



Effect of neutral nickel catalyst on cure process of silicon-containing polyarylacetylene



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ABSTRACT

The curing behavior of silicon-containing polyarylacetylene (PSA) with nickel acetylacetonate and triphenylphosphine ($\text{Ni}(\text{acac})_2/\text{PPh}_3$) as a catalyst was studied by differential scanning calorimetry (DSC), FTIR in situ monitoring and gel time analysis. The thermal stability of the cured PSA was performed on thermogravimeter. The results show that the catalytic effect of $\text{Ni}(\text{acac})_2/\text{PPh}_3$ on curing reaction of PSA is distinct. The peak temperature of cure reaction of PSA was decreased by 100 °C when the catalyst was added into the resin at a molar ratio of 100:1. The conversion ratio of the terminal alkynes in PSA cured with the catalyst is higher than that cured without catalyst during heating. The internal alkynes in PSA are apt to achieve when the catalyst is added in the early stage of curing process. The apparent activation energy of the gel process of PSA with the catalyst declined about 30%. The catalyst-added PSA was cured at lower temperature. The temperature at 5% mass loss and residual yield at 800 °C in N_2 of the cured PSA with the catalyst-added and catalyst-free are 615 °C and 89%, 618 °C and 90%, respectively.

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1. Introduction

Polyarylacetylene can be modified by the introduction of organic silicon to give a silicon-containing polyarylacetylene (PSA), which is a new kind of aromatic alkynes thermosetting resin. There are no volatile substances during the heat curing process of PSA resin, and the highly cross-linked network structure can be formed by thermal self-polymerization. Organic silicon modified polyarylacetylene can not only enhance the heat resistance, but also perform excellent mechanical properties, dielectric properties and high temperature ceramic performance [1–5]. With excellent properties, the cured PSA can be used as the high temperature resistant materials, wave-transmitting materials, semiconductor materials, and ceramic precursors and so on. It can be potentially applied in information, electronics and aerospace applications [6–10].

Late transition metal catalysts have been used in polymerization of aromatic alkynes. Diacetylenylbenzene and propargyl alcohol can be copolymerized by palladium-based catalyst to give a soluble copolymer [11]. In order to obviate releasing large amounts of heat, even explosion and undergoing severe shrinkage during the curing exothermic reaction of diacetylenylbenzene monomer, Katzman et al. used a metal nickel catalyst to cyclotrimerize the

diacetylenylbenzene and prepared an easy-to-process prepolymer [12]. Tseng et al. studied the curing process of polyarylacetylene prepolymerized by nickel catalyst and thermal reaction [13], the char yield at 800 °C of the cured prepolymer was 86%, and the temperature at 10% weight loss of the cured prepolymer was 685 °C. Meriwether et al. probed into the polymerization of acetylenyl compounds, and found that bis(triphenylphosphine) dicarbonylnickel could catalyze acetylenyl groups to cyclotrimerize and linearly polymerize [14]. Pasynkiewicz et al. investigated the mechanism of alkynes catalytic polymerization [15]. The polymerization of alkynes with nickelocene-based catalysts proceeds according to a coordination–insertion mechanism to form linear polymers and cyclic trimers. Ruthenium [16,17] and rhodium [18,19] complexes have been already used in researches on catalytic cyclotrimerization of terminal acetylenes. Ziegler catalyst was used to catalyze the cyclotrimerization of acetylenyl groups as well. The concentration of catalyst did not affect the molecular weight of polybenzene [20]. Late transition metal catalysts can not only catalyze polymerization of aromatic alkynes, but also be used to control the structure of polymer. Liu et al. has used late transition metal to cure polyarylacetylene to form the star structure of macromolecule [21]. Zhang et al. used rhodium catalyst to produce a linear polymer [22]. Nickel acetylacetonate has been used in the curing of the PSA resin, which could reduce the curing temperature of PSA resin, but had no impact on the thermal stability of cured PSA [23]. In this paper, authors use

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nickel acetylacetonate and triphenyl phosphine as a catalyst to study the conversion ratio of alkynyl groups in PSA during curing, and explore the catalytic curing process and thermal stability of the cured products.

2. Experimental

2.1. Material

Silicon-containing polyarylacetylene resin was prepared in terms of the Ref. [4] by Grignard process ($M_n = 1473$ by MALDI-TOF MS). Nickel acetylacetonate ($\text{Ni}(\text{acac})_2$) and triphenyl phosphine (PPh_3) were purchased from Shanghai Aladdin Reagents Co., Ltd. and used without further purification. Tetrahydrofuran (THF) was refluxed with sodium/benzophenone ketyl and was distilled under nitrogen before use.

2.2. Preparation of PSA with catalyst

The atmosphere in a 100 mL Schlenk flask was replaced with dry argon. The catalysts $\text{Ni}(\text{acac})_2$ and PPh_3 were quantitatively dissolved in dried THF in the flask, and the molar ratios of $\text{Ni}(\text{acac})_2$ and PPh_3 were 1:0, 1:1 and 1:2, respectively. Namely, the $\text{Ni}(\text{acac})_2/2\text{PPh}_3$ is designated to the molar ratio of 1:2. The PSA (2 g, 1.36 mol) was dissolved in 30 mL of THF in another 100 mL Schlenk flask under argon. A certain amount of the catalyst solution was injected into the PSA solution, and the mixture was magnetically stirred for 30 min at room temperature. THF in the solution was evaporated under vacuum at 45 °C to give a product.

2.3. Characterization

A matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrum was recorded using an A 4800 plus mass spectrometer (AB Sciex Germany) equipped with a solid laser ($\lambda = 355$ nm). PSA was dissolved in THF and mixed with matrix (anthracene) and cationization reagent (sodium iodide). The characteristics of thermal curing were studied by differential scanning calorimetry (DSC) on TA Q2000 at a heating rate of 20 °C/min. Samples approximately 1–2 mg were weighed accurately into aluminum sample pans, covered with an aluminum lid and sealed by crimping. Reference pans were prepared similarly, but without any sample in hermetic pans. The cure was monitored in situ by FTIR spectroscopy using a Nicolet 5700 FTIR spectrometer. The molten sample was coated on KBr round pellet to form a thin film. The coated KBr pellet was put into the hot cell of Thermo's HT-32 which was programmable to control heat rate. The sample was polymerized in HT-32 under air atmosphere. The cure reaction proceeded in the range from room temperature to 350 °C at a heating rate of 5 °C/min in the cell. The data of FTIR were gathered at an interval of 5 min. Each spectrum was the result of 16 scans with a resolution of 4 cm^{-1} . The gel time of the resins was measured in terms of ASTM D3056. The thermal stability of the cured resins was measured by thermogravimetric analysis (TGA) on Mettler-Toledo TGA/DSC1 thermogravimeter in the range between room temperature and 900 °C at a heating rate of 10 °C/min under a nitrogen purge with a flux of 60 mL/min. About 5 mg samples were weighed into ceramic crucibles.

3. Results and discussion

3.1. Catalytic cure of the PSA

Metal nickel complexes $\text{Ni}(\text{acac})_2$, $\text{Ni}(\text{acac})_2$ and PPh_3 were chosen to catalyze the curing of PSA under heating. Fig. 1 shows the DSC thermograms of the PSA and PSA with the catalysts. And

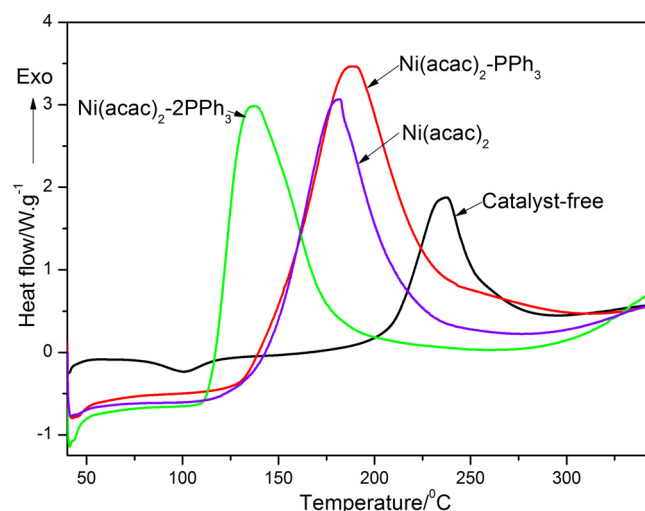


Fig. 1. Comparison of the DSC thermograms PSA and PSA with $\text{Ni}(\text{acac})_2\text{-PPh}_3$ catalyst at various molar ratio 1:0, 1:1 and 1:2, respectively.

the correlation analysis results are listed in Table 1. The DSC studies indicated that the cure of the PSA could occur via thermal self-polymerization, and the temperature of exothermic peak was over 230 °C; the ending temperature of curing process was over 250 °C. With the addition of $\text{Ni}(\text{acac})_2$ and PPh_3 , the temperature of exothermic peak of the PSA decreased apparently, especially it declined nearly 100 °C when the molar ratio of $\text{Ni}(\text{acac})_2$ and PPh_3 was 1:2. This observation suggests that $\text{Ni}(\text{acac})_2$ and PPh_3 catalyst can obviously reduce the curing temperature of PSA. The lowering cure temperature was also observed by Sukumaran et al. [24]. The curing reaction of azide and propargyl derivatives with catalyst was facilitated.

The $\text{Ni}(\text{acac})_2$ and PPh_3 catalyst with a molar ratio of 1 and 2 were used to cure the PSA. The DSC analysis on different dosage of the catalyst for curing PSA is shown in Fig. 2. Addition of $\text{Ni}(\text{acac})_2\text{-}2\text{PPh}_3$ to the PSA shifted the cure exotherm to lower temperature. The peak temperature of curing decreased with the increase of the molar ratio of $\text{Ni}(\text{acac})_2/2\text{PPh}_3$ and the PSA. The peak temperature of curing PSA catalyzed by $\text{Ni}(\text{acac})_2/2\text{PPh}_3$ is 120 °C when the molar ratio of PSA and $\text{Ni}(\text{acac})_2\text{-}2\text{PPh}_3$ is 50:1.

3.2. In situ FTIR monitoring of curing process

The complicated reactions of terminal alkynes will occur when heated. The different structures will form according to the different reaction mechanisms. However, the [2 + 2 + 2] cyclotrimerization of the terminal alkynes giving benzene ring structure is a primary polymerization [13]. In situ FTIR spectroscopy of the PSA cured by thermal self-polymerization and catalytic curing was carried out at progressively ascending temperature during heating. Fig. 3 shows FTIR spectra of the two PSA resins under non-isothermal curing. The gradually disappearing absorption bands of the carbon-hydrogen bond of terminal alkynes ($-\text{C}\equiv\text{C}-\text{H}$) at 3294 cm^{-1} are accompanied with increasing the curing temperature. However, the bands of the internal alkynes ($-\text{C}\equiv\text{C}-$) at 2156 cm^{-1} do not

Table 1
DSC results of PSA and PSA with the catalysts.

Sample	Peak temperature, T_p (°C)	ΔH (J/g)
Catalyst-free	233.5	344.7
$\text{Ni}(\text{acac})_2/0\text{PPh}_3$	179.2	419.5
$\text{Ni}(\text{acac})_2/1\text{PPh}_3$	185.3	521.5
$\text{Ni}(\text{acac})_2/2\text{PPh}_3$	134.5	378.7

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