Front. Chem. China (2006) 2: 203–206
DOI 10.1007/s 11458-006-0015-z

RESEARCH ARTICLE

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Synthesis and characterization of the B_3-monomer and hyperbranched poly(aryl ether ketone)s

Abstract Hyperbranched poly(aryl ether ketone)s were prepared by polymerization of hydroquinone (A_2) and 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene (B_3). 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 A_2 /B_3 mass ratio. The structure of the B_3 monomer was confirmed by MS, ^{1}H 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 B_3 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 AB_2 monomers. Baek and Tan [9] adopted the polymerization of AB_2+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 A_2+B_3 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 A_2 and B_3 monomers have much stronger intermolecular forces and chain entanglement forces than those of the polymers prepared from the polymerization of AB_2 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 A_2+B_3 polymerization, and we can adjust the properties by selecting the length and the structure of the A_2 unit. Thus, considering the molecule design, we designed and synthesized a kind of B_3 monomer, it can be used to prepared HPAEK, then we obtained HPAEK containing B_3 backbone, and studied the structure and the properties of the B_3 monomer and the polymer.

designed and synthesized a kind of B_3 monomer which can be used to prepared HPAEK, then we obtained HPAEK containing B_3 type of skeletal structure, and studied the structure and the properties of the B_3 monomer and the polymer.

2 Experimental

2.1 Materials and measurements

4,4′-Difluorobenzophenone was received from Yanji

Translated from *Acta Scientiarum Naturalium Universitatis Jilinensis*, 2005, 5 (in Chinese)

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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, K_2CO_3 and toluene were purchased from Beijing Chemical Factory; Diphenylsulfone was purchased from Yanbian Chemical Regent Plant and was purified before used.

^{1}H NMR spectra were recorded on a Bruker 500 MHz spectrometer, take $CDCl_3$ 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: $\eta_{iv}=\eta_{iv}(t/t_0)$.

2.2 Synthesis and characterization of 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene(B_3 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 K_2CO_3(13g). 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, dried, then the white powder B_3 monomer (13 g) was collected. The structure of B_3 monomer is shown in Fig. 1.

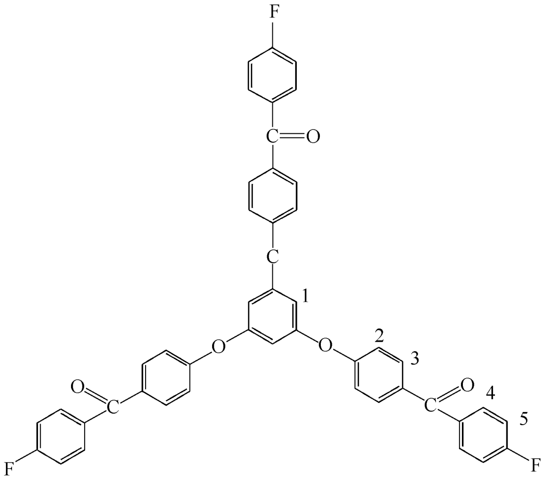

Fig.1 Structure of the B_3 monomer.

The IR spectrum is shown in Fig. 2, v/cm^{-1}:1,656, 1,596 (C=O), 1,238 (C-F); MS (EI^{+1}); *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; ^{1}H NMR ($CDCl_3$, δ, ppm): spectrum is shown in Fig. 3: δ_{H1} 6.612, δ_{H2}7.134, δ_{H3} 7.809, δ_{H4} 7.834, δ_{H5}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 B_3 monomer.

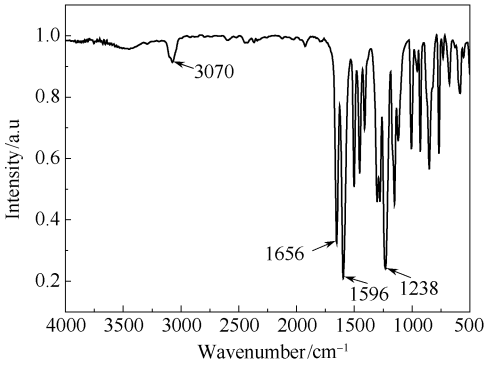

Fig.2 Infrared spectra of the B_3 monomer

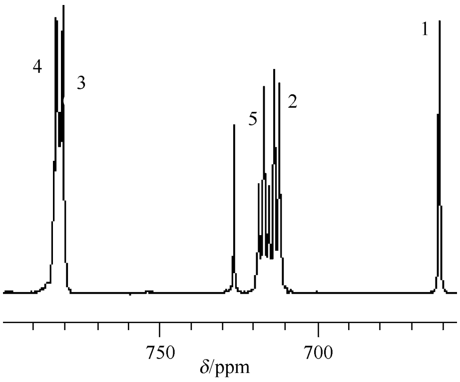

Fig.3 ^{1}H NMR of the B_3 monomer

2.3 Synthesis and characterization of the polymer

Hydroquinone (6.6 g), B_3 monomer (14.2g), fixed quantities of Na_2CO_3, K_2CO_3 and dipheny lsulfone were carried into a 250ml 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 N_2. 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 grayer powder polymer HPAEK-OH was obtained (the structure is shown in Fig. 4), η_{iv} 0.31 dL/g. If the quantities of hydroquinone and B_3

monomer were changed to 1.6 g and 14.2 g but kept the other reaction condition and dealing process the same as those of HPAEK-OH, the white powder polymer HPAEK-F was obtained (the structure is shown in Fig. 4), η_{iv} 0.12 dL/g. From Fig. 5 we can see that, the IR spectrum of HPAEK-OH exhibits obvious O–H characteristic absorption peak at 3,440 cm-^{1}, but HPAEK-F does not have it. The result illustrates that, HPAEK with different terminal groups can be prepared by changing the feed ratio of A_2 to B_3 monomer.

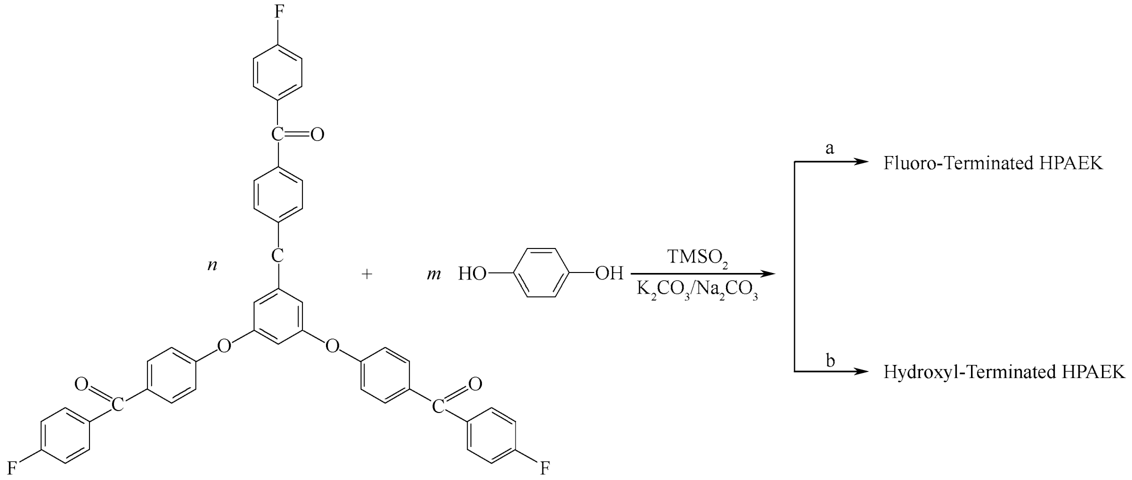

Fig.4 Chemical structure of the hyperbranched poly(aryl ether ketone)s (a) *m*:*n* =0.48(function group ratio);(b) *m*:*n* =2.03(function group ratio)

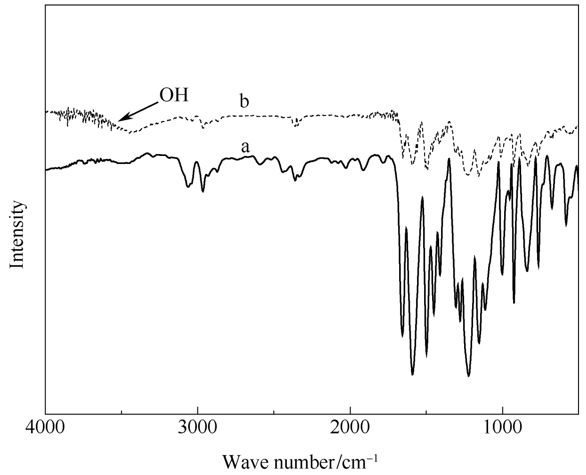

Fig.5 Infrared spectra of the HPAEK-F(a) and HPAEK-OH(b)

3 Results and discussion

3.1 Synthesis and properties of B_3 monomer

The preparation of B_3 monomers was by means of dropping the phloroglucinol dilute solution into the DMAc solution that contains a great deal of 4,4'-difluorobenzophenone. This kept the 4,4'-difluorobenzophenone monomer in the reaction system higher so that phenol-hydroxyl could react with the difluoro monomer and reduce the formation of low molecular polymers. In the structure of B_3 monomer, the electroaffinity of the monomer was increased because carbonyl and fluoro have strong electron-withdrawing effect, and its activity was similar to that of 4,4'-difluorobenzophenone.

3.2 Synthesis of hyperbranched polymers

HPEEK with different terminated groups was prepared by controlling the feed ratio of A_2 to B_3 in the nongel region. Therefore, gelation was effective. When A_2:B_3 (function group ratio) <0.5, fluoro-terminated (HPAEK-F) hyperbranched poly(ether ether ketone)s was obtained; when A_2:B_3 (function group ratio) >2.0, hydroxyl-terminated (HPAEK-OH) hyperbranched poly(ether ether ketone)s was obtained. In order to synthesize high molecular weight polymers, the feed ratio of A_2 to B_3 should approach the gel point as much as possible.

3.3 The inherent viscosity of the polymers

HPAEK prepared by the polymerization of A_2+B_3 cannot be dissolved in the routine organic solvent, but they can be dissolved in concentrated vitriol, so only concentrated vitriol can be adopted as the solvent to test the inherent viscosity of the polymer. HPAEK-OH and HPAEK-F have the same backbone structure and different terminal groups, but there are great differences between them. The inherent viscosity of HPAEK-OH is obviously higher than that of HPAEK-F. The reason lies in the fact that hyperbranched polymers contain lots of terminal groups, HPAEK-OH is terminated with hydroxyl, which belongs to polar function groups; it is easy to form hydrogen bonding between the polymer molecules and have strong intermolecular forces, hence HPAEK-OH has a higher inherent viscosity.

3.4 Thermal properties of the polymers

The thermal properties of polymer are the external exhibition of the internal molecular structure factor [11]. Figure 6 shows that the glass transition temperature of HPAEK-OH is 162 °C, and there is a rather obtuse melting peak (T_m=234 °C); HPAEK-F has only a T_g (T_g=114 °C), and it is far less than that of HPAEK-OH. This is because of the strong polar hydroxyl and the structure characteristic of hyperbranched polymers, it is easy to form hydrogen bonding in and between the HPAEK-OH molecules, the intermolecular forces are strong and the molecular chains are packing tightly, so HPAEK-OH has a higher glass transition temperature and certain crystallizability in contrast to HPEEK-F. Comparing their TGA curves (Fig. 7) we can know that, the thermal gravity temperature of HPAEK-F, with a 5% weight loss is 135 °C higher than that of HPAEK-OH. Because hyperbranched polymer ends contain a lot of function groups, the thermal stability of benzene-hydroxyl bond is much lower than that of benzene-fluoro bond.

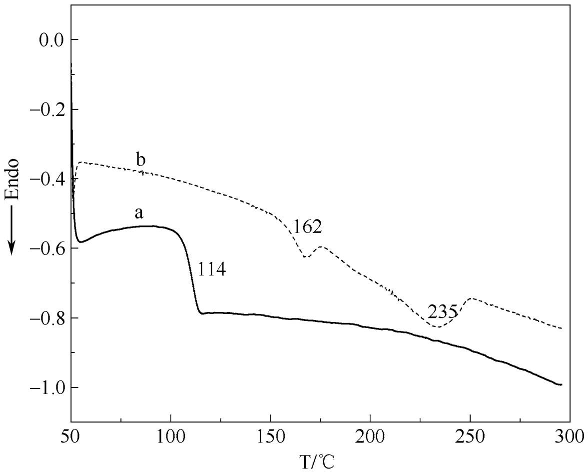

Fig.6 DSC of the HPAEK-F(a) and HPAEK-OH (b)

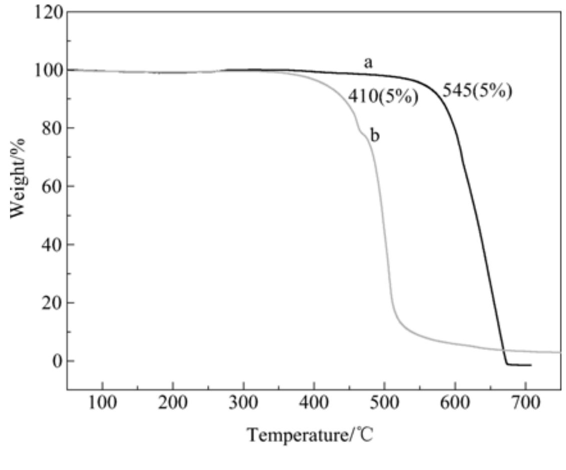

Fig.7 TGA of the HPAEK-F(a) and HPEEK-OH (b)

4 Conclusions

Based on nucleophilic substitution reactions, we synthesized a kind of B_3 fluoro-terminated monomer which can be used to prepare hyperbranched poly(aryl ether ketone)s. The structure of the B_3 monomer was confirmed by MS, ^{1}H NMR/IR. By means of A_2+B_3 type of polymerization, adopting 1,3,5-tris[4-(4-fluorobenzoyl) phenoxy] benzene as B_3 monomer and hydroquinone as A_2 monomer, different end-terminated hyperbranched poly(aryl ether ketone)s were prepared by using different ratio of A_2 and B_3. We found that the polarity of end groups have an effect on the thermal properties and the inherent viscosity of the polymer. This established a good foundation for preparing other kinds of hyperbranched poly(aryl ether ketone)s with different chain structure and end groups.

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