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Synthesis and Characterization of Poly(dimethylsilylene ethynylenephenyleneethynylene) Terminated with Phenylacetylene

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Summary

A novel easily processable resin, poly(dimethylsilylene ethynylenephenylene-ethynylene) $[\text{-Si(CH}_3)_2\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-C}\equiv\text{C-}]_n$ terminated with phenylacetylene, was developed. And the properties of the resulting resin were investigated. The resin was a viscous liquid and soluble in a variety of solvents. The cured resin showed high heat-resistant stability and high char yield. The cured resin was sintered at 1450°C and obtained sintered product was analyzed by FTIR, SEM and X-ray diffraction techniques and the results showed β-SiC were formed in the product.

Keywords:

inorganic-organic hybrid polymers; diethynylbenzene; silylene; heat-resistant resin; sinter

Introduction

Many engineers and scientists have focused on the highly heat-resistant polymers (d =1.0~1.5) which have good mechanical properties since 1930's. To heat-resistant polymers have many scientists paid a great attention since 1940's [1-5]. Up to now, a lot of high performance polymers such as polyimides, polybenzyimidazoles, polybenzothiazoles, polybenzoxazoles, etc. have been explored and been found their applications. However, they are not easy processed. Therefore, thermosetting resins with low molecular weight attract great attention of scientists in recent years. Combination of inorganic and organic units in a polymer chain, i.e. an inorganic-organic hybrid polymer, is a relatively new approach to develop heat-resistant polymeric materials. One of potential candidates would be a hybrid polymer containing silane and ethynyl or ethynylene with low molecular weight which could be able to crosslink at elevated temperature.

The polymers containing ethynyl or ethynylene groups are one kind of interesting resins. Some studies of silicon-containing polymers composed of [-SiR$_2$-C≡C-] (R= alkyl or phenyl) units have been reported because of their potential applications such as ceramic precursors and conducting materials [6-18]. There are a few cases reported in the literature on a polymer containing Si-H group in molecular chain. Itoh, et al. synthesized poly(phenylsilyleneethynylene-1,3-phenyleneethynylene) [-Si(Ph)H-C≡C-C$_6$H$_4$-C≡C-]$_n$ (abbreviated MSP), prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and m-diethynylbenzene in the presence of magnesium oxide. The results showed that the polymer had an extremely high thermal stability after cured[1, 2]. Poly[silyleneethynylene phenylene-ethynylene] terminated with phenylacetylene, C$_6$H$_5$-C≡C-[Si(Ph)H-C≡C-C$_6$H$_4$-C≡C]$_n$ -Si(Ph)H-C≡CC$_6$H$_5$ (abbreviated BLJ) [7], poly(phenylsilylene diethynylene) [-Si(Ph)H-C≡C-C≡C-]$_n$, and poly[methylsilyleneethynylene] [-Si(CH$_3$)H-C≡C-]$_n$ were synthesized and reported.

Researchers in our laboratory have been focused on the design and synthesis of novel polymers with low molecular weight and containing dialkyl silylene and ethynylenephenyleneethynylene units in a main molecular chain, which are inorganic-organic hybrid polymers expected to exhibit good mechanical, thermal, and oxidative properties. Using dialkyl silylene structure unit instead for alkyl silylene in synthesized polymers would decrease the crossing points of the polymers and then improve the mechanical property of the polymers. This paper presents the synthesis and characterization of poly(dimethylsilylene ethynylenephenyleneethynylene) terminated with phenylacetylene.

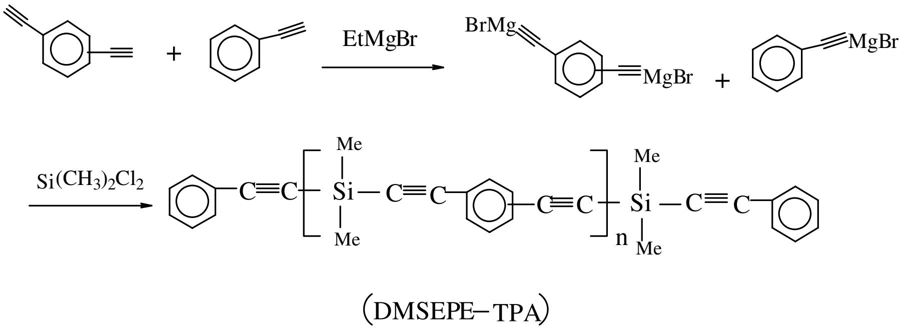
Experimental

1. Instrument

Infrared spectrum was obtained on Nicolet Magna model 550. ^{1}H-NMR spectrum was recorded in CDCl$_3$ on a BRUKER AVANCE 500 (500MHz) spectrometer operating at 500MHz. Chemical shifts were recorded relative to tetramethylsilane set at 0.0 ppm. Number average molecular weight (Mn) of polymers was measured in THF by gel permeation chromatograph (GPC) performed on a Waters 410 Chromatograph. Differential scanning calorimeter (DSC) analyses were performed with Universal V2.3 TA Instruments 2910 modulated system. The heating rate was 10K/min at a flow rate of nitrogen 15cm^3/min. Thermogravimetric analysis (TGA) was performed on a METTLER TGA/SDTA 851 analyzer with a heating rate of 10K/min. XRD spectrum was obtained on a Digaku (Japan) D/max 2550 VB/PC diffractometer. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6360LV microscope.

2. Preparation of poly(dimethylsilyleneethynylenephenyleneethynylene) terminated with phenylacetylene (DMSEPE-TPA)

A synthesis route to appropriate silicon-containing resins was showed in Scheme 1. Dimethyldichlorosilane, diethynylbenzene, and phenylacetylene were dried over 3A molecular sieves and distilled prior to use.



Scheme 1 The synthesis route of DMSEPE-TPA

An organic magnesium regent was prepared as follows: the magnesium metal ribbon (4.00g) was cut into small pieces and put into a 250ml three necked flask. The atmosphere in the flask was replaced by dry nitrogen gas. THF (40ml), which had been dried over sodium and then distilled, was introduced into the flask, a small piece of iodine was added, and the mixture was stirred to activate the reaction of magnesium. To the flask with the activated magnesium was a solution of 16.20g (148.68mmol) of ethyl bromide in THF (40ml) added dropwise at room temperature for about 3 hours. The mixture then was refluxed for 3 hours to produce ethylmagnesium bromide. To the reaction system was added a solution of 3.64g (35.65mmol) phenylacetylene (PhA) and 6.74g (53.47mmol) of m- / p-diethynylbenzene (DEB, m/p molar ratio was about 65/35) in 40ml THF dropwise at room temperature over 2 hours with stirring and the reaction was continued for an additional 3 hours at the refluxing condition to produce the intended and mixed organic magnesium reagents.

The polymerization reaction was subsequently performed. A solution of 9.20g (71.29mmol) of dimethyldichlorosilane in THF (40ml) was dropwise added to the above flask at room temperature over a period of 40 minutes with stirring. While the dimethyldichlorosilane was added the white solid Grignard reagents disappeared and the colour of the solution changed to celadon. The reaction was further developed for another 3 hours at the refluxing condition. Thereafter, THF was distilled out with an evaporator, 120ml of 2% aqueous solution of hydrochloric acid was added to the flask cooled with ice water, and the mixture in the flask was stirred for 1 hour. 70-80ml toluene was then added to the mixture. The resulting oil phase was separated by using a separatory funnel and washed with deionized water until the washed water was neutral. Then toluene was distilled off and an orange viscous crude product was obtained. The yield is 75%.

3. *Cure of DMSEPE-TPA*

The resin DMSEPE-TPA was weighted and kept in an oven at 200°C/4h +250°C/6h+300°C/5h+ 350°C/2h+385°C/5h to get a cured resin under air. IR spectrum of the cured resin was measured.

4. *Sintering of cured DMSEPE-TPA*

The cured DMSEPE-TPA resin was sintered under nitrogen at 420°C/0.5h + 800°C/0.5h+1200°C/0.5h+1450°C/12h.

Results and discussion

Characterization of DMSEPE-TPA

The resin (DMSEPE-TPA) which incorporate dimethyldichlorosilane unit into the main chain of polyarylene ethynylene was prepared by Grignard method[19]. In the flask phenylacetylene magnesium bromide (ph-C≡C-MgBr) and diethynylbenzene dimagnesium dibromide (BrMg-C≡C-ph-C≡C-MgBr) were allowed to react with the dimethyldichlorosilane to produce a resin with alternating -Si(CH$_3$)$_2$- and -C≡C-ph-C≡C- units and ph-C≡C- as end group (Scheme 1). The obtained resin was soluble in a variety of solvents, such as toluene, benzene, THF, acetone, chloroform, methanol, DMF and DMSO.

FT-IR spectrum for the resin was shown in Figure 1(a). It revealed a strong absorption at 2158 cm^{-1} which attributed to -C≡C- bond. A strong and sharp absorption for Si-CH$_3$ was at 1252 cm^{-1} and for -CH$_3$ stretching mode at 2961 cm^{-1}. The weak adsorption at 3060 cm^{-1} was due to the aromatic C-H stretch. ^{1}H-NMR (CDCl$_3$, ppm) spectrum of the resin showed a multiplet at 7.21-7.51 for C$_6$H$_4$ and 0.46-0.48 for Si(CH$_3$)$_2$. The molecular weight of the resin was determined by GPC (polystyrene standard), and the number average molecular weight Mn was 5230 with a polydispersity of 2.41.

FT-IR analysis of the cured resin was shown in Figure 1(b). The spectrum showed stretching vibration absorption band of ethynyl groups at 2158 cm^{-1} disappeared, and an absorption at 1600cm^{-1} attributed to –C=C- vibration increased. This indicated the reaction of ethynyl groups took place and resulted in the generation of olefinic structure [20~25]. A strong peak absorption at 1075, 1023cm^{-1} largely increased for the cured resin which might belong to the Si-ph (Diels-Alder cycloaddition[24, 25]) or Si-CH=CH$_2$ (trans CH wagging) indicated that the crosslinking reaction among the ethynylene groups occurred. A Si-CH$_3$ absorption band at 1252 cm^{-1} along with -CH$_3$ band at 2961 cm^{-1} remained. The absorptions at 1722, 3428cm^{-1} probably resulted from oxide products due to the partial oxidation of the resin during the cure process. IR cannot alone determine a structure. Our continuing efforts are currently

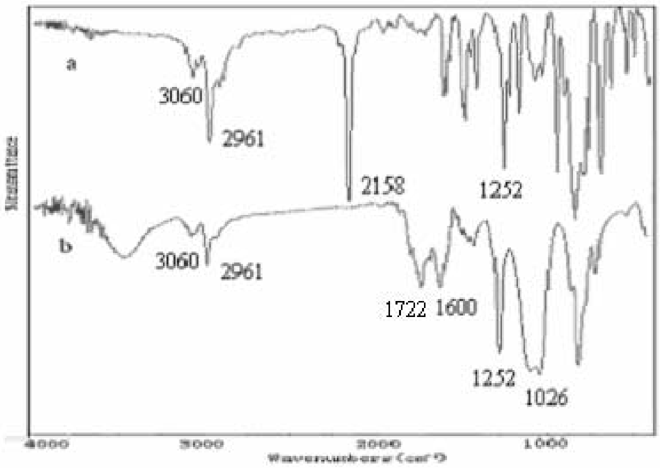


Figure 1 FT-IR spectra of DMSEPE-TPA before (a) and after (b) cure

focused towards further elucidating the complex reaction mechanisms involved in the curing.

The cure process of the ethynyl group has been widely investigated[20~25]. Analyses of solid-state ^{13}C-NMR, FTIR and ESR spectroscopies have brought some insight into the cure mechanism of ethynyl resins. The results demonstrated that the ethynyl resin underwent cyclotrimerization, hydrogen addition, Diels-Alder cycloaddition, etc, and formed a complex crosslinked structure like condensed polycyclic aromatic structure during the cross-linking process of the resin. But the cure reaction mechanism of ethynyl resins is still poorly understood. The insolubility of the cured resins increased the difficulties to clarify the structures of the crosslinked resin and then illustrate the curing mechanism.

Thermal behavior of DMSEPE-TPA resin and its thermal stability

Typical DSC curve of the resin measured under nitrogen was shown in Figure 2. As shown in the figure, there was an exothermic peak with the onset and top temperatures of 233°C and 339°C respectively which was attributed to a cross-linking reaction of the ethynyl groups. This indicated the curing of the resin began at over 233°C. The enthalpy of the cross-linking reaction of the resin was 291.2J/g, which was lower than that of BLJ resin (<400J/g) [7]. The low enthalpy was sometimes important and favourable to the control of heat released during the processability of the resin.

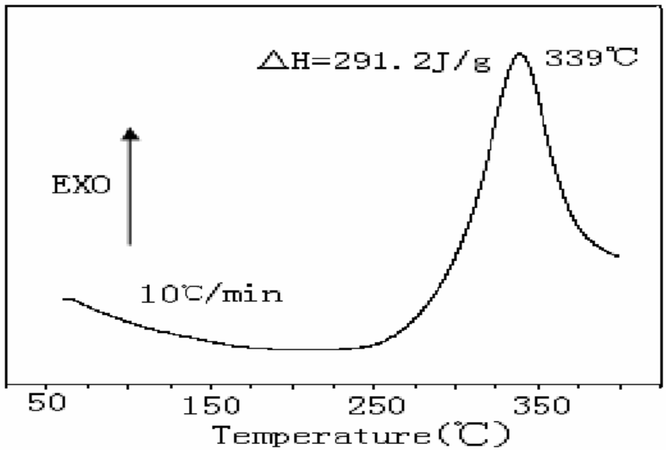


Figure 2 DSC curve of the resin DMSEPE-TPA

Thermal stability of the cured DMSEPE-TPA was determined by using TGA. TGA analyses were conducted under nitrogen and air separately. The results were shown in Figure 3 and Table 1. The decomposition temperature of the cured resin at 5% weight loss was 532°C and 485.6°C under nitrogen and air respectively. The decomposition residues of the cured resin at 800°C were 82.9% and 29.8% under nitrogen and air respectively. This illustrated the cured resin was thermally stable and easy to decompose under the attack of oxygen.

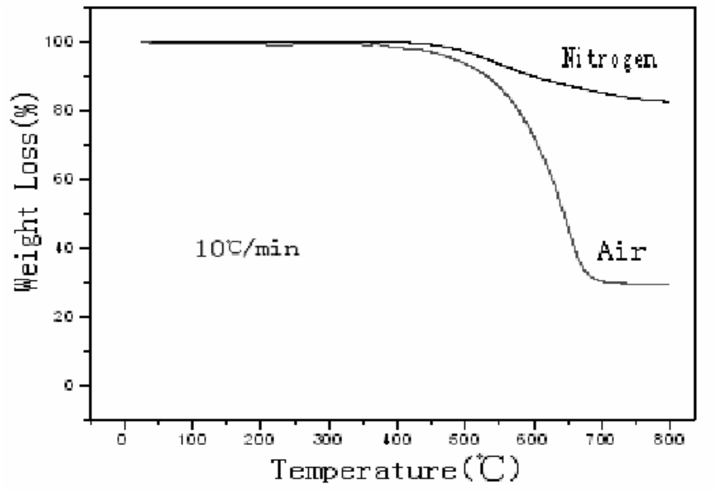


Figure 3 TGA curves of the cured resin in different atmospheres

Table 1 TGA Analysis Results of the Cured Resin in Different Atmospheres

Gas	Td_5°C) [a)]	Residue(%) at 700°C	Residue(%) at 800°C
N_2	532.0	85.8	82.9
Air	485.6	30.5	29.8

a) Td_5: Temperature of 5% weight loss

The formation of ceramics

The cured resin was sintered in a stove at temperature above 1000°C. The crosslinked structures of the resin were destroyed and the organic composition decomposed and inorganic composition remained. At last a ceramic was produced. X-ray diffraction patterns of various resins sintered at different temperatures were shown in Figure 4. As shown in the figure, there was a diffraction peak attributed to free carbon at defined angle 2θ =21.9° for samples sintered at 800°C, 1200°C and 1300°C, where interplanar distance was 4.06 Å. When the temperature arrived at 1300°C, a new peak appeared at 2θ = 35.6° and the intensity of the diffraction peak increased with the increase in temperature. At 1450°C, another two peaks at 2θ = 60.2° and 72.2° occurred. These three peaks with interplanar distances of 2.52, 1.54, and 1.31 Å attributed to β-SiC crystal. These results showed β-SiC ceramic had formed at the temperature above 1300°C. Figure 5 showed the FT-IR spectrum of the sintered resin. As shown in Figure 5, the absorption band at 825 cm^{-1} belonged to the stretching vibration of Si-C bond of SiC appeared. And the adsorptions at 951cm^{-1} and 1107cm^{-1} might attribute to the absorption of the C-C bond (because the resin was carbon rich), and Si-N bond (the cured resin was sintered under the N_2 atmosphere). The FT-IR result also demonstrated the SiC had positively formed.

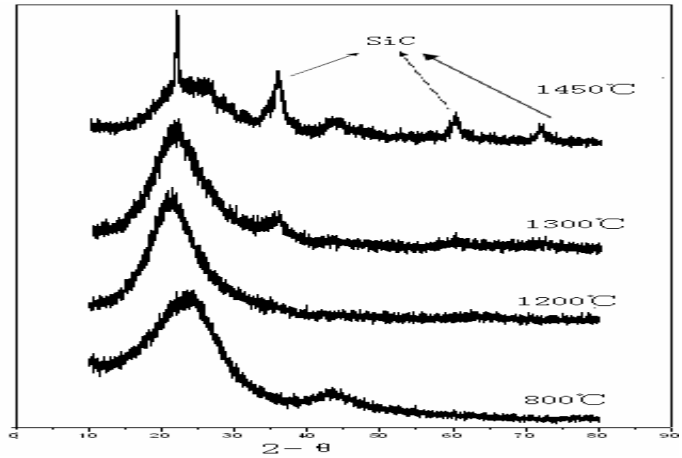


Figure 4 X-ray Diffraction patterns of cured DMSEPE-TPA resin sintered at various temperatures

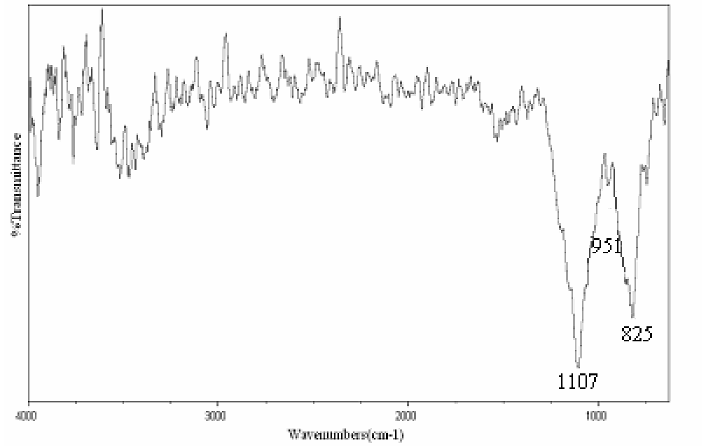
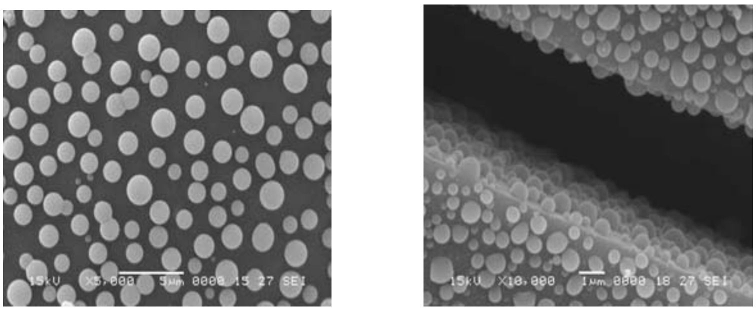


Figure 5 FT-IR spectrum of cured DMSEPE-TPA resin after sintered at 1450°C



a b

Figure 6 SEM microphotograph of the sintered resin

Direct evidence for the morphology of the sintered resin was obtained by scanning electron microscopy (SEM). The images of a sample were shown in Figure 6. As shown in the figure, there were a lot of isolated particles which were embeded in or grew out on the surface of the sintered resin orderly. The particle shape was spherical, and the diameter of the particle was mostly about 1μm (Figure 6 (a)). Figure 6 (b) showed that there were some cracks in the samples. This indicated that there were microspheres on all faces of the samples. Further investigation is being undertaken.

Conclusion

A novel resin poly(dimethylsilyleneethynylenephenyleneethynylene) terminated with phenylacetylene (DMSEPE-TPA) was prepared by the condensation reaction between dimethyldichlorosilane and organic magnesium reagent. The resin can be cured at the temperature above 233°C with a low enthalpy (291J/g). The decomposition temperature Td_5 of the cured resin arrived at 485.6°C and 532°C and the residue yields at 800°C were 29.8% and 82.9% under air and nitrogen respectively. The resin had high heat-resistant property. The cured resin was sintered at temperature above 1300°C and the β-SiC ceramic was formed.

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