SYNTHESIS AND THERMAL CHARACTERIZATION OF POLY(ETHER ETHER KETONE-co-ETHER NAPHTHALENE EHTER KETONE-co-ETHER DIPHENYL ETHER KETONE) RANDOM COPOLYMERS

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The chemical resistance and physical properties of poly(aryl ether ketone)(PAEK) have led to its broad industrial use. In order to obtain different properties of poly(arly ether ketone)s for various applications, structural modifications, such as functional group could be crosslinked or biphenyl units onto the main chain, have been attempted[1-5].

Experimental

Materials. 4,4'–difluoro diphenyl ketone (98%, industrial grade, supplied by Yanji Chemical Plant in China) was dried in vacuum oven at 70 centigrade for 6~10hr before it was used, diphenyl sulfone (98%, industrial grade, supplied by Yanji Chemical Plant in China) was recrystallized in acetone and then were dried in vacuum oven at 70 centigrade for 8hr, hydroquinone (98%, industrial grade, supplied by Yanji Chemical Plant in China), 4,4'-diphenol(99%, Analysis reagent) purchased from ACROS ORGANICS, 1,5–dihydroxy naphthalene (99%, Analysis reagent) purchased from ACROS ORGANICS in Belgium was dried 70 centigrade in vacuum oven for 6~10hr, K_2CO_3 (99%, Analysis reagent, purchased from Tianjin Chemical Reagent Plant in China) and Na_2CO_3 (99%, Analysis reagent, purchased from Shenyang Chemical Reagent Plant in China) were dried at 110 centigrade over 6hr. Except for diphenyl sulfone, the monomers and other reagents all were used without further purification.

Synthesis of polymers. In a three–neck round bottom flask, 0.20 mol 4,4'–difluoro diphenyl ketone and diphenyl sulfone were introduced and heated from room temperature to 160 centigrade quickly, and after the mixture was melted, 0.02mol 1,5–dihydroxy naphthalene, 0.02mol 4,4'-diphenol and 0.16mol hydroquinone and 0.20 mol catalysts(K_2CO_3 and Na_2CO_3)were added into the flask under stirring(under nitrogen atmosphere) then the mixture was heated to 200 centigrade. After keeping the temperature at 200 centigrade for 1 hr, the temperature of the reaction mixture was raised to 280~330 centigrade gradually, and the polymerization reaction carried out at this temperature for 1~3hr, then the hot mixture of products was poured into a large amount distilled water and the reaction was terminated. The products were pulverized, and were washed by acetone for several times to remove the solvent and were washed by distilled water for several times to remove the salt, and then were dried at 120 centigrade for 12hr, and the green–yellow powder polymers were obtained.

Characterization. The inherent viscosity was measured at 25 centigrade on a 0.05g/10mL solution of the polymers in 98% sulfuric acid using an Ubbelohde viscometer, the inherent viscosity was calculated by:

$$\eta_{inh} = C^{-1}Ln(t_1/t_0)$$

where C is the concentration of polymer solution in g/dL, t_1 and t_0 were the time that solution and solvent pass across the viscometer. The inherent viscosity of PNEEK(20%) used in this work was 0.96 .

Differential scanning calorimetry(DSC) measurements were carried out with a METTLER TOLEDO DSC 821e instrument with heating at 400 centigrade for 4min, a 10 centigrade/min cooling rate and a 20 centigrade/min heating rate in nitrogen. Degradations were carried out on 10-30mg powder copolymers, and contained within open aluminium pans air purging at PERKIN ELMER TGA-7.

Results and discussion

Synthesis of polymers. Poly(EEK-co-ENEK-co-EDEK) was synthesized by the nucleophilic substitution

reaction of 4,4'–difluoro diphenyl ketone containing hydroquinone, 4,4'-diphenol and 1,5–dihydroxy naphthalene. The hydrogen atoms connected to the ortho–position of halogen on the aryl rings are known to be acidic[6] . Attwood and his cowokers[7] have suggested that the proton abstraction reaction might appear during synthesizing poly(aryl ether ketone)s which could lead to branch and even gelation. In the investigated reaction system, the gelation would avoid at some reaction conditions so that the linear coplymers could be synthesized.

Thermal characterization. The glass transition temperature (Tg) of copolymer is higher and the melting temperature(Tm) is lower than PEEK, The increment of Poly(EEK-co-ENEK-co-EDEK) chain's rigidity was after containing more rigidity naphthalene moieties and biphenyl units that led to the increase of Tg, Tm fell down because naphthalene moiety construction unit is wrapping segment which destroied integrality and tighting stack of molecule chain. Figure 1 is the DSC curve of copolymer.

The thermal stability(Td) is measured by TGA from 30 centigrade to 650 centigrade. Td(5.0% and 10.0%) are similar with PEEK. Figure 2 is the Td curve of copolymer.

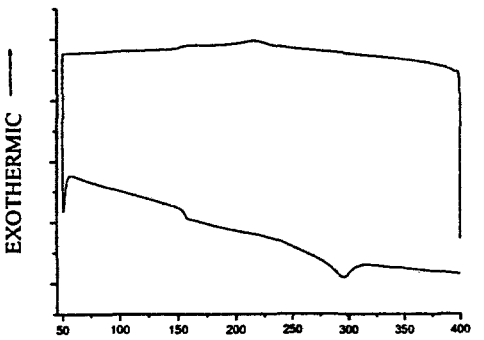

Figure 1

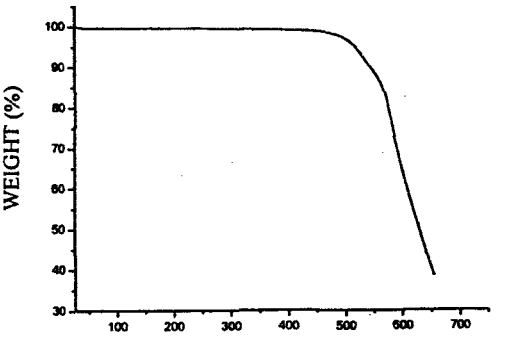

Figure 2

Keywords: thermal behavior, poly(EEK-co-ENEK-co-EDEK), 1,5-naphthalene ring, diphenyl units.

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Abstract: In this study, we have synthesized poly(EEK-co-ENEK-co-EDEK) random copolymers by the nucleophilic substitution reaction, the contents of naphthalene and diphenyl are 10% and 10%. Differential scanning calorimeter (DSC) and thermogravimetry (TG) have been used to investigate the thermal behaviors of copolymers with the aim of identifying those features which lead to thermal stability and instability.

摘要：本文主要讨论了含萘环及联苯结构聚芳醚酮无规共聚物的亲核取代合成方法。其中，萘环和联苯的理论含量各为 10%。并且应用 DSC 和 TG 两种实验手段对共聚物的热性能进行了测试，发现聚合物具有玻璃化转变温度高于 PEEK 和熔点明显低于 PEEK 以及热失重植和 PEEK 相似的特点。