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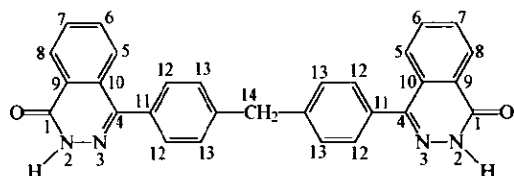
含亚甲基和双二氮杂萘酮结构的聚芳酮的合成与性能*

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关键词 聚芳酮, 聚杂萘酮, 4, 4'-亚甲基-[4-(1,4-亚苯基)杂萘-1(2H)-酮], 杂环聚合物

聚芳醚酮是一类重要的具有优异综合性能的工程塑料,它具有高的热稳定性、尺寸稳定性、耐溶剂性、好的加工性能和电性能,因而它经常作为复合材料的基质、粘合剂等被广泛的应用于航空、航天和电子等领域.近几十年来,人们付出了很大的努力去开发聚芳醚酮新品种^[1,2].本研究组以4-(4'-羟基苯氧基)-2,3-二氮杂萘-1(2H)-酮为缩聚单体制备了一系列的性能优良的聚芳醚酮^[3-6],在主链中引入高密度的氮杂萘酮结构是获得高热稳定性和良好溶解性的重要途径.由单体中含有更多的氮杂萘酮结构获得可溶解且耐温等级更高的聚芳酮是人们期待的目标. Hay 等人合成了含醚、硫醚及双二氮杂萘酮结构的单体,并用其合成了聚芳酮^[1].此类聚合物具有较好的耐热性能,玻璃化转变温度都在 300℃左右,但聚合物的分子量较低,且不溶于一般的有机溶剂.在聚合时,以二苯砜为溶剂,在 310℃左右反应,条件比较苛刻.本文基于分子设计的基本原则,合成了一种含有亚甲基和双二氮杂萘酮结构的新类双酚单体 4,4'-亚甲基-双[4-(1,4-亚苯基)杂萘-1(2H)-酮],不但能够在常见的聚合体系(NMP, 190℃)中获得聚芳酮,还保持了较高的耐热性,同时也增加了聚合物的溶解性.



1 试剂与仪器

二苯甲烷(化学纯,天津化学试剂二厂),无水三氯化铝(分析纯,北京国华试剂厂),冰醋酸(分

析纯,沈阳试剂一厂),二氯乙烷(分析纯,天津化学试剂一厂),水合肼($N_2H_4 \cdot H_2O$, 郑州化学试剂三厂),苯酚(分析纯,天津化学试剂一厂),4,4'-二氟二苯酮(聚合级),NMP经 0.3 nm 分子筛干燥后减压蒸馏后备用,无水 K_2CO_3 (分析纯,沈阳试剂三厂),甲苯(分析纯,沈阳化学试剂一厂).

实验采用 Varian INOVA 400 型核磁共振仪,溶剂 $CDCl_3$, TMS 为内标; Nicolet-20dx 型傅立叶红外光谱仪(KBr 压片); P.E.-7 DSC 分析仪,氮气环境下升温速率 10 K/min; TG/DTA220 型分析仪,氮气环境下升温速率 10 K/min; 元素分析经 Carlo ERBA Strumentazione, Model-1106 型分析仪测试; 特性粘度 η_{inh} 采用 NMP 溶剂, 25℃ 下由乌氏粘度计测定.

2 4,4'-亚甲基-双[4-(1,4-亚苯基)杂萘-1(2H)-酮]的合成

取 17 g (0.101 mol) 二苯甲烷和 30 g (0.202 mol) 邻苯二甲酸酐于三口烧瓶中,加入 100 mL $C_2H_4Cl_2$, 在低于室温下分批加入 60 g (0.45 mol) 无水 $AlCl_3$, 反应 3 h, 得黄色中间体; 将此中间体在环丁砜和氯苯混合体系中用水合肼在 120℃ 下关环, 得棕色双二氮杂萘酮粗品, 经冰醋酸重结晶得淡棕色双二氮杂萘酮, mp 338.10℃ (DSC), 总产率 60%. IR (cm^{-1}): 3106 (N—H), 2925 (CH_2), 1654 ($C=O$); ^1H -NMR (δ): H-2: 12.707 (s, 2H), H-8: 8.332 (m, 2H), H-6, 7: 7.843 ~ 7.712 (m, m, 2H, 2H), H-5: 7.725 (m, 2H), H-12: 7.512 (d, 4H), H-13: 7.468 (d, 4H), H-14: 4.159 (s, 2H); 元素分析: $C_{20}H_{20}N_4O_2$, 理论值: C, 76.29; H, 4.38; N, 12.27; 实验值: C, 75.28; H, 4.54; N, 11.35. 单体合成如图 1 所示.

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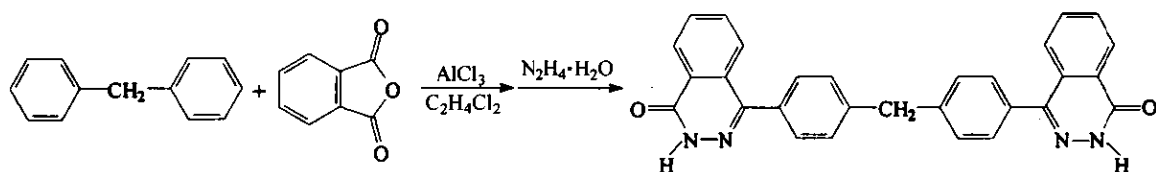


Fig. 1 Synthesis of the bis(phthalazinone) monomer

3 聚合物的合成与表征

准确称取 1.8259 g (4.0 mmol) 4,4'-亚甲基-双[4-(1,4-亚苯基)杂萘-1(2H)-酮], 0.8728 g (4 mmol) 4,4'-二氟二苯酮, 0.8847 g K_2CO_3 (6.4 mmol) 于带分水器的三口烧瓶中, 在氮气保护下加入 10 mL NMP, 20 mL 甲苯于 130℃ 下回流 3 h, 升温

于 190℃ 下反应 8 h, 停止反应, 将反应液倒入 100 mL 甲醇中, 得到长丝状白色聚合物. 以 NMP 为溶剂, 配成 15% 的溶液, 搅拌下, 倾入 5 倍体积的甲醇中进行精制, 过滤. 将白色粉末状聚合物于真空条件下 120℃ 烘干 48 h, 200℃ 下烘干 4 h. 其聚合反应如图 2 所示.

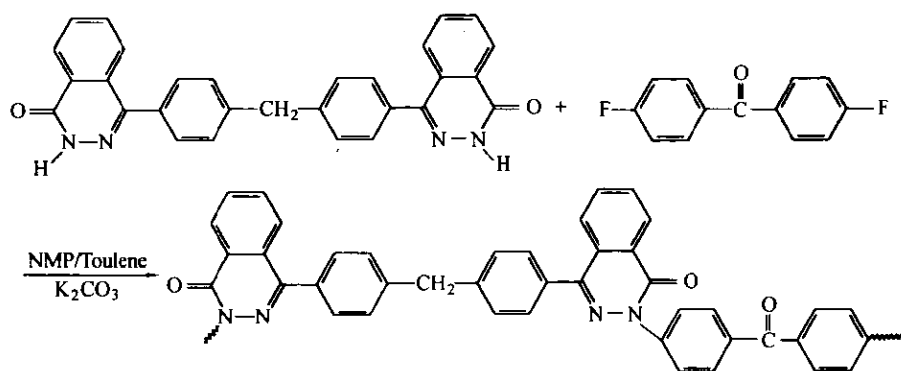


Fig. 2 Synthesis of poly(aryl ketone)

在 25℃ 下, 以 *N*-甲基吡咯烷酮为溶剂, 配成 0.5 g/dL 溶液, 测其特性粘度 η_{inh} 为 0.58 dL/g.

在图 3 和图 4 中, a 为单体的波谱, b 为聚合物的波谱. 对双二氮杂萘酮单体和聚合物的红外光谱进行比较, 在单体谱图中, 3160 cm^{-1} 处是 N—H 的吸收峰, 1654 cm^{-1} 处是内酰胺中羰基的特征吸收峰. 在聚合物的红外光谱中, N—H 的吸

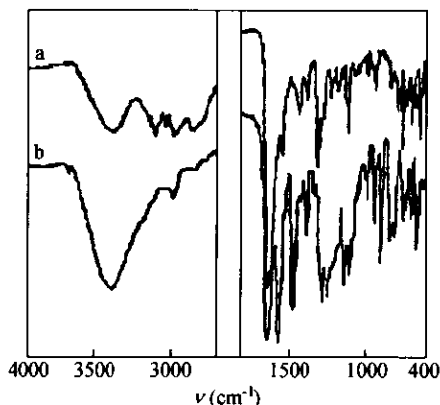
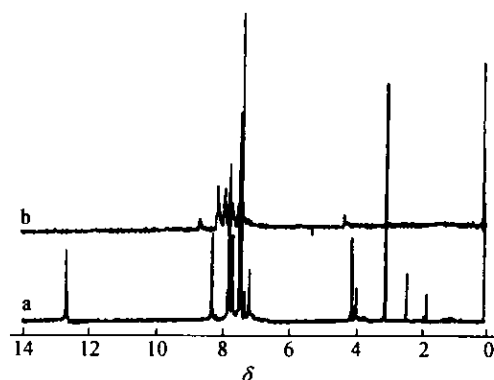


Fig. 3 FT-IR spectra of monomer and polymer

Fig. 4 ^1H -NMR spectra of monomer and polymer

收峰消失, 羰基的吸收峰也发生偏移. 对单体和聚合物的 ^1H -NMR 谱进行比较, 发现单体在 $\delta = 12.707$ 处的共振峰, 在聚合物的谱图中已经消失.

该聚合反应在 190℃ 下于 *N*-甲基吡咯烷酮 (NMP) 中反应 8 h, 即可得到高分子量的聚合物, 反应条件比较温和.

4 聚合物的溶解性能和耐热性能

表 1 列出了聚合物在一般有机溶剂中的溶解情况. 该聚合物可以在室温下溶于有机溶剂

NMP、间甲酚中, 但又不溶于 1,1',2,2'-四氯乙烷 (TCE)、*N,N*-二甲基乙酰胺 (DMAc)、二甲基亚砷 (DMSO).

Table 1 Solubility of the polymer

CHCl ₃	DMF	DMAc	DMSO	NMP	<i>m</i> -cresol	TCE	THF	Pyridine
±	-	-	-	+	+	-	-	-

+ Soluble, ± Partially soluble, - Insoluble; Testing condition: at room temperature

DSC、TG 的测试结果表明, 聚合物的玻璃化温度 (T_g) 为 258℃, 聚合物在氮气中 5% 热失重 ($T_{5\%}$) 为 431℃, 说明聚合物具有较好的耐热性. 从以上结果可知, 亚甲基的引入使聚合物的

耐热性能有所降低, 但对聚合物溶解性能有一定益处. 双二氮杂萘酮结构的扭曲和刚性的构型, 有利于聚合物溶解性的提高, 也保持了较好的耐热性能.

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SYNTHESIS AND PROPERTIES OF POLY(ARYL KETONE) CONTAINING BIS(PHTHALAZINONE) AND METHYLENE MOIETIES

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Abstract A new biphenol-like monomer, 4, 4'-methylenebis [4-(1, 4-phenylene)-phthalazin-1 (2H)-one] was synthesized from phthalic anhydride and diphenylmethane in two steps. In the first step, Friedel-Crafts reaction was carried out in 1, 2-dichloroethane between diphenylmethane and phthalic anhydride. The obtained product was used in the second step with hydrazine monohydrate added into its solution, followed by recrystallization in acetic acid. The melting point showed by differential scanning calorimetry of the bis(phthalazinone) monomer was 338.1 °C. The overall yield of the biphenol-like monomer was 60%. A new polyphthalazinone was prepared from 4, 4'-difluorodiphenylketone (DFK) and 4, 4'-methylenebis [4-(1, 4-phenylene)-phthalazin-1 (2H)-one] by solution polycondensation in *N*-methyl-2-pyrrolidone (NMP) with anhydrous K_2CO_3 as a catalyst. High molecular weight polymer was formed in 8 h at 190 °C. The polymer was refined by precipitation from its 15% NMP solution with methanol as the precipitating agent. The powder of the polymer was dried in a vacuum oven under 120 °C for 48 h and then under 200 °C for 4 h. The intrinsic viscosity of the polymer was 0.58 dL/g in NMP at 25 °C. The polymer showed high glass transition temperature (T_g) at 258 °C by DSC. The decomposition temperature for 5% weight loss ($T_{5\%}$) in nitrogen measured by thermogravimetric analysis occurred at 431 °C. The solubility of the polymer was investigated at room temperature. The polymer was soluble in NMP, *m*-cresol and partially soluble in chloroform, and insoluble in *N,N*-dimethylacetamide (DMAc) and dimethyl sulfoxide (DMSO). The methylene group and bis(phthalazinone) structure in the backbone of the polymer contribute much to the good solubility, and the rigid structure of bis(phthalazinone) retains its good thermal properties.

Key words Poly (aryl ether ketone), 4, 4'-Methylenebis [4-(1, 4-phenylene)-phthalazin-1 (2H)-one], Heterocyclic polymer