds when the curing temperature was beyond 360 °C. These results suggest that, in the presence of oxygen, benzene rings are formed from two $\text{C}\equiv\text{C}$ bonds, and the $\text{C}=\text{C}$ bonds changed into $\text{C}-\text{C}$ bonds with curing [25]. Thus, the introduction of unsaturated groups contributed to the lower thermal curing temperature of the phenylacetylsilanes and improved process conditions.

Conclusions

Vinyltriphenylethylnsilane and phenyltriphenylethylnsilane were synthesized as functional monomers. Spectral analysis confirmed the structures of the products.

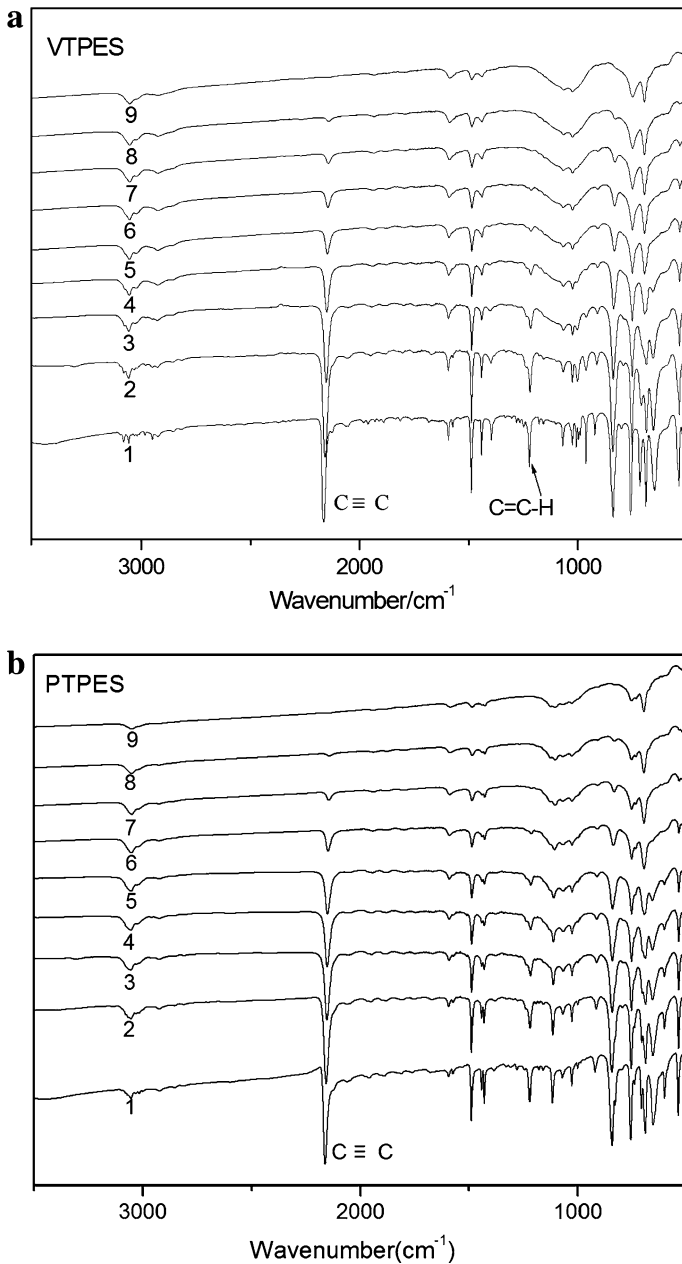


Fig. 6 FT-IR spectra of VTPES (a) and PTPES (b) at different curing temperatures: (1) 25 °C, (2) 150 °C, (3) 270 °C, (4) 300 °C, (5) 330 °C, (6) 360 °C, (7) 390 °C, (8) 420 °C, (9) 450 °C

The curing reactions were consistent with a first-order reaction according to the Kissinger method. The two monomers had a broad processing window for preparation of highly resistant materials by cyclotrimerization. The introduction

of unsaturated groups contributed to improving the process conditions for the phenylethynylsilane monomers.

Acknowledgments The authors gratefully acknowledge the support of the National Natural Science Foundation of China (NSFC) (Grant No. 50773017, 50973024).

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