Synthesis of Allyl-Ended Hyperbranched Organic Silicone Resin by Halloysite-Supported Platinum Catalyst

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ABSTRACT: A novel allyl-ended hyperbranched organic silicone resin (AHSR) was prepared successfully by hydrosilylation between phenyltriallylsilane and 1,1,3,3-tetramethyl disiloxane with halloysite-supported platinum (Pt–halloysite) as the catalyst. The chemical structure of the AHSR was characterized by ^{1}H-NMR and Fourier transform infrared spectroscopy, and its molecular weight was determined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry. The Pt–halloysite catalyst was prepared from chloroplatinic acid and halloysite by the simple wet impregnation method. The transmission electron micrographs of the catalyst showed that the platinum dispersed homogeneously into the halloysite nanotubes. Compared with the traditional homogeneous Speier and Karstedt catalysts, our heterogeneous Pt–halloysite catalyst demonstrated a higher catalytic activity, which was confirmed by IR monitoring of the attenuation of the Si—H stretching band. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: catalysts; composites; hyperbranched

INTRODUCTION

In recent years, there has been considerable interest in dendrimers and hyperbranched polymers because of their unique properties, including a low viscosity, high solubility, and less chain entanglement and better reactivity than linear polymers. Compared with dendrimers, hyperbranched polymers can be prepared by a faster and easier method; thus, they have become more important for society.[1–3] Hyperbranched organic silicone resins possess many special properties, including wide-range thermal stability, good resistance to oxidation, low surface tension and gas permeability, excellent dielectric properties, physiological inertness, and moisture resistance, and they have been applied widely in many branches of industry.[4] The organic functionalization of silicone materials and the synthesis of new functional polymers containing silicone are the two most important strategies for the development of organic silicone materials.

Since the discovery of hexachloroplatinic acid as a very efficient catalyst by Speier in 1957, hydrosilylation has become one of the most important reactions for preparing organosilicon materials in both industry and academia[5] because of its high yield, short reaction time, and negligible side products.[6] The hydrosilylation process has commonly been used in the catalytic crosslinking of polysiloxanes.[7] Homogeneous Speier and Karstedt catalysts have a high catalytic activity and good solubility in the products or solvents and are still used widely; however, they can be used only once, and the costly platinum cannot be recycled. Moreover, the heterogeneous platinum catalysts may be recycled many times, although their catalytic activity is generally lower. Such catalysts can be prepared by the process of platinum metals and their compounds or complexes supported on inorganic materials or polymers, including silica,[8] alumina, activated carbon, zeolite, and poly (methyl methacrylate).[9] Their low activities are attributed to the low dispersion of platinum on the supports.

Halloysite is a double-layered aluminosilicate mineral that has a predominantly hollow tubular structure. The diameter and length of the tubes are about 20–40 nm and 0.5–2.0 μm, respectively. Also, halloysite is an economically viable raw material that can be mined from a corresponding deposit as a raw mineral. It has found wide application because of its low cost, high specific surface area, and excellent chemical and thermal stability.[10,11] To our knowledge, this is the first report on the preparation of a heterogeneous platinum catalyst supported on halloysite and its use as a catalyst. In this study, we employed this compound to catalyze the synthesis of allyl-ended hyperbranched organic silicone resins (AHSRs), and it demonstrated a very high catalytic activity. On the basis of this experiment, we
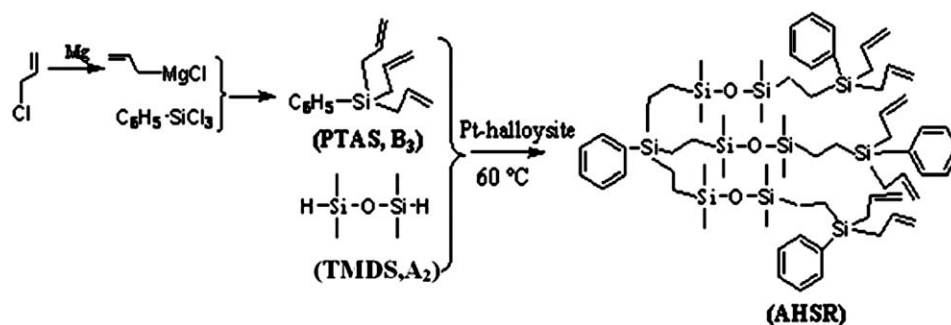
Figure 1 Synthetic scheme of AHSR. TMDS is 1,1,3,3-tetramethyl disiloxane; A2 means bifunctionality; B3 means trifunctionality

concluded that the halloysite-supported platinum (Pt–halloysite) composite could is a promising catalyst for future use.

EXPERIMENTAL

Materials and measurements

Tetrahydrofuran (THF) and 1,1,3,3-tetramethyl disiloxane (TMDS) were obtained from Sinopharm Chemical Reagent Corp. (Shanghai, China) and were used after distillation. Magnesium turnings, ammonium chloride, and other materials were all purchased from Tianjin Kermel Chemical Reagent Corp. Allyl chloride (AC) was obtained from Yueyang Petrochemical Co. Phenyltrichlorosilane (PTCS) was purchased from Zhejiang Zhongtian Chemical Corp. AC, TMDS, and PTCS were dried over 24 h by 4-Å molecular sieves before use.

Fourier transform infrared (FTIR) measurements were performed on a NEXUS 470 FTIR (Thermo Nicolet USA) spectrometer (KBr). ^{1}H-NMR spectra were measured in CDCl$_3$ on an AVANCE III-400 (Bruker) spectrometer with tetramethylsilane as an internal standard. The molecular weight was determined by an Applied Biosystems Voyager 4418 matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI–TOF MS, 1200HPLC-QTOF-MS USA Brucker dalton) spectrometer with acetone, 30% acetonitrile, and 0.3% acetic acid trifluoride as a mixed solvent (accelerating voltage = 20 kV, number of laser shots = 300/spectrum, laser repeating rate = 20.0 Hz, with sodium trifluoroacetate as the cationizing salt).

High-resolution transmission electron microscopy (TEM; Tecnai G2 20 S-TWIN, FEI, USA) was used to examine the morphology of the samples. X-ray photoelectron spectroscopy (XPS) analysis was performed on a Multilab 2000 spectrometer XPS (VG MultiLab 2000, UK) with an Mg Kα X-ray source (1253. 6 eV).

Synthesis of the Pt–halloysite catalysts

Halloysite powder (200 g) was immersed in 250 mL of H$_2$O$_2$ (30 wt %) for about 12 h, and the mixture was filtered. The filter cake was washed twice with deionized water. Then, 50 mL of deionized water was mixed with the filter cake and centrifuged for 5 min at 4800 rpm/min at room temperature. Purified halloysite was obtained after the supernatant solid was taken out and baked for about 5 h at 400°C.

For the preparation of the Pt/halloysite composite, 0.2 wt % Pt^{4+} (on the basis of the total of the composite) was used through the experiments. Chloroplatinic acid (0.08 g) and isopropyl alcohol (2.42 g) were charged into a three-necked flask equipped with a stirrer, condenser, thermometer, and nitrogen inlet and stirred for 1 h at room temperature. Then, 15.0 g of purified halloysite and 50 mL of ethanol were added to the flask and reacted for 10 min with 700-W ultrasound radiation, and then, 0.2 g of NaHCO$_3$ was added and reacted for 10 min under ultrasonic conditions and stirred for 24 h at room temperature. The reaction mixture was put into a rotating evaporator
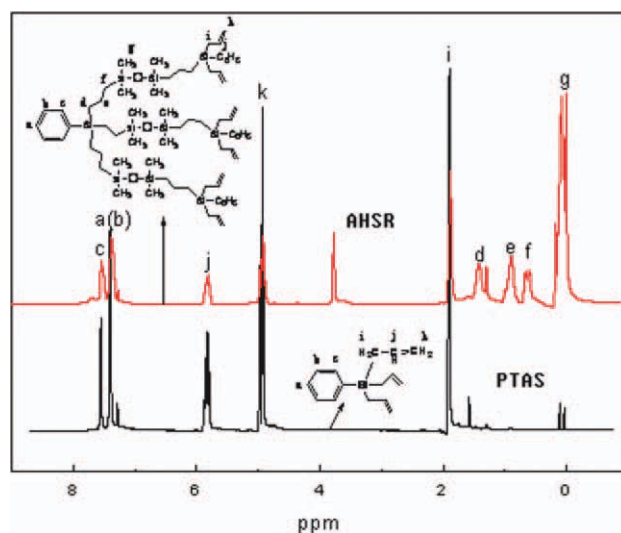

Figure 2 ^{1}H-NMR spectra of PTAS and AHSR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
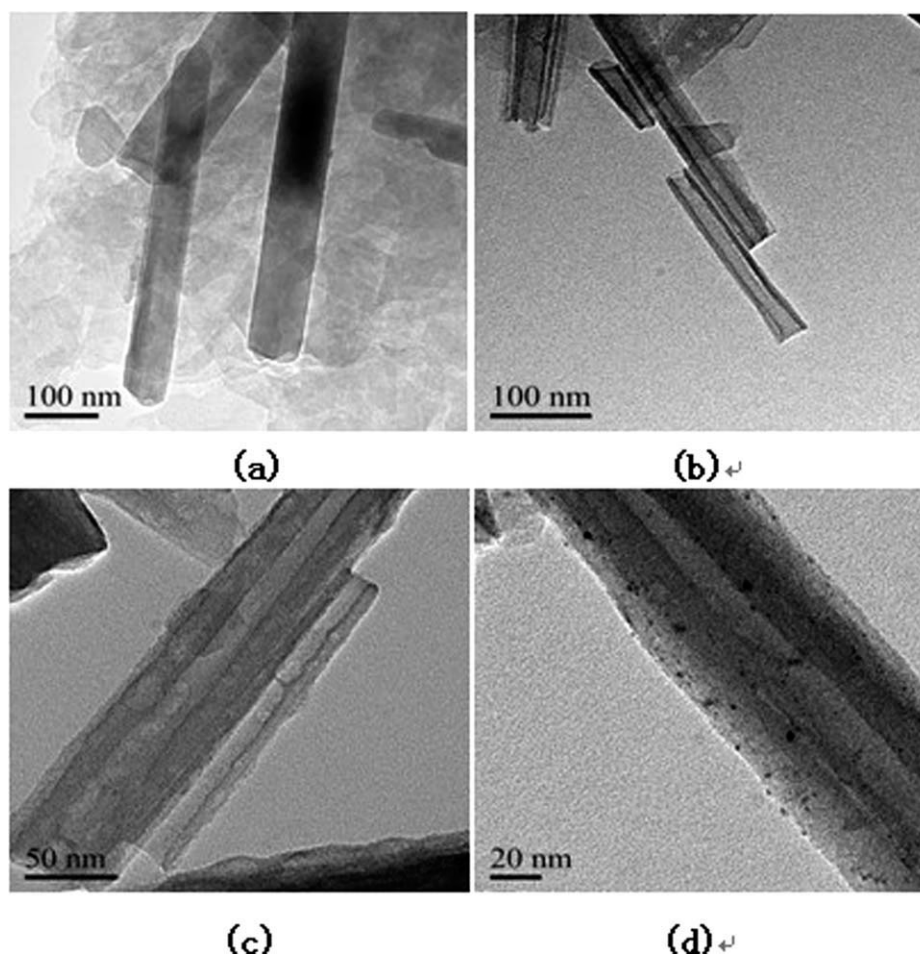
Figure 3 TEM micrographs of the (a) crude halloysite, (b) purified halloysite, (c) Pt–halloysite composite, and (d) reduced Pt–halloysite catalyst by H_2.

under a pressure of 3–5 mmHg at 60–70°C after the reaction mixture was passed through a pressurized filter and the filter cake was washed twice with 5 mL of deionized water. Finally, a yellowish, loose solid Pt–halloysite (70.5 g) was obtained.

Synthesis of AHSR

The synthesis scheme of the AHSR is shown in Figure 1.

To synthesize the AHSR, the route and recipe are described as follows: 5.37 g (0.22 mol) of magnesium turnings, 20.00 g of THF, and 0.05 g of iodine were added to a four-necked flask equipped with stirrer, cooler, thermometer, and nitrogen inlet. A mixture of 13.00 g (0.17 mol) of AC and 20.00 g of THF was added dropwise into the flask and reacted for 2 h at 40°C under a nitrogen atmosphere. The residual magnesium turnings were filtered, and the excess AC was removed under a pressure of 500–600 mmHg at 40°C. The Grignard reagent of AC was obtained with a yield of about 75%.

PTCS (15.00 g, 0.07 mol) and Grignard reagent of AC (50.11 g, 0.50 mol) were added to a three-necked flask equipped with a stirrer, cooler, and thermometer and reacted for 24 h in an ice bath at about 0°C. Then, 50 mL of saturated NH$_4$Cl solution was added to the flask, and the mixture was filtered. After the previously layered mixture was washed twice with 10 mL of deionized water, the filtrate was dried for 12 h by 5.00 g of MgSO$_4$. Yellowish liquid phenyltriallylsilane (PTAS; 18.29 g) with a yield of 91.5% was obtained after the solvent THF was removed under a pressure of 3–5 mmHg at 100°C for 60 min.

PTAS (5.00 g, 0.0219 mol), TMDS (2.21 g, 0.0164 mol), and Pt–halloysite catalyst (1.4 g) were added to a three-necked flask equipped with a stirrer, cooler, and thermometer and reacted for 2 h at 60°C. A yellowish liquid AHSR with a yield of 92.9% was obtained after the solvent THF was removed under a pressure of 3–5 mmHg at 140°C for 60 min.

PTAS (^{1}H-NMR, δ): 1.89–1.91 (—CH_2—CH=CH$_2$), 4.91–4.98 (—CH$_2$—CH=CH_2), 5.78–5.89 (—CH$_2$—CH=CH$_2$), 7.39–7.56 (—C$_6$$H_4$).

Figure 5 Conversion of the hydrosilylation versus reaction time. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
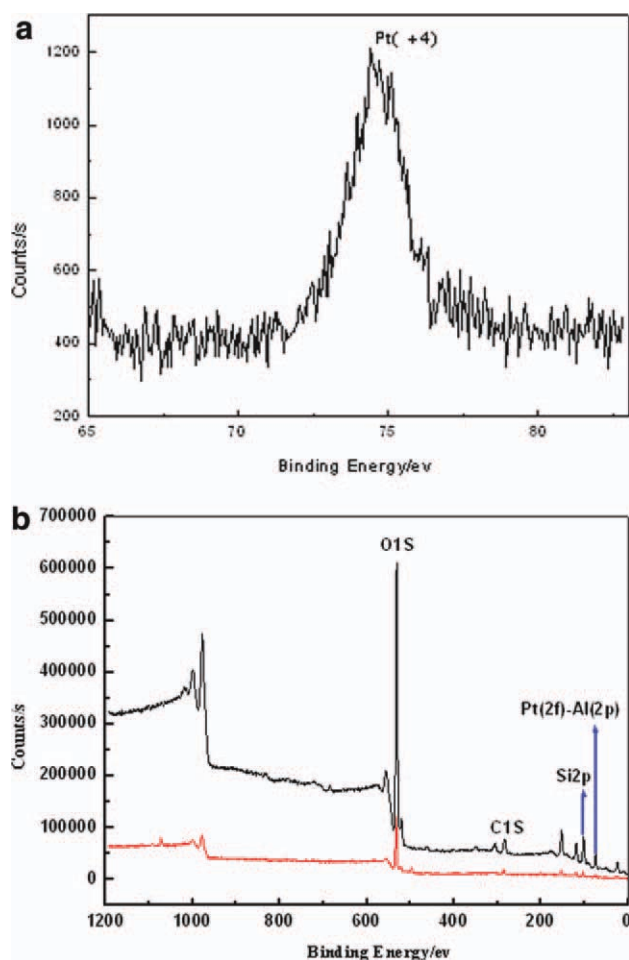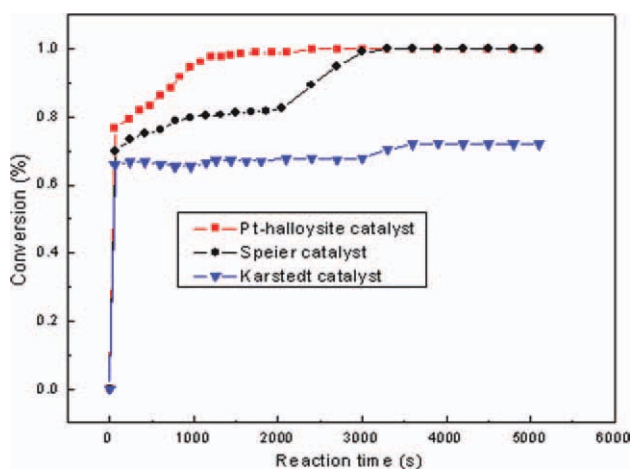
Figure 4 XPS spectra of Pt^{4+} on the (a) Pt–halloysite and (b) Pt–halloysite composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

tively. Figure 3(c) shows the chloroplatinic acid impregnated halloysite. To determine the distribution of Pt^{4+} on halloysite, the Pt–halloysite was was treated and observed under TEM. The treatment is described as follows: the Pt–halloysite catalyst was baked for 3 h at 300°C in a pipe furnace under the flow of pure hydrogen at a heating rate of 2°C/min from 25 to 300°C. Pt^{4+} in the Pt–halloysite was reduced to Pt(0), as confirmed by the platinum nanoparticles observed in Figure 3(d). The diameter of the Pt(0) nanoparticles was under 10 nm, and they were homogeneously dispersed inside the halloysite nanotubes. The visible Pt particles derived from Pt^{4+} showed that there existed Pt^{4+} in the Pt–halloysite composite. The XPS scans of Pt^{4+}[12] and the Pt–halloysite composite microspheres are shown in Figure 4. The occurrence of Pt^{4+} (Pt 2f) in Figure 4(a) and Pt 2f, O 1S, Si 2p, and Al 2p in Figure 4(b)

AHSR (^{1}H-NMR, δ): 0.01–0.17 (—Si—CH_3), 0.60–0.67 (C$_6$H$_5$—Si—CH_2—CH$_2$—), 0.90 (C$_6$H$_5$—Si—CH$_2$—CH_2—CH$_2$—), 0.89–1.00 (C$_6$H$_5$—Si—CH$_2$—CH$_2$—CH_2—), 1.60–1.91 (—CH_2—CH═CH$_2$), 4.89–4.98 (—CH$_2$—CH═CH_2), 5.80–5.86 (—CH$_2$—CH═CH$_2$), 7.39–7.56 (C$_6$H$_4$).

The ^{1}H-NMR spectra of PTAS and AHSR are shown in Figure 2.

RESULTS AND DISCUSSION

Effects on the preparation of the Pt–halloysite composite

The TEM micrographs of the crude halloysite and purified halloysite are shown in Figure 3. From the TEM images, it could be clearly seen that there were some clays and impurities beside the nanotubes in the crude halloysite [Fig. 3(a)]. After purification, the nanotubes of the halloysite were very clear [Fig. 3(b)], and the length and diameter of the regular nanotubes were 0.5–1.5 μm and 20–30 nm, respec-
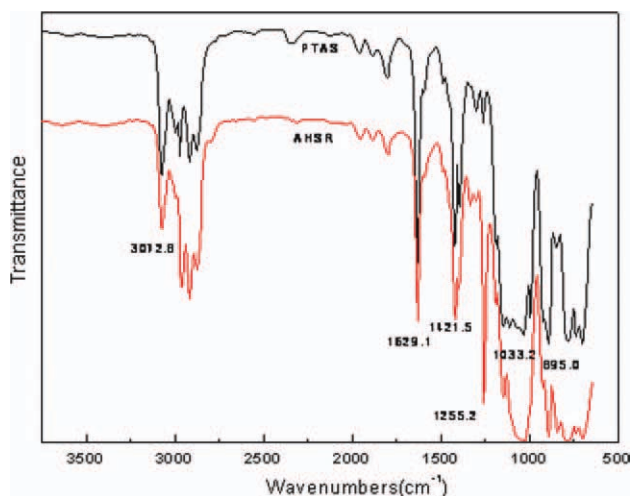

Figure 6 FTIR spectra of PTAS and AHSR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
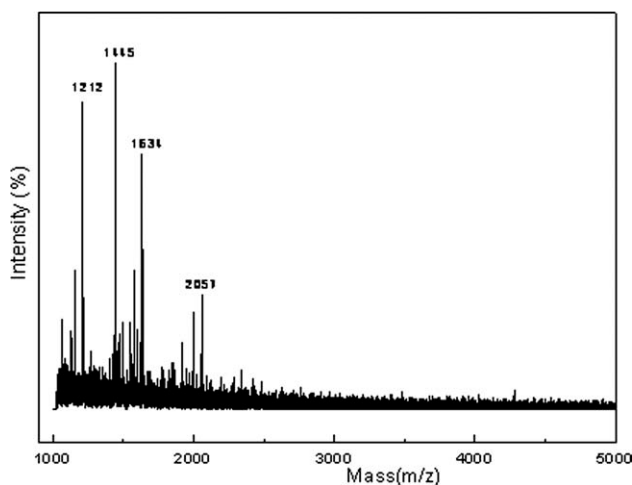
Figure 7 MALDI–TOF MS spectra of the AHSR.

further confirmed the formation of the Pt–halloysite composite.

Catalytic activity of the Pt–halloysite composite was studied by *in situ* FTIR measurement. The relationship between the conversion of the Si—H bond of TMDS and reaction time is shown in Figure 5. The conversion was calculated by the area ratio of the Si—H to the other unchanged bond's area. Compared with the traditional homogeneous Speier[13] and Karstedt catalysts,[14] under the same reaction condition and same amount of Pt^{4+} content, the Pt–halloysite catalyst showed a much higher catalytic activity, and the conversion could be controlled by the reaction time. The high hydrosilylation activity of the Pt–halloysite catalyst was attributed to the high specific surface area, so the Pt^{4+} complex could be dispersed over all of the channels of the halloysite tubes. Therefore, the catalytic activities were enhanced accordingly.

PTAS and AHSR synthesized by the catalysis of the Pt–halloysite composite

The FTIR spectra of PTAS and AHSR are shown in Figure 6. All of absorption peaks of the phenyl at 3073 and 1424 cm^{-1}, the —CH=CH$_2$ group at 1629 cm^{-1}, the —CH$_3$ group at 2940–2960 cm^{-1}, the Si—O—Si group at 1033 cm^{-1} (the curve of PTAS), and the Si—C group at 850–900 cm^{-1} are shown[15] in Figure 6.

MALDI–TOF MS can be used to measure the molecular weight of hyperbranched polymers.[16] In this study, MALDI–TOF MS was also used to determine the molecular weight of our hyperbranched polymers. The MALDI–TOF MS spectrum of the AHSR is shown in Figure 7. The main peaks were observed at $m/z = 1212$, 1445, 1634, and 2058. According to the reaction mechanism of PTAS and TMDS, the molecular weights of the this AHSR and the greater allyl groups bearing AHSR were, respectively, 1316.63 and 3493.06 g/mol.

CONCLUSIONS

In summary, a novel, heterogeneous, high-catalytic-activity halloysite-supported Pt catalyst was obtained by a simple wet impregnation method from halloysite and chloroplatinic acid. With the nano-Pt–halloysite catalyst, a novel liquid AHSR was synthesized successfully from hydrosilylation between PTAS and TMDS. The nano-Pt–halloysite catalyst had a higher activity than those of traditional Speier and Karstedt catalysts, and the degree of hydrosilylation could be controlled by the reaction time.

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