

双邻位甲基取代聚芳醚酮酰亚胺的合成与性能研究*

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摘 要 N,N' -(4,4'-二苯甲烷)-二偏苯三甲酰亚胺酰氯(DIDC-M)分别与4,4'-二(2,6-二甲基-苯氧基)二苯酮(o -Me₂-DPOBP)和4,4'-二(2,6-二甲基-苯氧基)三苯二酮(o -Me₂-DPOTPDK)进行低温溶液共缩聚,合成了两种含双邻位甲基侧基和主链含亚胺结构的聚醚酮醚酮酰亚胺(o -Me₂-PEKEKI-P_a)及聚醚酮醚酮酰亚胺(o -Me₂-PEKKEKI-P_b)共聚物.用FT-IR,¹H-NMR,DSC,TGA和WAXD对共聚物的结构和性能进行了表征.研究表明P_a和P_b均为非晶态结构;具有较高的玻璃化转变温度(P_a为240℃,P_b为237℃);能溶解于DMF、DMAc、NMP、二氯甲烷、氯仿等普通有机溶剂中,溶剂挥发后成膜性良好,可制成透明薄膜.共聚物P_a,P_b的拉伸强度分别为80.0 MPa,51.8 MPa,断裂伸长率6.9%,4.6%,杨氏模量2.0 GPa,1.8 GPa.

关键词 聚芳醚酮酰亚胺,共缩聚,双邻位甲基,结构和性能

聚酰亚胺(PI)、聚芳醚酮(PEK)均属高性能高分子材料,由于具有优良的耐高温、化学稳定性、优异的力学性能和电绝缘性能,已广泛应用于航空、航天、核工业、电子电器以及汽车制造等高新技术领域^[1].由于PI不溶于普通溶剂中,吸湿性较大^[2],采用热固化成型温度高达300℃以上;而PEK由于分子链规整性好,熔融温度高,不溶于常见的溶剂中,加工成型较困难,使其应用受到了一定的限制.为了改善PI,PEK的加工等性能,国内外对溶剂型以及热塑性的高性能材料做了大量的研究工作^[3].常用的方法是在主链中引入半柔性基团,如-Si-,SO₂-,O-CO-,C(CF₃)₂-等^[4,5],或引入扭曲的非共平面结构单元以降低大分子链的规整性^[6-9].本文从分子设计角度出发,合成了 N,N' -(4,4'-二苯甲烷)-二偏苯三甲酰亚胺酰氯(DIDC-M),将其分别与4,4'-二(2,6-二甲基-苯氧基)二苯酮(o -Me₂-DPOBP)和4,4'-二(2,6-二甲基-苯氧基)三苯二酮(o -Me₂-DPOTPDK)进行低温溶液共缩聚,合成了两种含双邻位甲基侧基和主链含亚胺结构单元的聚醚酮醚酮酰亚胺(o -Me₂-PEKEKI-P_a)及聚醚酮醚酮酰亚胺(o -Me₂-PEKKEKI-P_b)共聚物.试图将聚芳醚酮和聚酰亚胺的优良性能结合在一起,刚性的酰亚胺环及侧甲基可较大幅度地提高聚合物的 T_g .研究表明,合成的两种共聚物均为非晶态,能

溶于常见的有机溶剂中, T_g 比PEEK(143℃)、PEKK(163℃)有较大幅度提高,采用延流法可制成透明的薄膜.树脂可望在薄膜电容器材料、柔性线路板、密封材料、绝缘材料等领域得到应用.

1 实验部分

1.1 主要原料

无水AlCl₃,分析纯,上海金山兴塔化工;1,2-二氯乙烷(DCE):工业品,重蒸后加0.4 nm分子筛干燥备用; N -甲基吡咯烷酮(NMP):工业品,CaH脱水后减压蒸馏,加0.4 nm分子筛干燥备用.

1.2 主要仪器

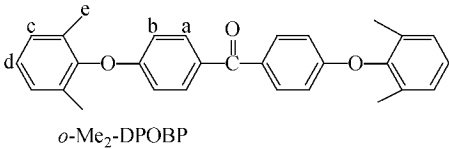
红外光谱,Perkin-Elmer SP one FT-IR 光谱仪, KBr压片;核磁共振,Bruker Vance 400 M Hz 型核磁共振仪(CDCl₃四甲基硅烷为内标);X-Ray,日本理学电机 DMAX-III A 型 X-射线衍射仪, CuK α 40 kV/30 mA,2 θ = 4 ~ 40°;差动扫描量热仪,Perkin-Elmer Pyris 1 DSC,氮气气氛,气体流速为20 mL/min,升温速率10 K/min;TG,岛津 DT-40 型热分析仪,升温速率为15 K/min,氮气气氛;对数比浓粘度(η_{inh}),配成0.5 g/dL的DMAc溶液,在30℃恒温水槽中用乌氏粘度计测定,按 $\eta_{inh} = c^{-1} \ln t_1/t_0$ 计算;力学性能测试采用SANS微机控制电子万能试验机(CMT8102,深圳市新三思材料

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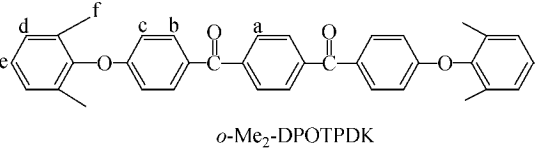
检测有限公司).

1.3 单体的合成

o-Me₂-DPOBP 和 *o*-Me₂-DPOTPDK 参考文献



[10]的方法合成,熔点分别为 205 ~ 206℃和 194 ~ 195℃,经 FT-IR、¹H-NMR(图谱数据见表 1)证明有如下结构:



DIDC-M 参考文献[11]的方法合成,熔点为 276 ~ 277℃,经 FT-IR、¹H-NMR(数据列于表 1)证

明有如下结构:

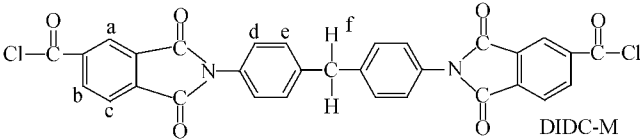


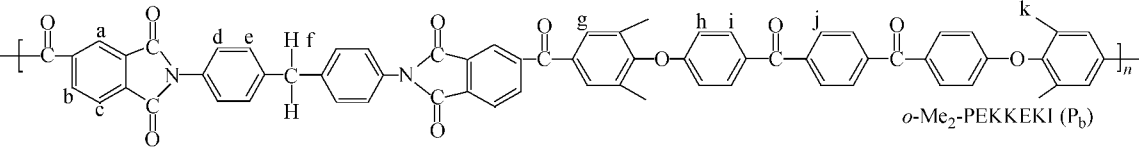
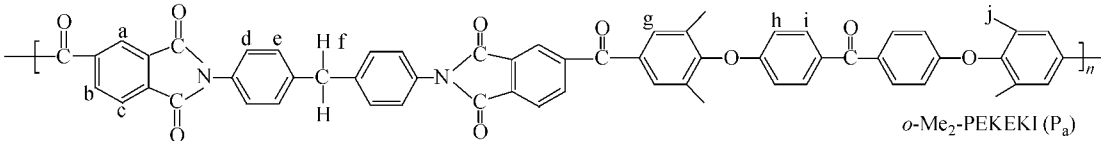
Table 1 FT-IR and ¹H-NMR spectra data of monomers

Monomer	FT-IR (KBr,λ,cm ⁻¹)	¹ H-NMR (CDCl ₃ ,δ)
<i>o</i> -Me ₂ -DPO BP	2918 (m,CH ₂ -H),1660 (s,-CO-), 1590,1496 (s,Ar-H),839 (ms,Ar-1,4)	7.773 ~ 7.793 (4H _a ,d,J = 8.0 Hz), 6.837 ~ 6.857 (4H _b ,d), 7.112 ~ 7.163 (4H _c ,2H _d ,m), 2.165 (12H _e ,s)
<i>o</i> -Me ₂ -DPO TPDK	2919 (m,CH ₂ -H),1658 (s,-CO-),1589, 1499, 1401 (s,Ar-H),840 (ms,Ar-1,4)	7.831 ~ 7.863 (4H _a ,4H _b ,m), 7.123 ~ 7.160 (4H _c ,2H _d ,m), 6.866 ~ 6.895 (4H _e ,d), 2.16 (12H _f ,s)
DIDC-M	1776 (s,-CO-N-CO), 1717 (s,-CO-), 1377 (m,CN), 1096 (m,-CO-), 750 (s,C-Cl)	8.690 (2H _a ,s), 8.535 ~ 8.554 (2H _b ,d,J = 7.6 Hz), 8.104 ~ 8.123 (2H _c ,d,J = 7.6 Hz), 7.384 ~ 7.393 (8H _{d,e} ,d), 4.122 (2H _f ,s)

1.4 共聚物的合成

参考文献[12]的方法,将 17.6 g 无水 AlCl₃ 和 20 mL 二氯乙烷(DCE)置于带有氮气导出入管和搅拌器的三口瓶中,在 - 5 ~ 0℃ 下滴加适量的 NMP 和 30 mL DCE,搅拌 0.5 h,至溶液澄清后分别加入 4.14 g (0.01 mol) *o*-Me₂-DPOBP,5.83 g (0.01 mol) DIDC-M. 于 - 15℃ 的冰盐浴中反应

1 h,室温下反应 10 h,滴加适量二苯醚封端,2 h 后用甲醇猝灭,将树脂捣碎,依次用 10% 甲酸、10% 氨水、去离子水洗涤数次后,用甲醇抽提,烘干,真空下 100℃ 干燥 6 h,得黄色粉末状树脂 P_a,收率 ≥ 98%. 用同样的方法合成 P_b. P_a,P_b 的结构单元如下所示:



1.5 共聚物薄膜的制备

将树脂溶于 DMAc 中,配成 5% 的溶液,在洁净的玻璃板上流延成膜,溶剂挥发后,脱膜.薄膜依次用丙酮、乙醇浸泡 24 h,120℃ 下真空干燥 2 h,在 180℃ 下进行热处理 2 h,将膜裁成试样条进行力学性能测试.

2 结果与讨论

2.1 共聚物的结构分析

FT-IR 和¹H-NMR 测试数据及归属列于表 2. 由表可知,二种共聚物具有预期的结构,由于 P_a 和 P_b 具有相似的结构,其红外特征吸收峰基本相同.

Table 2 FT-IR, ¹H-NMR spectrum data of copolymers

Copolymer	FT-IR (KBr, λ, cm ⁻¹)	¹ H-NMR (CDCl ₃ , δ)
P _a	2922 (m, CH—H, CH ₂ —H); 1660 (s, —CO—); 1779, 1725 (s, —CO—N—CO), 1384 (m, CN); 1246 (s, Ar—O—Ar)	8.319 (2H _a , s); 8.244 ~ 8.261 (2H _b , d, J = 6.8); 8.108 ~ 8.127 (2H _c , d, J = 7.6); 7.404 ~ 7.435 (8H _{d,e} , d, d); 4.128 (2H _f , s); 7.617 (4H _g , s); 6.884 ~ 6.906 (4H _h , d, J = 8.8); 7.814 ~ 7.835 (4H _i , d, J = 8.4); 2.227 (12H _{j,s})
		8.300 (2H _a , s); 8.224 ~ 8.242 (2H _b , d, J = 7.2); 8.098 ~ 8.107 (2H _c , d, J = 7.2); 7.384 ~ 7.416 (8H _{d,e} , d, d); 4.109 (2H _f , s); 7.604 (4H _g , s); 6.891 ~ 6.913 (4H _h , d, J = 8.8); 7.793 ~ 7.869 (8H _{i,j} , d, d); 2.213 (12H _k , s)

2.2 WAXD 分析

图 1 为共聚物 P_a, P_b 经 200℃ 热处理 1 h 后测得的广角 X-射线衍射图. 两种共聚物均出现一个弥散的峰, 无晶体晶面衍射出现, 这是由于在分子主链引入了酰亚胺结构单元和双邻位甲基侧基, 增加了大分子的自由体积, 链的规整性降低, 难以达到结晶所要求的有序排列, WAXD 分析表明两种共聚物均属非晶态结构.

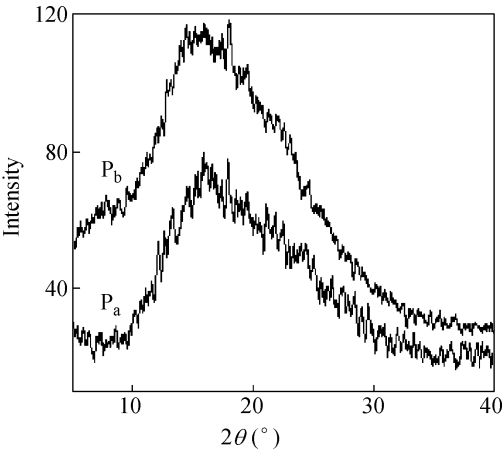


Fig. 1 WAXD curves of copolymers

2.3 共聚物的热分析

DSC 分析如图 2, 结果列于表 3, 由表可知, 两种共聚物的 T_g 与聚芳醚酮酮 (PEKK)^[12] 聚芳醚酮醚酮酮 (PEKEKK)^[13] 相比, 均有较大幅度地提高. 这是由于在分子主链引入刚性的酰亚胺环结构单元以及双邻位甲基侧基, 阻碍了主链分子的内旋转, 使大分子链的构象数减少以及构象的转换能垒增加的缘故. DSC 曲线上未出现熔融结晶峰, 这与 WAXD 分析结果一致. P_a, P_b 用熔点法测其软化温度, P_a 为 310 ~ 330℃, P_b 为 290 ~ 312℃, 树脂可以采用模压法加工成型.

热失重分析见图 3, 实验数据见表 3. 两种共聚物的 T_d 与 PEKK^[12]、PEKEKK^[13] 相比有所下降, 可能是由于甲基侧基对分子共轭平面产生了一定的张力, 以及甲基和主链上亚甲基与芳环相比热

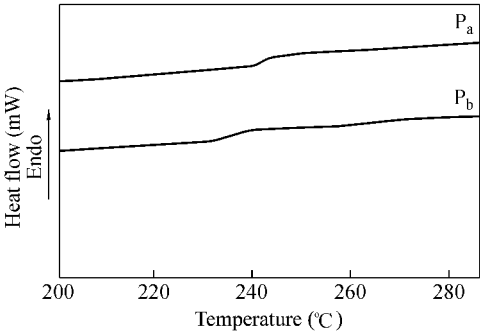


Fig. 2 DSC curves of copolymers

Table 3 Properties of copolymers

Copolymer	η _{inh} (dL/g)	T _g (°C)	T _m (°C)	T _s (°C) ^a	T _d (°C) ^b	T _d (°C) ^c
P _a	0.61	240		310 ~ 330	466	513
P _b	0.90	237		290 ~ 312	464	529
PEKK ^d	0.77	163	341		575	
PEKEKK ^e	0.81	160	380		530	

^aSoft temperature; ^{b,c} Lost weight of 5%, 10%; ^d Lit. ^[11] (TPC/IPC = 70%/30%); ^e Lit. ^[12]

氧化稳定性较低所导致的. 但两种共聚物的 T_d 均在 464℃ 以上, 仍属于耐热性良好的有机高分子材料.

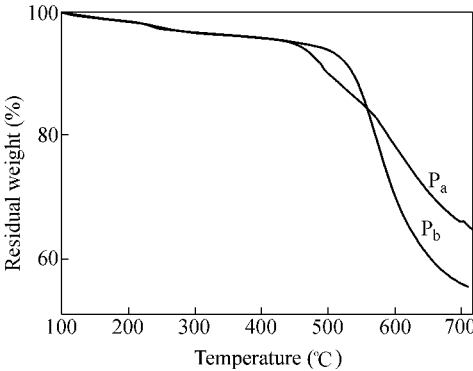


Fig. 3 TG curve of copolymers

2.4 溶解性试验

表 4 为 P_a, P_b 溶解性测试结果, 两种共聚物的溶解性与 PEKK^[12]、PEKEKK^[13] 树脂相比有了明显的改善, 共聚物除能溶于浓硫酸外, 还能溶于酰

Table 4 Solubility of copolymers									
Copolymer	DMF	DMAc	NMP	CHCl ₃	CH ₂ Cl ₂	C ₂ H ₄ Cl ₂	C ₂ H ₂ Cl ₄	C ₆ H ₅ OH/C ₂ H ₂ Cl ₄ (1:1)	H ₂ SO ₄ (Conc.)
P _a	+	+	+	+	+	+	+	+	+
P _b	+	+	+	+	+	+	+	+	+
PEKK ^a	—	—	—	—	—	—	—	—	+
PEKEKK ^b	—	—	—	—	—	—	—	—	+

+ :Soluble ; — :Insoluble ;^aLi^[12] ;^bLi^[13]

Table 5 Mechanical properties of copolymers			
Copolymer	Tensile strength (MPa)	Young's module (GPa)	Elongation at break (%)
P _a	81.0	2.0	6.9
P _b	51.8	1.8	4.6

好的溶解性,可以采用溶剂法加工成型,如延流或涂布成膜等.

2.5 共聚物的力学性能

P_a 和 P_b 的力学性能测试结果列于表 5,由表可知共聚物薄膜具有较好的力学性能.

胺类和卤代烃有机溶剂中.树脂在卤代烃中有较

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STUDY ON SYNTHESIS AND PROPERTIES OF POLY(ARYL ETHER KETONE IMIDE) HAVING BIS(*o*-METHYL) PENDENT GROUPS

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Abstract Three novel monomers were synthesized and confirmed by FT-IR and $^1\text{H-NMR}$. *N,N'*-(4,4'-diphenylmethane)bistrimellitamide diacid chloride (DIDC-M) was synthesized by acidylated the 4,4'-bis(*N*-Trimellitamide)-diphenylmethane, which obtained from trimellitic anhydride with 4,4'-diaminodiphenylmethane (DDM). 2,2',6,6'-Tetremethyl-4,4'-diphenoxy diphenylketone (*o*-Me₂-DPOBP) and 2,2',6,6'-tetremethyl-4,4'-diphenoxy-triphenyldiketone (*o*-Me₂-DPOTPDK) were prepared by aromatic nucleophilic substitution reaction by 2,6-dimethylphenol with 4,4'-difluorodiphenylketone and 4,4'-difluorotriphenyldiketone respectively at the presence of sodium hydroxide, using DMSO as solvent at 200°C.

Two novel poly(aryl ether ketone imide) copolymers containing bis(*o*-methyl) moieties were prepared by low temperature solution polycondensation of DIDC-M with *o*-Me₂-DPOBP or *o*-Me₂-DPOTPDK, in 1,2-dichloroethane (DCE) and at the presence of AlCl₃ and *N*-methyl-2-pyrrolidone (NMP) as catalyst. The structure of copolymers (P_a, P_b) obtained were characterized by FTIR and $^1\text{H-NMR}$. Differential scanning calorimetry (DSC) analysis indicated that the copolymers showed high glass transition temperature (T_g) 240°C and 237°C, respectively. The single T_g 's in the DSC cures suggested that no microphase separation occurred in the block copolymer. The copolymer also showed a high thermal stability with 5% weight-loss temperatures in excess of 464°C in nitrogen, while 10% weight-loss temperature over 513°C, according to thermogravimetric analysis (TG). Wide-angle X-ray diffraction (WAXD) studies revealed that P_a and P_b were amorphous, which agreed with the results of DSC, and as a result of introducing the rigid imido structure or non-planar methyl pendent to polymer backbone, the regularity of macromolecular chain destroyed. The soluble behaviours of the copolymers were tested qualitatively at room temperature in common organic solvents. It showed that the copolymers have good solubility in the following solvents, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), NMP, dichloromethane, tetrachloroethane and chloroform. Flexible and colorless films were easily obtained by solution casting with DMAc as solvent. Tensile strength, elongation at break and Young's module of P_a were 80.0 MPa, 6.95%, and 2.0 GPa, respectively, and for P_b were 51.8 MPa, 4.6%, and 1.8 GPa, respectively. So introducing methyl pendent groups in the polymer main chain and copolymerization with novel monomers are efficient methods to synthesis high performance advanced materials. Furthermore, the copolymers contain methyl pendant group as a potential functional group, which can be converted into aldehyde or carboxylic acid, so it provides an original way to prepare functional PI/PEK copolymer's.

Keywords Poly(aryl ether ketone imide), Copolymerization, Bis(*o*-methyl) pendent, Structure and properties