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Synthesis and characterization of the B₃-monomer and hyperbranched poly(aryl ether ketone)s

Abstract Hyperbranched poly(aryl ether ketone)s were prepared by polymerization of hydroquinone (A₂) and 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (B₃). The gelation of hyperbranched poly(aryl ether ketone)s was effectively avoided. Hydroxyl-terminated (HPAEK-OH) and fluoro-terminated (HPAEK-F) hyperbranched poly(aryl ether ketone)s were prepared by using different A₂/B₃ mass ratio. The structure of the B₃ monomer was confirmed by MS, ¹H NMR/IR. The glass transition temperatures of the HPAEK-F and HPAEK-OH are 114°C and 162°C respectively. Thermal stability of HPAEK-F is higher than HPAEK-OH.

Keywords B₃ monomer, hyperbranched poly(ether ether ketone)s, hydroxyl-terminated, fluoro-terminated

1 Introduction

Hyperbranched polymers are highly branched macromolecules with three-dimensional architecture. They have many excellent properties, such as good solubility, low melting viscosity, and large amount of terminal functional groups [1]. Due to their unique chemical and physical characteristics, this kind of material will have broad application prospects in the aspect of the exploitation and application of function materials, and have become a focus in the area of macromolecular science over the past 10 years [2, 3]. Hyperbranched poly(aryl ether ketone)s is one of the hyperbranched polymers. Miller et al. [4], Chu and Hawker [5, 6], and Shu et al. [7, 8] prepared it by reaction of AB₂ monomers. Baek and Tan [9] adopted the polymerization of AB₂+AB to obtain the linear-hyperbranched copolymer and adjusted the AB monomer content to improve the thermal properties and the crystallizability of the polymer. However, the preparation of HPAEK via the A₂+B₃ type of polymerization has not been reported yet. It is reported that [10], while preparing hyperbranched polymers, which are made of the same repeating units, the polymers prepared from the polymerization of A₂ and B₃ monomers have much stronger intermolecular forces and chain entanglement forces than those of the polymers prepared from the polymerization of AB₂ monomers, and in macroscopic behavior, the former exhibits higher heat resistance and glass transition temperatures than the latter. Moreover, it is easy to control the variety of the end groups in the A₂+B₃ polymerization, and we can adjust the properties by selecting the length and the structure of the A₂ unit. Thus, considering the molecule design, we designed and synthesized a kind of B₃ monomer, it can be used to prepared HPAEK, then we obtained HPAEK containing B₃ backbone, and studied the structure and the properties of the B₃ monomer and the polymer.

2 Experimental

2.1 Materials and measurements

4,4’-Difluorobenzophenone was received from Yanji...
Chemical Plant; phloroglucinol (m.p. is 216~218 °C) was purchased from Shanghai Chemical Factory; N,N-dimethylacetamide (DMAc) was obtained from Tianjin chemical reagent plant; hydroquinone, phenol, K₂CO₃ and toluene were purchased from Beijing Chemical Factory; Diphenylsulfone was purchased from Yanbian Chemical Regent Plant and was purified before used.

¹H NMR spectra were recorded on a Bruker 500 MHz spectrometer, take CDCl₃ as solvent; mass spectra were obtained on an American TRACE MS mass spectrograph, sample directly tested. For thermal properties testing, differential scanning calorimetry (DSC) was performed on a Mettler Toledo DSC 821, under an atmosphere of nitrogen at a heating rate of 10 K/min. Element analysis was performed on a Perkin Elmer 2400 analyzer. Infrared spectra were recorded on a Nicolet Impact 410 spectrometer, KBr disc. Viscosity was tested by Ubbelohde viscometer, with concentrated vitriol (0.01 g/dL) as solvent, 25±1 °C, use the equation: \[ \eta_v = \eta_v(t/t_0). \]

2.2 Synthesis and characterization of 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene(B₃ monomer)

A mixture dilute solution of phloroglucinol (0.06 mol) and DMAc (30 ml) was acutely stirred at 165 °C, then tardily added into a turbid solution of 4,4'-difluorobenzophenone (0.84 mol), DMAc (700 ml) and K₂CO₃ (13 g). After that, continue to a reflux temperature for 6 h. The liquid was poured into an aqueous solution of hydrochloric acid, filtered, and a primrose yellow solid was collected. It was washed with a great deal of alcohol at room temperature with the procedure being repeated several times to remove the excess 4,4'-difluorobenzophenone. The solid was heated at reflux with a mixture of alcohol and water to remove the residual 4,4'-difluorobenzophenone. The solid was heated at reflux with a mixture of alcohol and water to remove the residual 4,4'-difluorobenzophenone, dried, then the white powder B₃ monomer (13 g) was collected. The structure of B₃ monomer is shown in Fig. 1.

The IR spectrum is shown in Fig. 2, v/cm⁻¹: 1,656, 1,596 (C=O), 1,238 (C-F); MS (EI⁺): m/z: 721; DSC experiment (m.p.131); element analysis calculated value (%), C 74.93, H 3.75; the measure value (%), C 73.64; H 3.77; ¹H NMR (CDCl₃, δ, ppm): spectrum is shown in Fig. 3: δ₁H 6.612, δ₁H 7.134, δ₁H 7.809, δ₁H 7.834, δ₁H 7.168; the hydrogen chemical shifts adscription and the ratio of peak area are in agreement with the theoretical calculation, therefore, it’s proved that the target product is B₃ monomer.

Fig.1 Structure of the B₃ monomer.

2.3 Synthesis and characterization of the polymer

Hydroquinone (6.6 g), B₃ monomer (14.2 g), fixed quantities of Na₂CO₃, K₂CO₃ and diphenylsulfone were carried into a 250 ml three-neck flask equipped with a mechanical stirrer, a thermometer and a water absorbent filter paper. The mixture was heated at 160 °C (1 h), 180 °C (1 h), 200 °C (1 h), 260 °C (3 h), 280 °C (2 h) under N₂. The reaction product is poured into deionized water and crushed. The polymer was washed with acetone and methanol to remove the solvent and the low molecular polymer then washed with hot deionized water to remove the salt which was imbedded in the polymer. It was then dried and a gray polymer polymer HPAEK-OH was obtained (the structure is shown in Fig. 4), \[ \eta_v = 0.31 \text{ dL/g.} \] If the quantities of hydroquinone and B₃