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A series of hyperbranched poly(ether ether ketones) with different chain length between branching point (L) were prepared using a A$_2$ + B$_3$ methodology, in which the A$_2$ is hydroxyl-terminated PEEK oligomer. The L affects the properties of the polymers such as the inherent viscosity, the degree of crystallinity, the thermal properties of the polymers etc. The polymer with a L$_2$ ≈ 8 had T_g (122.4°C), T_c (200.2°C), and broad T_m (247.4°C). With the increment of L, up to the point L$_2$ ≈ 20 and L$_2$ ≈ 35, the polymers become semi-crystalline, with a melting point of 300.9°C and 317.9°C, respectively. Their wide angle X-ray scattering (WAXS) pattern indicated that their crystal structure is exactly the same as that of the linear homopolymer.

1. Introduction

Hyperbranched polymers are getting increasingly more attention due to their unique features such as three-dimensional architecture, low melting viscosity, good solubility, and a large amount of terminal functional groups (1). This kind of material may be potentially used as coating additives (2), drug and gene deliveries (3), electroactive and photochemical molecular devices (4), optical waveguide materials (5), conductive materials, "building blocks" of functional materials (6), etc. Since the hyperbranched polymer can be prepared by one-step polycondensation of AB$_2$-type monomers; it is well known that it is easier to be obtained than the analogous dendrimer. However, most of the AB$_2$ monomers are unavailable commercially and have to be synthesized by the researchers themselves. Therefore, only a few hyperbranched polymeric materials are commercially available in a large scale with relatively low cost. To overcome this problem, it is necessary to develop a new synthetic strategy for hyperbranched polymers. Over the past decade, researchers have begun to focus towards the polycondensation of A$_2$ and B$_3$ monomers, within them the notable examples were reported by Jikei, (7−9), Fréchet,

(10), Voit (11), and Long (12, 13), it involved the synthesis of hyperbranched polymers from the reaction of A$_2$ + B$_3$ and their applications.

Hyperbranched poly(aryl ether ketone) (HPAEK) is a kind of hyperbranched polymers. Miller et al. (14), Chu and Hawker (15, 16), Cho et al. (17) and Shu et al. (18, 19) have synthesized the hyperbranched poly(aryl ether ketone)s through the self-polymerization of AB$_2$ monomer. Baek (20, 21) reported the acquirement of linear-hyperbranched copolymer through the copolymerization of AB$_n$ + AB monomers and showed the influences of content of AB monomer in the improvement of its thermal properties, solubility and crystallization of resulting materials. The preparation of HPAEK via the 'A$_2$ + B$_3$' approach was far less reported. However, one of the advantages of this approach is that the polymer performance was able to be controlled through adjusting structure and chain length of A$_2$, furthermore, the structure of the polymer's aggregative state was also able to be controlled. The disadvantage of this approach is the generation of gelatin at the end of polymerization process. To avoid the problems aforementioned, this work represents a novel strategy to prepare a series of hyperbranched poly(ether ether ketone)s by changing the length and molecular weight of A$_2$ unit, performing direct polycondensation close to the gel point, further investigating the relationship of the chain length between branching points with thermal properties and crystallinity of hyperbranchend poly(ether ether ketones) (HPEEKs).

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2. Experimental

2.1 Materials

Phloroglucinol (m.p. is 216–218°C) was purchased from Shanghai Chemical Factory. Diphenylsulfone (98%), hydroquinone (DP, 98%) and 4,4′-difluorbenzophenone (BF, 98.5%) were purchased from Changzhou Huashan Chemical Co., Ltd. (Jiangsu Province, P. R. China) and were purified before use. Anhydrous sodium carbonate (98%), anhydrous potassium carbonate (99%) and N,N-dimethylacetamide (DMAc) were obtained from Tianjin Chemical reagent plant.

2.2 Measurements

IR spectra were recorded on a Nicolet Impact 410 spectrometer. Mass spectra were obtained on an American TRACE MS mass spectrograph. ^{1}H-NMR was carried out on a Bruker 510 (500 MHz) spectrometer. Glass transition temperature (T_g) was measured with a Mettler Toledo DSC821[e] at a heating rate of 10°C/min in N_2 atmosphere. Thermo-gravimetric analysis (TGA) was conducted on a NetzchSta449c system at a heating rate of 10°C/min in N_2 atmosphere. Wide-angle X-ray diffraction (WAXD) powder patterns were recorded with a Rigaku RU-200 diffractometer using Ni-filtered Cu Kα radiation (40 kv, 100 mA, λ = 0.15418 nm). The inherent viscosities of the oligomers and polymers were measured in a 0.1 wt% H_2SO_4 solution at 25°C.

2.3 Synthesis of 1,3,5-Tris[4-(4-fluorobenzoyl) phenoxy]Benzene(B₃)

Phloroglucinol (10.08 g) and 4,4′-difluorobenzophenone (226.70 g) were dissolved in 650 ml of DMAc and 60 ml of toluene in a 1000 ml three-necked flask fitted with a mechanical stirrer, nitrogen inlet, thermometer, and a condenser. Potassium carbonate (20.00 g) was subsequently added. The suspension was heated to 140°C under a nitrogen atmosphere for 4 h. The toluene was distilled from the flask. The reaction was stirred for 8 h at 152°C. The mixture was poured into

5000 ml of deionized water. The solution was filtered off, white crystals were obtained after recrystallization from mixed solutions of acetone and ethanol. Yield: 58%. m.p.: 131°C (DSC). m/z: 721. Elem. Anal. Calcd for $C_{45}H_{27}O_6F_3$ (721.3 g/mol): C, 74.93%; H, 3.75%; Found: C, 73.64%, 3.77%; IR (KBr, cm^{-1}): 1645, 1596 (C=O); 1227 (C-F); 1155 (C-O). ^{1}H-NMR (CDCl₃), δ (ppm): 6.61 (s, 3H), 7.11–7.13 (d, 6H), 7.17 (d, 6H), 7.81–7.83 (d, 12H).
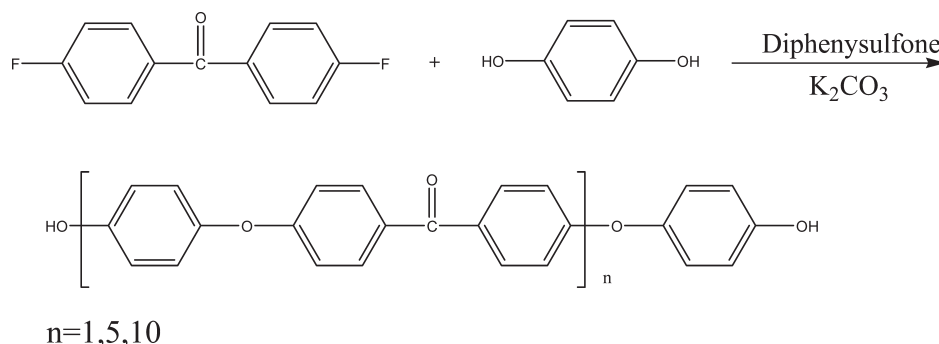
2.4 Synthesis of the PEEK Oligomers

Dihydroxy-terminated PEEK oligomers were prepared by the reaction of hydroquinone and 4,4′-difluorbenzophenone in diphenylsulfone in the presence of Na_2CO_3, K_2CO_3 according to the procedures presented in the literature (Scheme 1) (22, 23).

The synthetic methods based on Carothers' equation and basic properties for the PEEK oligomers are shown in Table 1. It was found that the average polymerization degree (Xn) affected the viscosity (η_{iv}) and melting point (T_m) of oligomers. Table 1 shows that oligomers with a high Xn characterized with high T_m and η_{iv}.

2.5 Synthesis of Hyperbranched Poly(ether ether ketone)s (HPEEK) with Various Chain Lengths of Branching Point

Synthesis of hyperbranched poly(ether ether ketone)s (HPEEK) was conducted in a 100 ml three-necked round bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet, and a water absorbent filter paper, and the flask was charged with 1,3,5-tris[4-(4-fluorobenzoyl)phenoxy] benzene (0.01 mol), 0.0072 mol of oligomer OH-BF-1, 0.0076 mol of mixture of potassium carbonate and sodium carbonate, and diphenylsulfone. The same procedure as was mentioned above for the copolymerization of dihydroxy-terminated A₂ oligomers (OH-BF-5, OH-BF-10, respectively) and B₃ monomer was carried out, the mixture was heated from room temperature to 180°C and kept for 2-3 h, then to 220°C and kept for 2–3 h, then to 280°C and kept for 2–3 h, and finally to 300°C and kept for 2–3 h. The

n=1,5,10

Sch. 1. Synthesis of the PEEK oligomers.

Table 1. Properties of the PEEK oligomers

| Oligomers	[BF] (mol)	[DP] (mol)	Xn	η_{iv} (dL/g)	T_m (°C)
OH-BF-1	0.0077	0.10	1	0.07	223.33
OH-BF-5	0.0677	0.10	5	0.11	300.01
OH-BF-10	0.0818	0.10	10	0.14	332.24

copolymer solution was then poured into water. After it was cooled, the precipitate was crushed, washed thoroughly by hot acetone and distilled water several times, and dried at 120°C for 24 h. The synthesis of polymers is shown in Scheme 2. Unfortunately, the copolymers was insoluble in common solvents, therefore, the application of NMR technique was precluded in the determination of the degree of branching, distribution of the linear, dendritic and terminal units. The objective of this work is to investigate the relationship between properties and chain length of branching point (L). Presume that the chain length between two focal points in the Scheme 2 is the chain length of branching point (L). Here, we presume that L contains one phenyl ether (−o−⬡) unit or one phenyl ketone ($-\overset{O}{\underset{||}{C}}$−⬡) unit as a

repeating unit. According to this assumption, when A_2 is OH-BF-1 (n = 1), $L_1 \approx 8$, consider this polymer as P1; When A_2 is OH-BF-5 (n = 5), $L_2 \approx 20$, consider this polymer as P2; then n = 10, $L_3 \approx 20$, as P3.

3. Results and Discussion

3.1 Polymerization

Flory (24) reported that gel formation depends on the stoichiometry of the monomers, the extent of reaction, and step-growth polymerization reactions which involved a mixture of difunctional (A_2) and trifunctional (B_3) monomers and
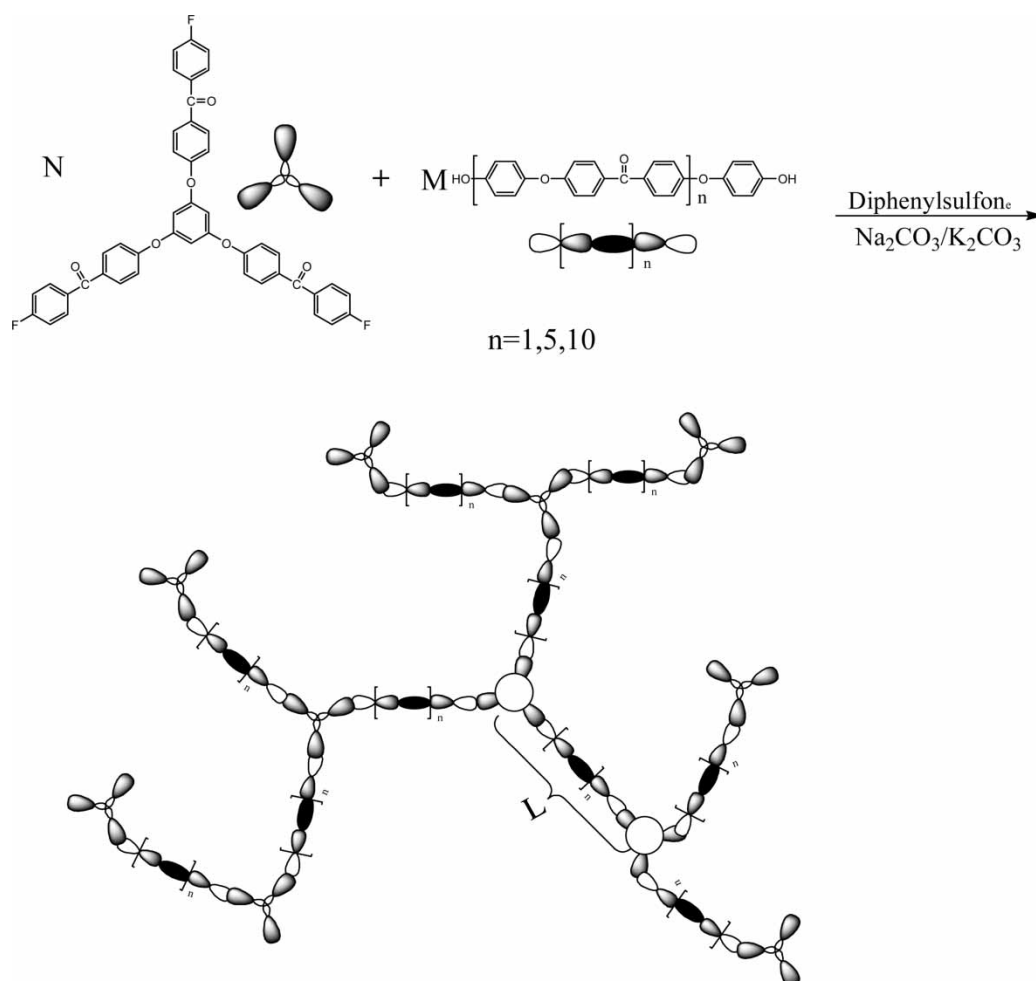
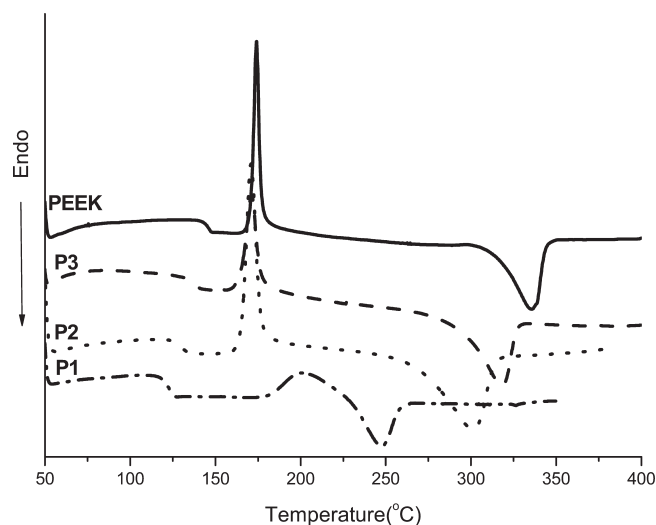
Sch. 2. Synthesis of the HPEEKs.

Fig. 1. DSC curves of linear PEEK and HPEEKs.

further leads to the formation of hyperbranched or crosslinked polymer. According to the theory of Flory et al., $A_2 + B_3$ system is based on the following assumptions: (1) the equal reactivity of all A groups, as well as B groups, in both monomers and the growing polymers; (2) the exclusive reactivity of A groups with B groups; and (3) no intramolecular cyclization and chain termination in the process. The range of feeds with the functional group ratios of A_2 to B_3 (1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene) at critical gel point can be calculated by using the following equation:

$$\frac{1}{(a-1)(b-1)} \leq r_A \leq (a-1)(b-1) \tag{1}$$

where r_A is the ratio of functional group A_a to B_b initially present in the reaction mixture, a and b are functionality numbers of monomer A_a and B_b, respectively. Substituting the values of $a = 2$ and $b = 3$ in Equation (1), then Equation (1) becomes:

$$0.5 \leq r_A \leq 2.0 \tag{2}$$

Flory showed that when $r_A \leq 0.5$, even if ρ_A (extent of reaction) = 1; or $r_A \geq 2.0$, ρ_B (extent of reaction) = 1, gel

formation is impossible. In this paper, we use $r_A = 0.48$ to prepare B_3-terminated hyperbranched poly(ether ether ketone)s with various chain lengths between branching point. The solid content by weight of oligomer $A_2 + B_3$ polymerization reactions is around 25% to 30%.

3.2 Relationships between Inherent Viscosity and Chain Length of Branching Point

Kakimoto, (9) has demonstrated that hyperbranched polyimides obtained by $A_2 + B_3$ polymerization have a loose-packing, low branching density topology. It is reasonable to think that hyperbranched polymers obtained by $A_2 + B_3$ polymerization could penetrate through one another to form a certain extent of chain entanglement and strong intermolecular interaction, giving the rise to a glass transition temperature, solution viscosity, and thermal stability higher than that of hyperbranched polyimides having the same repeating unit by AB_2 self-polymerization. The relationship between inherent viscosity η_{iv} and chain length of branching point is shown in Figure 1 and Table 2. The inherent viscosity of hyperbranched polymers is from 0.19 to 0.24, which is lower than that of linear PEEK, and the data of intrinsic viscosities between three HPEEK reveals the increment trend with the chain length of branching point (L) increases. Two factors are as below: (1) the molecular weight of HPEEK increases with the increasing oligomer "L"; (2) according to Kakimoto's belief, the HPEEK has more loose-packing and lower branching density topology with an increasing of L, which lead to stronger intermolecular force and chain entanglement.

3.3 Relationships between Thermal Properties and Chain Length of Branching Point

The glass-transition temperatures (T_g) of the linear and hyperbranched PEEK polymers were determined by DSC. The scans were run on the powder samples after they had been heated to 350°C in the DSC chamber and allowed to cool to ambient temperature under a nitrogen purge. The DSC results are also shown in Figure 1 and Table 2. The DSC results reveal an increasing trend in T_g values as the chain length of branching point increases (L). The P3 displayed a T_g at 138.0°C, which is 15.6°C higher than that of P1, but

Table 2. Properties of the linear PEEK and HPEEKs with various chain lengths between branching point

Polymers	$\eta_{iv}{}^a$ (dL/g)	$T_g{}^b$ (°C)	$T_c{}^b$ (°C)	$T_m{}^b$ (°C)	ΔH (J/g)	$T_d{}^c$ (°C)
P1	0.19	122.4	200.2	247.4	−10.47	576
P2	0.22	133.2	171.3	300.9	−30.64	573
P3	0.24	138.0	171.2	317.9	−42.58	544
PEEK	0.30	145.3	174.3	336.5	−32.37	585

[a]Intrinsic viscosity determined in oil of vitriol at 25 ± 0.1°C.
[b]Glass transition temperature (T_g), crystallization temperature (T_c), and melting temperature (T_m) determined by DSC with a heating rate of 10°C/min.
[c]The temperature at which 5% loss occurred on a TGA thermogram obtained with heating rate of 10°C/min in N_2.
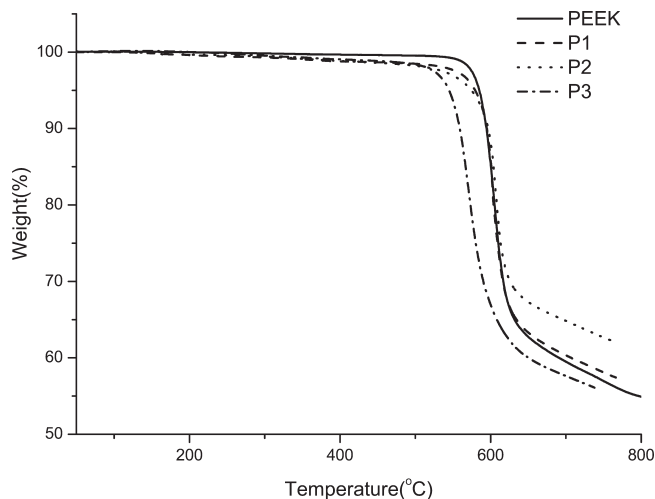
Fig. 2. TGA thermograms for linear PEEK and HPEEKs.

slightly lower (7°C) than that of linear PEEK. The copolymer P1 showed a blunt cooling crystallization peak at 200°C, and slightly broad melting peak at 247°C. With an increase of chain length of branching point, while $L_3 \approx 20$ and $L_3 \approx 35$, the P2 and P3 show a sharp cooling crystallization peak at 171°C, and sharp melting peak at 301°C and 318°C, respectively. By comparing T_m between P1, P2, and P3, the results show an increasing trend of T_m values as the chain length of branching point increases.

The thermal stability of the HPEEKs copolymers was determined by thermogravimetric analysis (TGA) on the powder sample in nitrogen atmosphere. The results are shown in Figure 2 and Table 2. It is obvious that the P1 and P2 show fairly good thermal stability. The P3 are less thermally stable than the corresponding P1, P2 and linear PEEK. This is likely related to the molecular weight distribution and hydroxyl-terminated of long chain oligomers

A_2 leading to the B_3-terminated imperfection of the polymers.

3.4 Relationships between Crystalline Degree and Chain Length of Branching Point

All samples were characterized with an X-ray diffraction technique to determine their degrees of crystallinity which is similar to the thermal analysis data (Fig. 3). The P1, P2, and P3 displayed peaks at 7.76 Å, 7.20 Å, 6.83 Å, and 4.10 Å, which have similar peak positions observed for the linear PEEK, but their intensities show an increasing trend as the chain length of branching point increases.

4. Conclusions

Three hydroxyl-terminated PEEK oligomers were synthesized. A series of hyperbranched poly(ether ether ketone)s with various chain lengths between branching point based on A_2 (PEEK oligomers) and B_3 (1,3,5-tris[4-(4-fluorobenzoyl)phenoxy]benzene) were prepared through a typical one-step polymerization method. The relation of chain lengths between branching point (L), crystallization and thermal properties have been studied. It was found that the chain lengths L greatly affected the crystallization and thermal properties of the polymers. The T_g of hyperbranched poly(ether ether ketones) is between 122.4°C and 138.0°C, and the melting point is between 247°C and 318°C. The thermal stability of the HPEEKs copolymers is weakened as the chain length between branching point increases.

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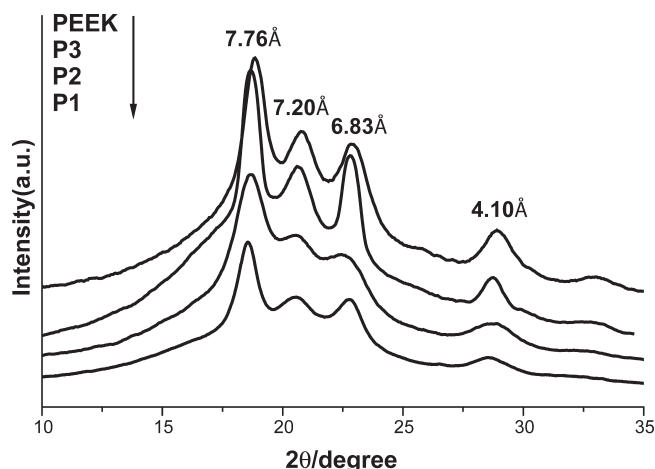
Fig. 3. WAXD diffraction curves for linear and HPEEKs.

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