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High heat-resistant linear propargyl ether-terminated polymers containing Si–H group: synthesis, characterization, and properties

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Abstract

Two kinds of novel linear propargyl ether-terminated polymers containing Si–H group, poly[(phenylsilylene)propargyl-bisphenol A] and poly[(phenylsilylene)propargyl-bisphenol S], were synthesized successfully by the dehydrogenative cross-coupling reaction of dipropargyl ethers of different bisphenols and phenylsilane. The structures of the resulting polymers were confirmed by Fourier transform infrared (FT-IR) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The molecular weights of the polymers were estimated by gel permeation chromatography. The polymers had excellent solubility and outstanding processability. Thermal curing behavior of the polymers was studied by differential scanning calorimetry (DSC) and FT-IR spectra. Thermal stability of the cured polymers was also investigated by DSC and thermogravimetric analysis. The results showed that the values of glass transition temperature of the cured polymers are above 380°C.

Keywords

Propargyl, phenysilylene, thermosets, thermal properties

Introduction

In the recent years, the alkynyl-terminated resins with good thermal stability and processability have been under investigation. Many alkynyl-terminated resins have been widely used in the aerospace and electronics as matrix resins of composites, adhesives, coatings, and so on.[1] Currently, the resins terminated with alkynyl groups mainly include the acetylene-terminated resins (ATRs), the phenylacetylene-terminated resins, and the propargyl-terminated resins (PTRs). The ATRs are hydrophobic materials with low water absorption, good thermal stability, and excellent physicomechanical properties.[2–4] However, their applications are limited by difficult multistep preparation process in low yield, high price,[4] and narrow processing window.[5] The phenylacetylene-terminated resins have better thermal and thermo-oxidative stability and wider processing window than the ATRs.[6–8] However, major disadvantages of these resins are their high price and high curing temperatures (above 350°C).[9–13] Compared to ATRs and phenylacetylene-terminated resins, the PTRs can offer better comprehensive performance. The PTRs have many advantages, such as low cost and low water sensitivity of monomers, moderate curing temperature, curing process without volatiles, low water absorption, high thermal stability, and excellent mechanical properties of the cured products.[4,5,14] Therefore, more and more attentions have been focused on the study of various kinds of the PTRs.

In 1971, Hay[15] synthesized dipropargyl ethers by reacting dihydric phenol with a propargyl halide in the presence of a base. Subsequently, Picklesimer[16] and Inbasekaran and Dirlikov[17] synthesized the propargylether-terminated resins in different ways. In 1990, Dirlikov reported of PTRs based on different biphenols, which possessed attractive properties such as a glass transition temperature (T_g) of above 300°C, excellent isothermal thermostability, low water absorption, low dielectric constant and dissipation factor, excellent physicomechanical properties, low cost, and so

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on.[4] Subsequently, many researchers studied the thermal curing mechanism[18–23] and oxidative polymerization[24–26] of the propargylether-terminated monomers. Currently, the main propargylether-terminated monomers or polymers include propargylether-terminated ester-imide prepolymers (T_g of above 225°C),[27,28] polybenzoxazines (T_g of above 295°C),[26,29] addition-curable propargylether-containing phenolic resins (T_g of higher than 370°C),[30,31] and so on.

To further improve heat resistance of the propargylether-terminated resins, it is a good way to introduce some reactive groups into the structures of the resins. There are many reactive groups such as Si–H, Si–Cl, and Si–OR. Among these groups, Si–H bond can react with many groups such as C=C, C≡C, C=O, OH, NH, and C≡N,[32] which can increase the cross-linking density to improve the T_gs of the cured products. These silicon-containing groups have good thermal stability because silicon atom can form inorganic compounds, for example, SiC or SiO_2.[32] Therefore, introducing these silicon-containing reactive groups into the polymer structures can further improve the heat resistance. Currently, many polymers containing [–SiR_2–C≡C–] (R = alkyl or phenyl) units have been reported. However, there are a few reports in the literature of a polymer containing Si–H group. Itoh et al.[32–34] synthesized poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [–Si(Ph)H–C≡C–C_6H_4C≡C–]$_n$, whose low-viscosity was about 10 Pa s in the temperature range of 140–152°C. Buvat and coworkers[35,36] prepared poly[silylene ethynylene–phenylene ethynylene] C_6H_5–C≡C–[Si(Ph)H–C≡C–C_6H_4–C≡C]$_n$–Si(Ph)H–C≡CC_6H_5 that could withstand high temperatures up to 600°C. Other heat-resistant polymers containing Si–H group, poly[(-methyl silylene) ethynylene] [–Si(CH_3)H–C≡C–]$_n$[37] and poly[(phenyl silylene)–diethynylene)] [–Si(Ph)H–C≡C–C≡C–]$_n$,[38] were also synthesized and reported. All these polymers containing –Si(R)H– units in the main chain had extremely high thermal stability. However, the cost of the polymers was high.

In this article, the method of molecular design was used to synthesize new structure polymers that had advantages of both the propargyl ether-terminated resins and the polymers containing Si–H group. Two new kinds of linear propargyl ether-terminated polymers containing Si–H group in the main chain were synthesized. The structures of the polymers were confirmed by Fourier transform infrared (FT-IR) and proton-nuclear magnetic resonance (^{1}H NMR). Thermal curing behavior of the polymers was studied by differential scanning calorimetry (DSC) and FT-IR. The processability and thermal stability were also investigated.

Experimental

Materials

Dipropargyl ether of bisphenol A (DPEBA, melting point (mp): 80–81°C), dipropargyl ether of bisphenol S (DPEBS, mp: 191–192°C), and phenylsilane ($PhSiH_3$, refractive index (n_D^{20}) = 1.5125) were synthesized according to the methods reported previously.[4,17,39] Lithium aluminum hydride ($LiAlH_4$) and diethylene glycol dimethyl ether (DGDE) were purchased from Tianjin Fine Chemicals Institute (Tianjin, China). $LiAlH_4$ was purified by mixing with anhydrous ether (mass ratio 1:5), slowly stirring and refluxing for several hours under nitrogen, and then filtering and drying under reduced pressure at 60°C to obtain white crystals prior to use. DGDE was distilled and dried by 3 A molecular sieves prior to use.

Synthesis of PBAS

DPEBA (5.93 g, 19.50 mmol), $LiAlH_4$ (0.039 g, 1.03 mmol), and DGDE (7.5 mL) were mixed in a 50-mL three-necked flask equipped with a condenser, mechanical stirrer, and nitrogen protection at room temperature. Then $PhSiH_3$ (2.22 g, 20.50 mmol) was added to the flask after about 30 min with stirring. The reaction system was kept to react at 120°C for 20 h with refluxing, stirring, and N_2 protection in an oil bath. The reaction mixture was cooled to room temperature and poured into 1 N hydrochloric acid and then extracted with toluene. The organic layer was separated, dried by anhydrous sodium sulfate, and then removed solvent by rotary evaporation to get the crude product. After drying at 60°C for 50 h, poly[(phenylsilylene)propargyl-bisphenol A] (PBAS) was obtained as a yellow viscous liquid. Yield: 6.58 g, 67%; weight-average molecular weight (M_w): 5473. Using essentially the same procedure and employing DPEBA (4.03 g, 13.25 mmol), $LiAlH_4$ (0.025 g, 0.66 mmol), DGDE (5.0 mL), and $PhSiH_3$ (1.43 g, 13.25 mmol), poly[(phenylsilylene)propargyl-bisphenol A] (PBAS-1) was obtained as a brown solid. Yield: 3.49 g, 64%. M_w: 90,170. The structure of PBAS was confirmed by FT-IR and ^{1}H NMR spectroscopy.

FT-IR (potassium bromide (KBr)): cm^{-1} = 3293 (≡CH stretching), 2140 (Si–H and C≡C stretching), 1428, 1000 (Si–Ar deformation), 1362, 1379 (C–CH_3 bending), 1242 (Ar–O– stretching), 1027 (–O–C– stretching).

^{1}H NMR (deuterated chloroform ($CDCl_3$), 300 MHz): δ (ppm) = 1.58 (s, CH_3), 2.45 (s, ≡C–H), 4.62 (m, CH_2), 4.89 (m, SiH_2), 5.25 (m, Si–H), 6.62–7.80 (m, Ar–H).

Synthesis of PBSS

Using essentially the same procedure and employing DPEBS (3.65 g, 11.20 mmol), $LiAlH_4$ (0.025 g, 0.66 mmol), DGDE (15 mL), and $PhSiH_3$ (1.27 g, 11.77 mmol), poly[(phenylsilylene)propargyl-bisphenol S] (PBSS) was obtained as a brown solid. Yield: 3.7 g, 75%. M_w: 5693. The structure of PBSS was confirmed by FT-IR and ^{1}H NMR spectroscopy.

FT-IR (KBr): cm^{-1} = 3270 (≡CH stretching), 2128 (Si–H and C≡C stretching), 1430, 1000 (Si–Ar

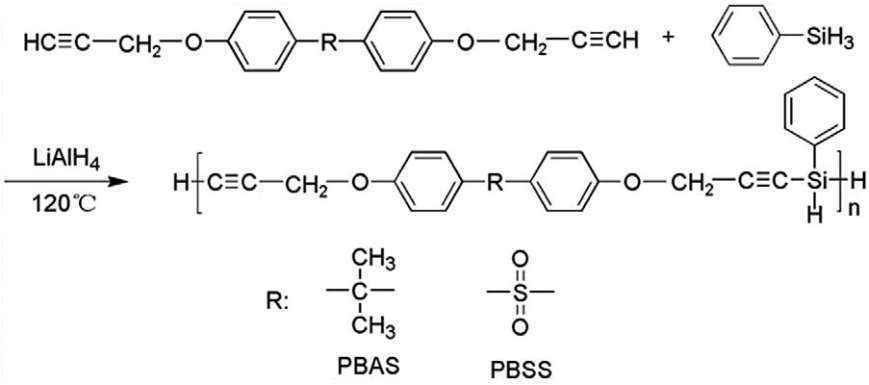

Figure 1. Synthesis of PBAS and PBSS. PBAS: poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S].

Table 1. Average molecular weights of the resulting polymers.

Sample	DPEBA (or S) (mmol)	$PhSiH_3$ (mmol)	Molar ratio DPEBA (or S)/$PhSiH_3$	Molecular Weight		
				M_w[a]	M_n[a]	PDI[b]
PBAS	19.50	20.50	0.95	5473	2218	2.47
PBSS	11.20	11.77	0.95	5693	2804	2.03
PBAS-1	13.25	13.25	1.00	90170	28450	3.17

PBAS: poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S]; DPEBA: Dipropargyl ether of bisphenol A; $PhSiH_3$: phenylsilane; M_w: weight-average molecular weight of polymer; M_n: number average molecular weight of polymers; PDI: polydisperity index.
[a] Measured by gel permeation chromatography in tetrahydrofuran and using polystyrene as the standard.
[b] PDI = M_w/M_n.

deformation), 1386, 1148 (O=S=O stretching), 1242 (Ar–O– stretching), 1018 (–O–C– stretching).

^{1}H NMR (dimethyl sulfoxide (DMSO-d_6), 300 MHz): δ (ppm) = 2.49 (s, ≡C–H), 4.62 (m, CH_2), 4.89 (m, SiH_2), 5.97 (m, SiH), 6.89–7.81 (m, Ar–H).

Measurements

FT-IR spectra were recorded using FT-IR spectrometer (Nicolet model NEXUS-470, USA) at a wavelength of 400–4000 cm^{-1} with 4 cm^{-1} resolution in solid state as KBr pellets. ^{1}H NMR spectra were recorded on a spectrometer (model FX-90Q, JEOL, USA) using $CDCl_3$ or DMSO-d_6 as solvent at room temperature. Polymer M_w and number-average (M_n) molecular weights were determined by gel permeation chromatography (GPC) in tetrahydrofuran (THF) at a flow rate of 1 mL min^{-1} using a system chromatograph analysis apparatus (Waters 515-2410) with polystyrene standard. DSC and thermogravimetric analysis (TGA) were carried out in argon atmosphere on a Jupiter simultaneous thermal analyzer (NETZSCH model STA 449C, Germany) with a heating rate of 20°C min^{-1}. Bohlin Advanced Rheometer (model Gemini 200, Malvern Company, UK) was used to study the rheological properties of the polymers with a shear rate of 0.1 s^{-1} at the heating rate of 5°C min^{-1}.

Results and discussion

Synthesis of PBAS and PBSS

The linear propargyl ether-terminated polymers containing Si–H group, PBAS and PBSS, were synthesized by the dehydrogenative cross-coupling reaction of dipropargyl ethers of bisphenols and $PhSiH_3$, as shown in Figure 1. The average molecular weights of the polymers based on different bisphenols were determined by GPC using polystyrene as the standard. The detailed data obtained from GPC analyses are summarized in Table 1. As shown in Table 1, M_w of PBAS and PBSS were 5473 and 5693 with polydispersity index (PDI) between 2.47 and 2.03, respectively. By adjusting the ratio of DPEBA and $PhSiH_3$, PBAS-1 could be obtained with high molecular weight (M_w = 90,170).

The structures of PBAS and PBSS were characterized by FT-IR and ^{1}H NMR spectroscopy. Figure 2 shows the FT-IR spectra of PBAS and PBSS. PBAS and PBSS contained characteristic absorption bands of ≡CH at 3293 and 3270 cm^{-1}, respectively. The characteristic absorptions owing to both Si–H bond and C≡C bond at 2140 and 2128 cm^{-1} were also observed, respectively. The deformation vibration absorption peaks of Si–Ar appeared at around 1430 and 1000 cm^{-1}. The similar absorption peaks of –Ar–O–C– exhibited at around 1240 cm^{-1} (ν–Ar–O–) and 1030 cm^{-1} (ν–O–C–). Furthermore, in the FT-IR spectrum of

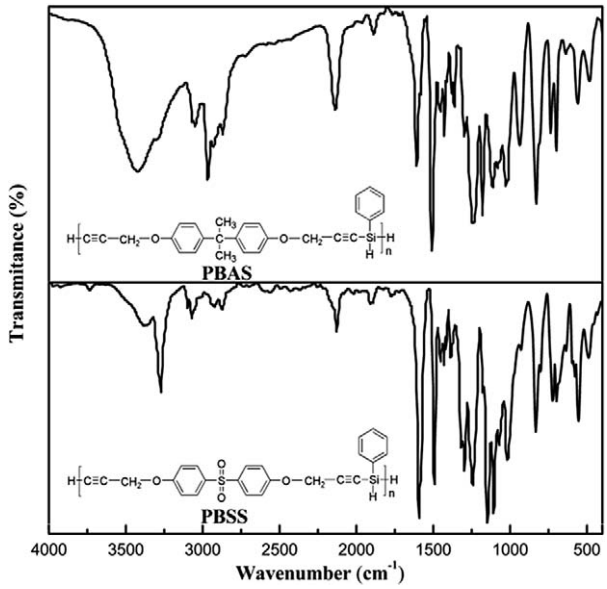

Figure 2. FT-IR spectra of PBAS and PBSS. PBAS: poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S].

PBAS, the characteristic double peaks of $–C(CH_3)_2–$ group appeared at 1362 and 1379 cm^{-1}, while O=S=O group of PBSS showed absorption at 1386 and 1148 cm^{-1}.

The ^1H NMR spectra of PBAS and PBSS are shown in Figure 3. PBAS and PBSS contained some identical groups with similar characteristic peaks. The peaks from 6.62 to 7.81 ppm were assigned to protons of phenyl groups, whereas the peaks at 4.62 ppm were caused by $–CH_2–$. The peaks of ≡C–H appeared at 2.45 and 2.49 ppm, and those of SiH_2 group appeared at 4.89 ppm and Si–H group appeared at 5.25 and 5.97 ppm. The characteristic peak at 1.58 ppm in the spectrum of PBAS was attributed to $–C(CH_3)_2–$ in the backbone. Both FT-IR and ^1H NMR agreed well with the structures of novel polymers as expected.

Solubility of the resulting polymers

By adjusting the molar ratio of DPEBA or DPEBS and $PhSiH_3$, the resulting polymers with different molecular weights in different physical states could be obtained. For example, PBAS was a yellow viscous liquid, while PBAS-1 was a brown solid. The solubility of the resulting polymers in several commonly used organic solvents at 3.0% (w/v) is listed in Table 2. The results showed that PBAS and PBSS were soluble in the test solvents including toluene, acetone, chloroform, and THF. PBAS-1 was partially soluble in chloroform, THF, and acetone because of its high molecular weight. The good solubility should be resulted from the flexibility of propargyl ether group in the polymer structure. Moreover, the polymers based on two different bisphenols were moldable and soluble in many solvents of low-boiling point. The low-viscosity viscous liquid states and excellent solubility facilitated the processing properties of the polymers, which could be used for resin transfer molding (RTM) process and filament winding.

Dynamic rheological behavior of the resulting polymers

The dynamic viscosity behaviors were measured by the rheometer, which showed that the resulting polymers

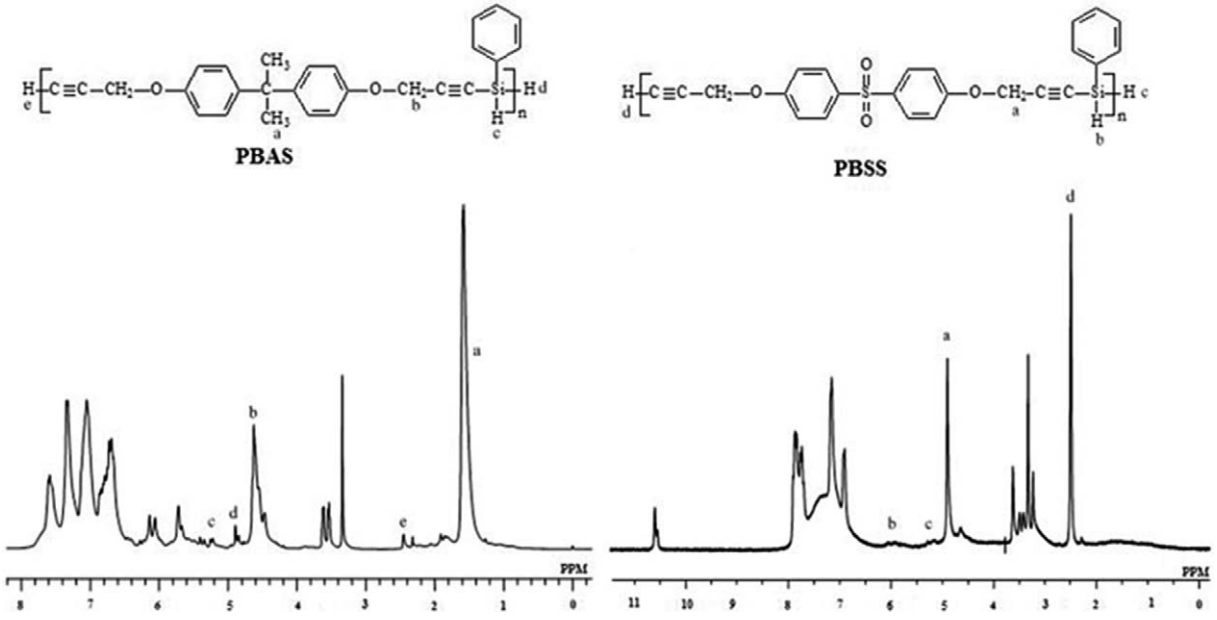

Figure 3. ^1H NMR spectra of PBAS and PBSS. PBAS: poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S]; ^1H NMR: proton-nuclear magnetic resonance.

Table 2. Solubility of the resulting polymers.[a]

	Solvent				
Polymer	Toluene	Acetone	Chloroform	THF	Ethanol
PBAS	++	++	++	++	+
PBSS	++	++	++	++	−−
PBAS-1	++	+−	+−	+−	−−

PBAS; poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S]; THF: tetrahydrofuran.
[a]Qualitative solubility was determined at 3.0% (w/v); ++: soluble at room temperature; +−: partially soluble at room temperature; +: soluble on heating; −−: insoluble even on heating.

exhibited excellent flow-ability. The viscosity–temperature curves of monomer DPEBA, polymers PBAS, and PBAS-1 are shown in Figure 4. The curves showed an initial viscosity decrease as the temperature increased, then stabilized and finally increased suddenly when the gelation occurred. The viscosity of PBAS was below 1 Pa s in the temperature range of 78–274°C. Compared to DPEBA, PBAS had excellent flow-ability and a broad processing window around 200°C, which illustrated that Si–H group attaching directly to propargyl ether group in the way of σ bond to obtain the linear polymers could not reduce the flow-ability. Low viscosity, a broad processing window, and excellent solubility permitted PBAS to be applicable to a variety of techniques, for example, RTM, compression molding, and autoclave molding for fabricating composites. The viscosity of PBAS-1 was lower than 10 Pa s in narrow temperature range of 130–140°C, which showed that the rheological behavior was affected by the molecular weight. PBAS-1 was fusible and moldable, and it was possible to be used for compression-molding and melt-spinning.

Thermal curing behavior of the resulting polymers

Thermal curing behavior of the resulting polymers was examined by DSC under argon atmosphere at a heating rate of 20°C min^{-1}, which showed that PBAS and PBSS exhibited similar DSC thermograms. The two polymers showed only an exothermic peak on the DSC curves with maximum at about 270°C. We had studied the non-isothermal curing

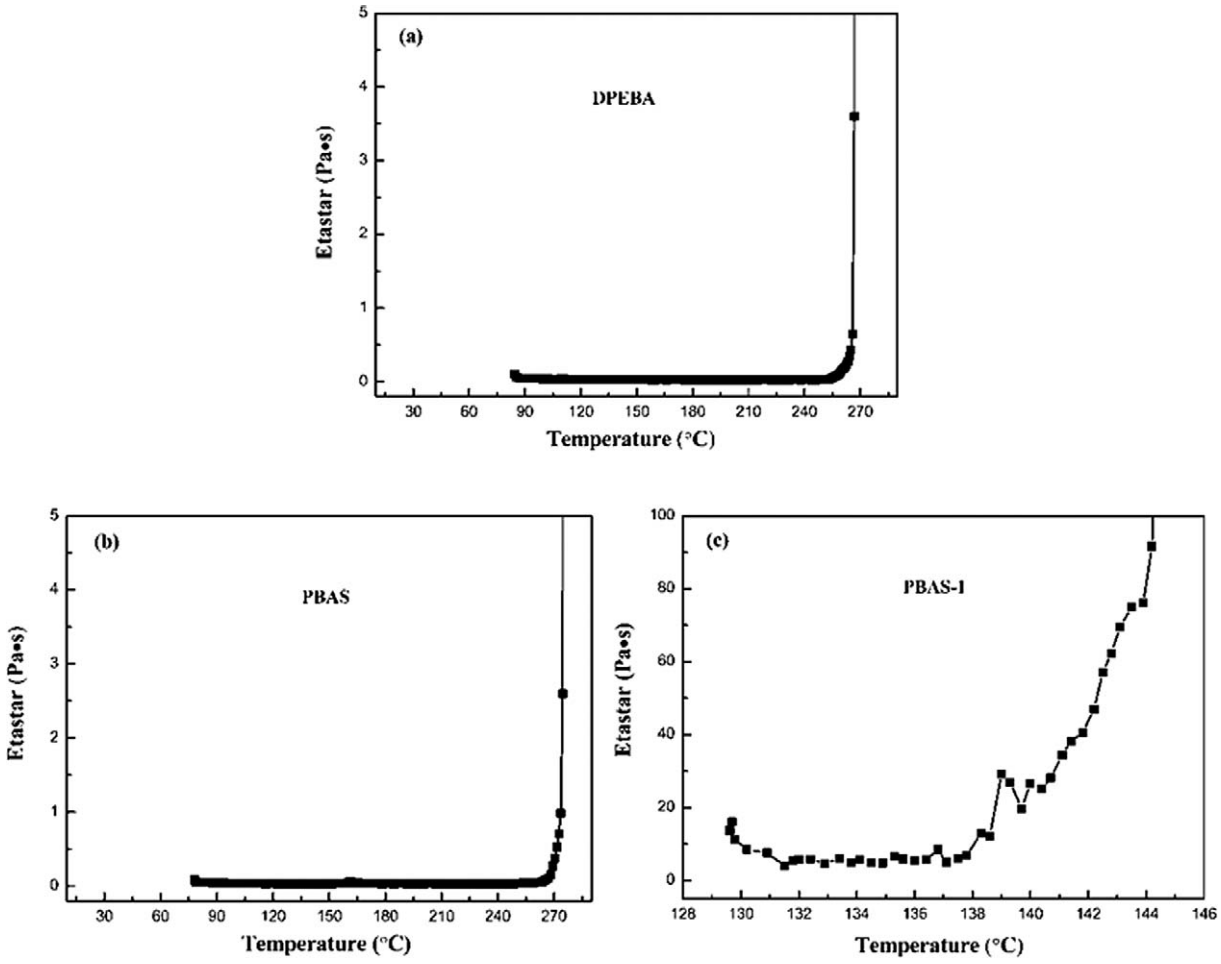

Figure 4. Viscosity–temperature curves of the monomer and the resulting polymers.

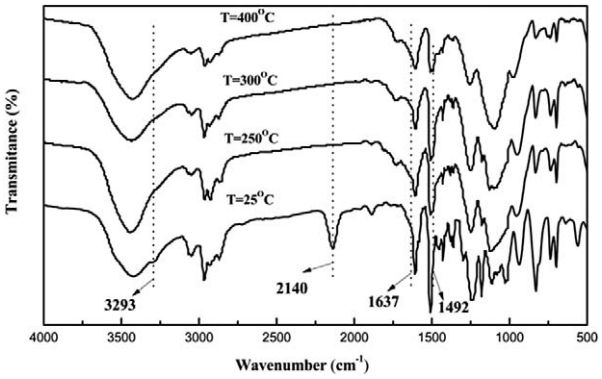

Figure 5. FT-IR spectra of PBAS after curing at different temperature for 8 h. PBAS: poly[(phenylsilylene)propargyl-bisphenol A]; FT-IR: Fourier transform infrared.

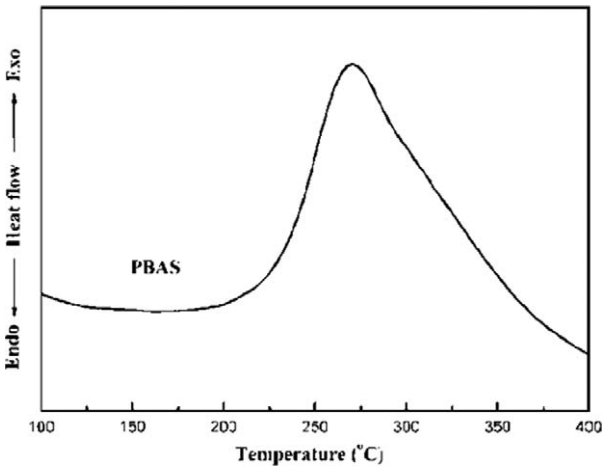

Figure 6. DSC thermogram of PBAS. DSC: Differential scanning calorimetry; PBAS: poly[(phenylsilylene)propargyl-bisphenol A].

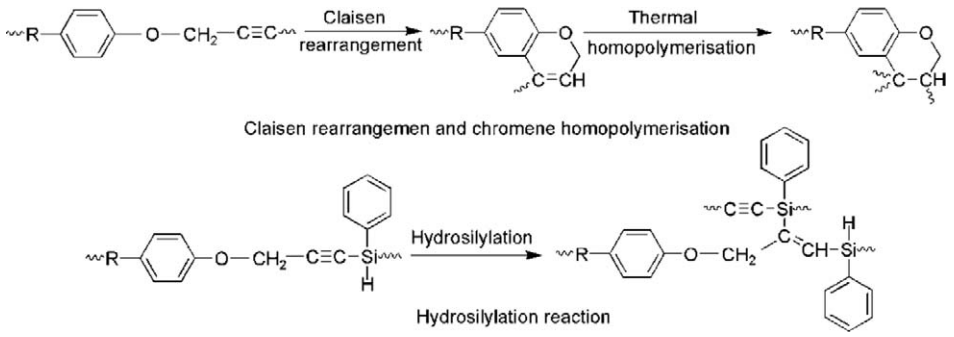

Figure 7. Curing mechanism of the resulting polymers.

kinetics of poly[(phenylsilylene)propargyl-hexafluoroiso bisphenol A] (PBAFS)[40] by Kissinger, Ozawa, and Friedman methods, founding that the cure reaction of PBAFS was *n*th-order in nature with activation energy of 132.4 KJ mol^{-1}. The reaction order for n and A were 1.17 and 1.24×10^{12} min^{-1}, respectively. In this article, the curing behavior of the propargyl ether-terminated polymers was investigated by PBAS as an example.

The FT-IR spectra of PBAS after curing at different temperature for 8 h were recorded in Figure 5. As shown in Figure 5, the infrared absorption peaks of ≡C–H at 3293 cm^{-1} and of C≡C and Si–H at 2140 cm^{-1} disappeared after curing at 250°C for 8 h. Instead, two new absorption peaks appeared at 1637 and 1492 cm^{-1} corresponding to C=C and aromatic ring of 2H–chromene, respectively. After curing at 300 and 350°C for 8 h, the absorption peaks of 2H–chromene at 1637 and 1492 cm^{-1} disappeared, which showed that the homopolymerization of 2H-chromene occurred. The results of FT-IR spectra indicated that the hydrosilylation reaction between Si–H and C≡C bonds, the Claisen rearrangement reaction, and the chromene homopolymerization all existed.

Figure 6 shows the DSC thermogram for the PBAS. Obviously, only a broad exothermic peak was observed in the DSC curve with a maximum at 271°C. The only one curing exothermic peak showed that the hydrosilylation reaction involved the Si–H and C≡C bonds and the Claisen rearrangement reaction of phenyl propargyl ether took place within the same temperature range.[40] Thus, the curing mechanism of the propargyl ether-terminated polymers containing Si–H group could be proposed in Figure 7, which showed the existence of two reactions at the same time.

Thermal properties of the cured polymers

The resulting polymers based on different bisphenols were cured in convective air oven without a catalyst as follows: 180°C for 16 h; 250°C for 4 h; 300°C for 6 h; and 400°C for 2 h. T_g values of the cured products were tested by DSC with a heating rate of 20°C min^{-1} in argon atmosphere. Thermal stability was determined by TGA. TGA curves of the cured polymers are shown in Figure 8. The detailed data obtained from the TGA and DSC analyses are summarized in Table 3. It showed that the cured polymers based on different bisphenols had the T_g values of above

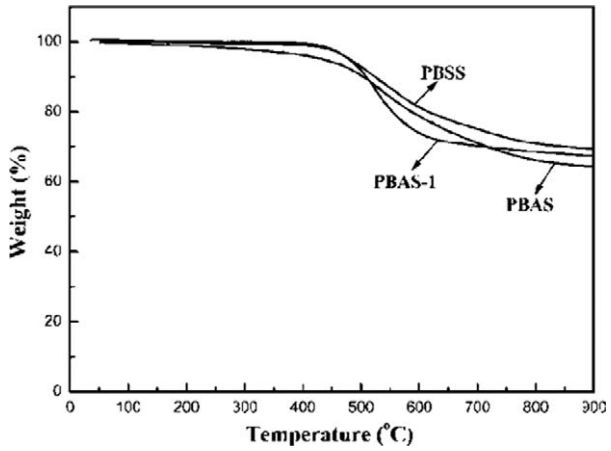

Figure 8. TGA curves of the cured resulting polymers. TGA: Thermogrametric analysis.

380°C. Such high T_g values illustrated that the propargyl ether-terminated polymers had good heat resistance and could be applied at high temperature conditions.

TGA curves of the cured polymers (Figure 8) displayed the temperatures of 5% weight loss (T_{d5}) in argon atmosphere above 437°C, which were much higher than those of the corresponding dipropargyl ether of bisphenols. This might be attributed to high reactivity of Si–H group, which resulted in a dense network by the hydrosilylation reaction between Si–H and C≡C. All polymers had high char yields (> 65%) at 900°C in argon atmosphere, implying their potential application as precursor for Si–C-based ceramics. Thermal stability was determined by the backbone structures and the cross-linking densities of the cured products. The thermal stability of O=S=O group (in PBSS) was better than $-C(CH_3)_2-$ group (in PBAS), which was in agreement with the T_{d5} values. The data from thermal analysis showed that the resulting polymers had fairly high thermal stability. Compared to PTRs (Table 3), the polymers with Si–H and propargyl ether group in the main chain had better thermal stability, which was mainly caused by the increase in cross-linking density and formation of thermally stable structure. Therefore, the introduction of Si–H group into the main chain of the propargyl ether-terminated resins could further improve the heat resistance indeed.

Conclusions

Two kinds of novel linear propargyl ether-terminated polymers containing Si–H group in the main chain were successfully synthesized via the dehydrogenative cross-coupling reaction. The structures of the polymers were confirmed by FT-IR and ^{1}H NMR. M_w of PBAS, PBAS-1, and PBSS were 5473, 90,170, and 5693, respectively, with PDIs between 2.03 and 3.17. The polymers had excellent solubility in commonly used organic solvent. Extremely high thermal stability was confirmed by DSC and TGA. The cured polymers exhibited good thermal stability with a T_g of above 380°C. The degradation temperatures at 5% weight loss (T_{d5}) were 437–481°C and the char yields at 900°C in argon atmosphere were higher than 65%. The introduction of Si–H group into the propargyl ether-terminated resins could obtain new linear polymers with good processability and high heat resistance.

Table 3. Thermal analysis data of the cured PTR monomers and the cured polymers.

	PTR monomers			Polymers		
Data	DPEBA[4,41]	DPEBS[41]	Data	PBAS	PBSS	PBAS-1
T_g (°C)[a]	~300	–	T_g (°C)[a]	384	440	404
T_{ini} (°C)[b]	340	350	T_{d5} (°C)[c]	437	481	478
Char yield (%)[d]	43	67	Char yield (%)[e]	65	70	67

DPEBA: Dipropargyl ether of bisphenol A; DPEBS: Dipropargyl ether of bisphenol S; PTR: propargyl-terminated resins; PBAS; poly[(phenylsilylene)propargyl-bisphenol A]; PBSS: poly[(phenylsilylene)propargyl-bisphenol S]; T_g: glass transition temperature; T_{ini}: initial decomposition temperature.
[a] T_g measured by differential scanning calorimetry at a heating rate of 20°C min^{-1} in argon atmosphere.
[b] Initial decomposition temperature at a 10°C min^{-1} heating rate in nitrogen atmosphere.
[c] Temperature at a 5% weight loss at a 20°C min^{-1} heating rate.
[d] Residual weight percentage at 700°C in nitrogen atmosphere.
[e] Residual weight percentage at 900°C in argon atmosphere.

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