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Preparation of Grafted Microspheres of Pan/cpva with Chemical Crosslinking Method

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Abstract: The graft polymerization of acrylonitrile on CPVA microspheres were performed in an acidic solution polymerization system by using cerium ammonium sulfate as initiator and grafted microspheres PAN/CPVA were prepared. The chemical structure were adequately characterized with infrared spectrum (FTIR) and Scanning Electron Microscope (SEM). Effects of various factors such as reaction time, reaction temperature, the concentration of the initiator were all examined. The experimental results show that under suitable conditions (the temperature was 45°C and the concentration of the initiator was $6.7 \times 10^{-3} \text{ mol L}^{-1}$), the grafted microspheres PAN/CPVA with graft degree of $27 \text{ g } 00\text{g}^{-1}$ can be obtained.

Key words: cerium ammonium sulfate, chemical crosslinking, grafted microspheres

INTRODUCTION

Microsphere materials especially polymer microsphere materials have been widely used in many fields of science and technology (Rasuli *et al.*, 2008; Oster *et al.*, 2001; Liu *et al.*, 2006; Bicak *et al.*, 2001; Yang *et al.*, 2005), because they have many advantages such as larger specific surface area but not easy to reunite, good mechanical properties, solvent resistance and reuse performance compared with microspheres with nanometer and larger particles such as ion exchange resin microspheres (Bayramoglu *et al.*, 2007; Yavuz *et al.*, 2006; Bayramoglu and Arica, 2005). Functional polymer microspheres with excellent biocompatibility used for the immobilization of biological macromolecules and enzymes (Xu *et al.*, 2006; Perez *et al.*, 2006), drug controlled release (Krizova *et al.*, 2005), the separation of biological macro-molecules and DNA (Rittich *et al.*, 2006) gradually become research hotspot. Crosslinked microspheres of Polyvinyl Alcohol (CPVA) were widely used in biomedical sciences because of biocompatibility. While, the CPVA microspheres grafted from different polymers made it useful in different functional biomedical microspheres materials with multi-purpose. These materials were widely used in separation of biological macromolecules, immobilization, tissue engineering, blood purification therapy, intelligent drug delivery and other areas (Dincer and Telefoncu, 2007; Bodugoz-Senturk *et al.*, 2009; Nho *et al.*, 2005). In this study, the graft polymerization of acrylonitrile on CPVA microspheres were performed in an acidic solution polymerization system by using cerium ammonium sulfate as initiator and grafted microspheres PAN/CPVA were prepared. The influence of various factors on the particle size and

performance of micro-spheres were mainly examined, providing valuable reference for preparing grafted PAN/CPVA microspheres with good sphericity and controllable particle size. The research results have certain reference value for the fields such as biomedicine, biochemical engineer, biochemical analysis and related research of enzyme catalysis.

EXPERIMENTAL

Materials and instruments: CPVA micro-spheres (prepared by reverse phase polymerization); Ceric ammonium sulfate (analytical pure) was purchased from Tianjin Bodi Chemical Company; Acrylonitrile (AN, analytical pure) was purchased from Tianjin Fucheng Chemical Reagent Factory. The instruments used in this study were as follows: 438 VP scanning electron microscope (SEM, LEO Company of UK). XSZ-4 Binocular biological microscope with micrometer (Taiyuan Optical Instrument Factory). 1700 Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Company of United States). ZK-82A vacuum oven (Shanghai Experimental Instrument Factory); TG 328 B electronic balance (Shanghai Balance Instrument Factory).

Preparation of grafted PAN/CPVA micro-spheres: 0.20 g crosslinked microspheres were added in the 4-neck flask equipped with stirrer, reflux condenser and thermometer. And then 50 mL DMF was added to make the microspheres swollen for 12 h, followed by adding 2.7 mL acrylonitrile, 20 mL aqueous solution contained 0.33 g^{-1} ceric ammonium sulfate and 0.7 mL sulfuric acid. The microspheres were reacted for 6 h under stirring and nitrogen gas for shielding. Microspheres were separated

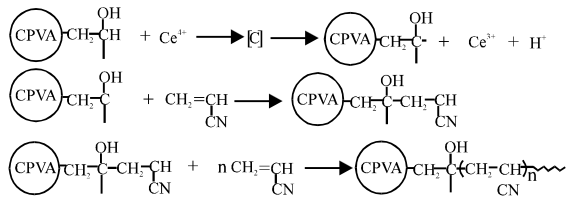


Fig. 1: Preparation reaction of PAN/CPVA microspheres

by filtration, washed several times with DMF to remove impurities and by-products and then washed with distilled water at room temperature, dried in vacuum drying oven to constant weight to obtain grafted microspheres. The preparation reaction of grafted PAN/CPVA microspheres were shown in Fig. 1.

Characterization of CPVA microspheres: The chemical structure of microspheres before and after grafted PAN were characterized using infrared absorption spectra. The morphology, particle size and size distribution were observed using Scanning Electron Microscope (SEM). The graft degree GD ($\text{g } 100 \text{ g}^{-1}$) of polyacrylonitrile on surface of PAN/CPVA microspheres was measured by the gravimetric method, calculated as the following formula. Where m_1 (g) was the quality of crosslinked microspheres CPVA and m_2 (g) was the quality of grafted PAN/CPVA microspheres.

$$\text{GD} = \frac{m_2 - m_1}{m_1} \times 100$$

RESULTS AND DISCUSSION

FTIR spectra of the CPVA microspheres and grafted microspheres PAN/CPVA: The FTIR spectra of CPVA microspheres and grafted microspheres PAN/CPVA were shown in Fig. 2. As can be seen from the Fig. 2, the stretching vibration absorption peak of hydroxyl (hydrogen bond association state) appeared at 3444 cm^{-1} , the symmetric and asymmetric stretching vibration absorption peak of main chain methylene- CH_2 appeared at 2950 cm^{-1} and 2910 cm^{-1} , the bending vibration absorption peak of the main chain methine- CH -appeared at 1411 cm^{-1} and the backbone absorption peaks of polyvinyl appeared at 947 cm^{-1} . The absorption peaks were also found after acetal ether forming reaction, such as the ether bond absorption peak at 1150 cm^{-1} and the residual aldehyde absorption peak at 1720 cm^{-1} . All absorption peaks demonstrated the chemical structure of microspheres CPVA. As can be seen from the FTIR spectra of grafted microspheres PAN/CPVA, the characteristic absorption peak of hydroxyl at 3444 cm^{-1} was significantly weakened and the stretching vibration absorption peak of nitrile group (weak vibration absorbing absorption of $\text{C} = \text{N}$)

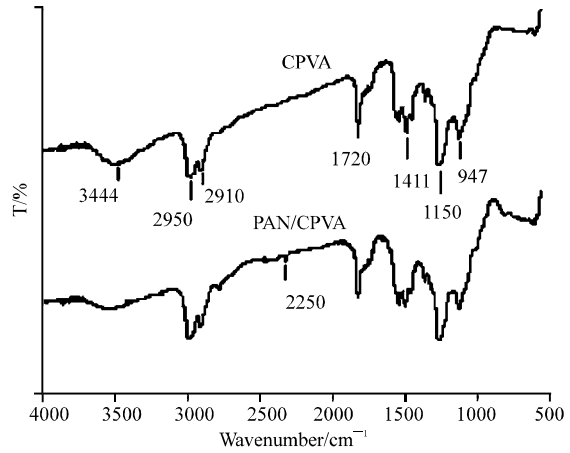


Fig. 2: FTIR spectra of CPVA and PAN/CPVA microspheres

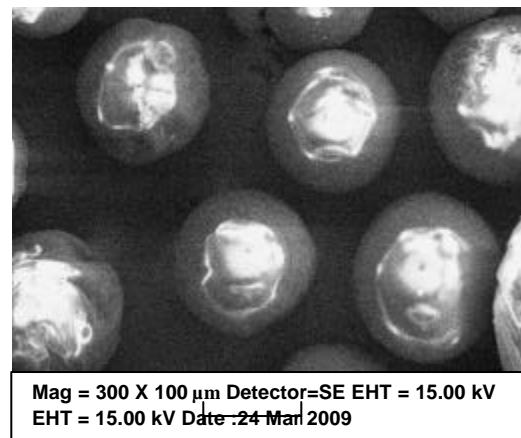


Fig. 3: SEM image of CPVA and PAN/CPVA microspheres

appeared at 2250 cm^{-1} . The changes in the spectral peaks fully demonstrated the surface graft polymerization of acrylonitrile to form grafted microspheres PAN/CPVA was successful.

Morphology of CPVA microspheres: The SEM photograph of CPVA and PAN/CPVA microspheres were shown in Fig. 3. As can be seen from the Fig. the microspheres CPVA showed good sphericity and uniform particle size. After grafted polymerization, the sphericity of microspheres PAN/CPVA (B) Remained good but the surface seemed to be rather rough which was due to the surface of the CPVA microspheres grafted from the macromolecular chains of PAN.

Effects of various factors on graft degree of PAN/CPVA microspheres: Effect of reaction time: It was shown the graft degree of PAN/CPVA microspheres changed curve

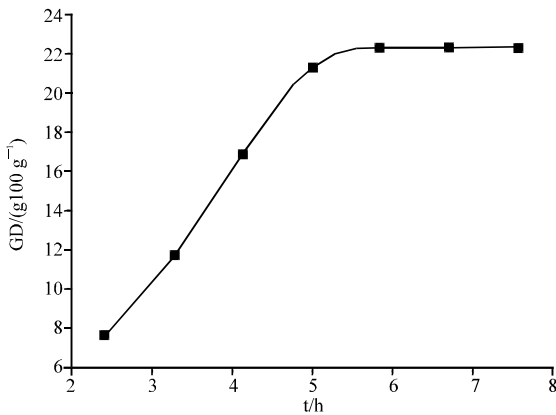


Fig. 4: Effect of reaction time on graft degree of PAN/CPVA microspheres

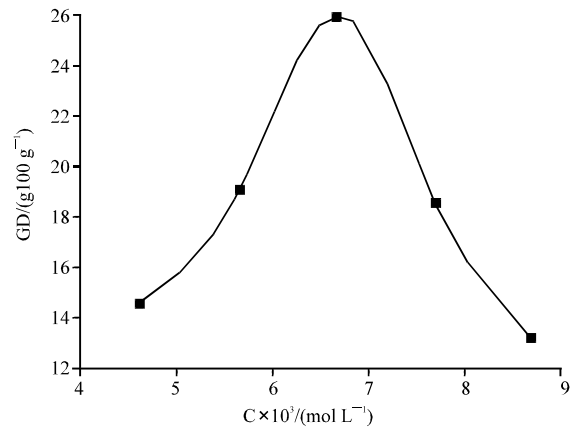


Fig. 6: Effect of cerium salt concentration on graft degree of PAN/CPVA microspheres

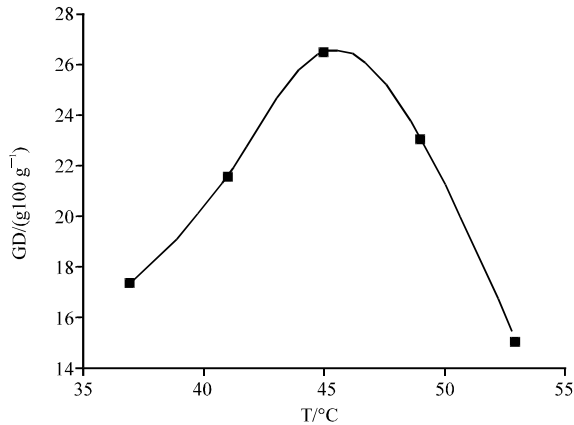


Fig. 5: Effect of temperature on graft degree of PAN/CPVA microspheres

with the reaction time in Fig. 4. As can be seen from the Fig. the graft degree increased constantly with the reaction time. When reacted for 5 h, the change of graft degree was gradually slow and no change for reacted for 6 h. The reason was that the polymer layer formed on the surface of microsphere caused by the long-chain entanglement of the polymer, producing a base power degree. So the monomer can not be activated by the contact point of the polymer layer, causing no graft polymerization, the graft degree did not change after 6 h. Selected 6 h as the suitable reaction time in the research.

Effect of reaction temperature: It was shown the graft degree of PAN/CPVA microspheres changed curve with the temperature in Fig. 5. As can be seen from the Fig, the graft degree was increased with increasing temperature at lower temperature and reached maximum (27.07g 100g⁻¹) at 45°C. While the degree was decreased with the

temperature rised. The reason was that in the range of low temperature, the reaction rate of chain initiator and the chain growth speeded up with elevated temperature, causing increased graft degree. While, the reaction rate of chain transfer and chain termination were also accelerated with elevated temperature, so when the temperature was higher than 45°C, the rapid chain transfer and chain termination reactions led to the total rate of graft polymerization decreased, causing the graft degree reduced. Obviously, in this graft polymerization system, 45°C was suitable reaction temperature.

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Effect of cerium salt concentration: It was shown the graft degree of PAN/CPVA microspheres changed curve with ceric ammonium sulfate concentration when other reaction conditions were fixed in Fig. 6. It can be found that the graft degree first increased and then decreased

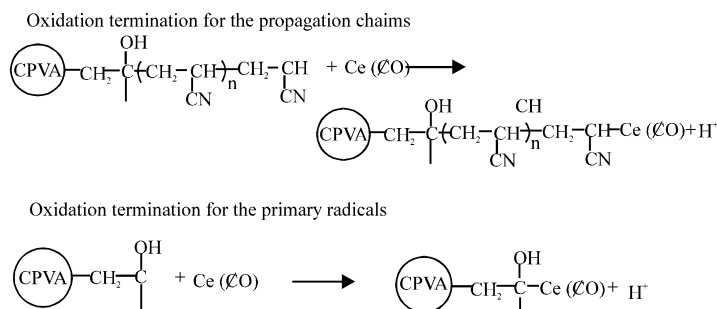


Fig. 7: The schematic of reaction mechanism

with increasing concentration of ceric ammonium sulfate. And the microsphere with graft degree of 25.89 g 100 g⁻¹ can be obtained when the concentration of ceric ammonium sulfate was 6.7×10⁻³ mol L⁻¹. The reason was that the "oxidative terminated" occurred in the process of cerium salt radical initiated polymerization, while the primary radicals can also be inactivated for oxidative termination during the process. The reaction mechanism was shown in Fig. 7.

When the concentration of cerium salt was smaller, more primary radicals were produced on the surface of microspheres with the initiator concentration increased, accelerated the graft polymerization, thus increasing the graft degree. While, when the cerium salt concentration was too large, the oxidation termination reaction speeded up, especially a large number of primary radical termination were oxidation terminated, reducing the number of active sites, so the graft polymerization rate slowed down and the graft degree reduced. Therefore, select 6.7×10⁻³ mol•L⁻¹ was the appropriate concentration of cerium salt in the research.

CONCLUSION

The grafted microspheres PAN/CPVA with controllable particle size were successfully prepared when the graft polymerization of acrylonitrile on CPVA microspheres were performed in an acidic solution polymerization system by using cerium ammonium sulfate as initiator. The main factor affected the ball performance of the reaction system were reaction time, reaction temperature and concentration of cerium salt. For the preparation of grafted microspheres PAN/CPVA with graft degree of about 27g 100 g⁻¹ for further use, the suitable conditions were as follows, the temperature was 45°C reacted for 6 h and the cerium salt concentration was 6.7×10⁻³ mol•L⁻¹.

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