Synthesis and Properties of High-performance Homo- and Copolyimides Based on 2,5-bis(4-aminophenyl)-pyrimidine

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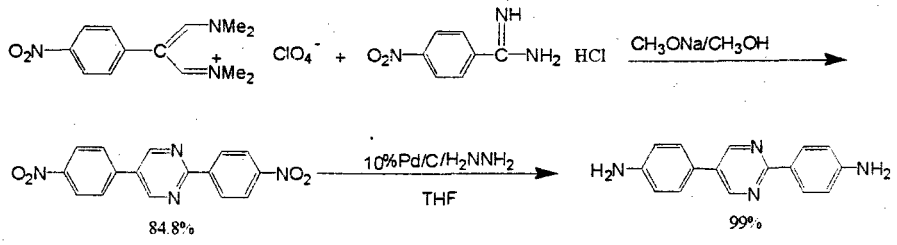
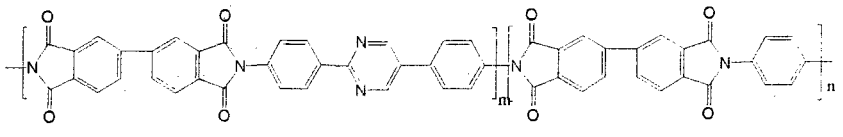
Aromatic polyimides have been extensively investigated for their excellent thermal stability and high mechanical properties, along with their good chemical resistance and electrical properties[1]. Therefore, they are used for the wide-spread materials, such as coatings, films, fibers, and matrix resins for advanced composites, etc. In the later of 1990s, Russian researchers reported a series of polyimide fibers based on 2,5-bis(4-aminophenyl)pyrimidine(2,5-PMR) with the properties similar to that of polybenzoxazole(PBO, Zylon) [2-4]. However the comprehensive properties of the PIs has not been revealed.

Recently, we synthesized a series of diamines containing the 2,5-disubstituted pyrimidine with high yield through simple reactions as shown in Scheme 1.



Scheme 1 Synthesis of 2,5-bis(4-aminophenyl)pyrimidine

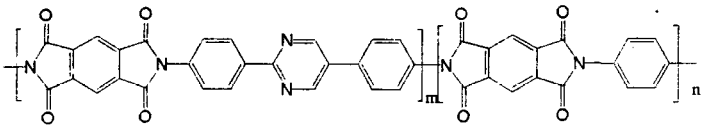
The homoPI were prepared by the polycondensation of 2,5-PMR and pyrimelltic dianhydride (PMDA) or 3,3`,4,4'-biphenyl tertracarboxylic dianhydride (BPDA). In the case of the copolymer synthesis, a part of 2,5-PMR was replaced by 1,4-phenylenediamine(PDA). The PIs were produced by two-step method. In the first step, poly(amic acid)(PAA) were prepared from 5(w/w)% [PMDA-PDA/2,5-PMR(n/m)] or 10(w/w)%[BPDA-PDA/2,5-PMR(n/m)] solution of monomers in N,N-dimethylacetamide(DMAC) at room temperature for 24h . The intrinsic viscosity of PAA solution ranging from [η]=2.07-5.67dl/g. In the second step, the PI films were obtained by thermal imidization of PAA films at 400℃. The properties of the PI films are listed in Table I and Table II. The figures in parenthese show the molar ratio of PDA/2,5-PMR. All the polyimides thus prepared have very high thermoxidative stability.



BPDA-PDA/2,5-PMR

Table I Properties of PI films made fromBPDA-PDA/2,5-PMR

BPDA-PDA/2,5-PRM(n/m) (mol)							
				TGA(wt%) (air)		TGA(wt%) (N2)	
n/m	viscosity of PAA(dl/g)	Tβ (℃)	Tg(℃)	5%(℃)	10%(℃)	5%(℃)	10%(℃)
0/100	3.09	173.4	318.4	573.3	600	573.3	603.1
25/75	2.83	159.9	300.3	588.4	606.5	587.1	609.5
50/50	2.52	172.6	301.9	564.7	591.4	577.6	593.9
80/20	2.12	160.1	306.5	556.5	578.3	564.7	591.4
90/10	2.07	170.2	318.1	534.5	560.3	568.9	582.6



PMDA-PDA/2,5-PMR

Table II Properties of PI films made from PMDA-PDA/2,5-PMR

PMDA-PDA/2,5-PRM(n/m) (mol)						
			TGA(wt%) (air)		TGA(wt%) (N2)	
n/m	viscosity of PAA(dl/g)	Tg(℃)	5%(℃)	10%(℃)	5%(℃)	10%(℃)
0/100	5.67	410.2	545.3	584.9	546.8	588.1
25/75	4.42	484.2	577.5	590.1	563.9	587.1
50/50	3.45	456.9	573.7	592.3	555.2	588.1
75/25	2.66	452.5	548.3	578.5	552.7	581.6

References

[1] C. E. Sroog, Prog. Polym. Sci., 16, 561(1991).

[2] Mihailov, G.M., Korzawin, L.N., Lebejeva, M.F. and Baklagina, Yu.G., J. Pract. Chem., (Russ.), 71(12), 2040(1998).

[3] T. E. Sukhanova, Yu. G. Baklagina, V. V. Kudryavtsev, T. A. Maricheva, F. Lednicky, Polymer 40, 6265-6276(1999)..

[4] Mihailov, G.M., Lebejeva, M.F., Baklagina, Yu.G., and Maricheva, T.A., J. Pract. Chem., (Russ.), 73(3), 472(2000).

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基于 2,5-二(4-氨基苯)嘧啶高性能共聚和均聚酰亚胺的合成及性能表征

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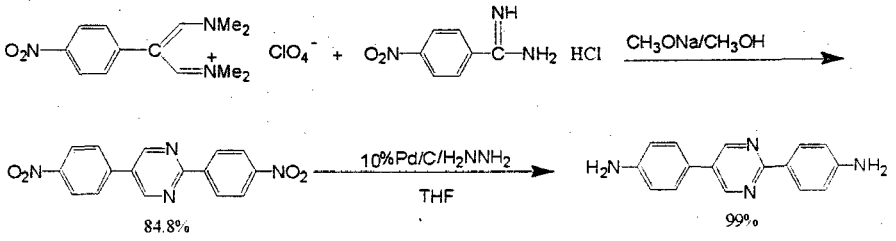
芳香聚酰亚胺因其优异的耐热性和机械性能以及良好的化学稳定性和介电性能而被广泛得用于涂料，薄膜，纤维，复合材料等高分子材料[1]。二十世纪九十年代末，苏联工作者报道了一系列性能与聚苯并噁唑（PBO, Zylon）纤维[2,3,4]相似的聚酰亚胺纤维。但是并未涉及这些聚酰亚胺其他的性能。

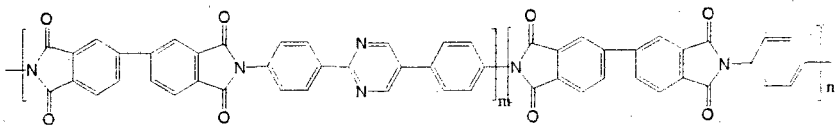
最近我们用简单易行的反应合成了一系列含 2，5－二取代嘧啶的二胺且产率较高，具体反应如下（schem1）：



Scheme 1

均聚聚酰亚胺由 2,5-二(4-氨基苯)嘧啶(2,5-PMR)与均苯二酐（PMDA）或联苯二酐（BPDA）聚合而成，对于共聚聚酰亚胺，其中一部分 2，5－PMR 被对苯二胺（PDA）取代共聚而成。聚酰亚胺通过两步法合成，第一步以 DMAc 作溶剂[PMDA-PDA/2,5-PMR(n/m)]

在固含量 5(w/w)% ，[BPDA-PDA/2,5-PMR(n/m)] 在固含量 10(w/w)%室温下形成聚酰胺酸（PAA）。聚酰胺酸的粘度变化范围为[η]=2.07-5.67dl/g。第二步，在 400℃使聚酰胺酸薄膜热亚胺化得到聚酰亚胺薄膜。聚酰亚胺薄膜的性能列于 Table I 和 Table II。其中圆括号中的数字代表 PDA 与 2,5-PMR 的摩尔比。由表格中的数据可看出这样得到的聚酰亚胺具有很高的热氧化稳定性。



BPDA-PDA/2,5-PMR

Table I Properties of PI films made fromBPDA-PDA/2,5-PMR

BPDA-PDA/2, 5-PRM(n/m) (mol)							
				TGA(wt%) (air)		TGA(wt%) (N2)	
n/m	viscosity of PAA(dl/g)	Tβ (℃)	Tg(℃)	5%(℃)	10%(℃)	5%(℃)	10%(℃)
0/100	3.09	173.4	318.4	573.3	600	573.3	603.1
25/75	2.83	159.9	300.3	588.4	606.5	587.1	609.5
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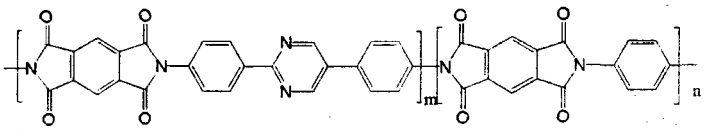

PMDA-PDA/2,5-PMR

Table II Properties of PI films made from PMDA-PDA/2,5-PMR

PMDA-PDA/2, 5PRM(n/m) (mol)									
			TGA(wt%) (air)		TGA(wt%) (N2)		elogation (%)	tensile strength (MPa)	modulus (GPa)
n/m	inherent viscosity of PAA(dl/g)	Tg(℃)	5%(℃)	10%(℃)	5%(℃)	10%(℃)			
0/100	5.67	410.2	545.3	584.9	546.8	588.1	10.1	254	5.66
25/75	4.42	484.2	577.5	590.1	563.9	587.1	***	***	***
50/50	3.45	456.9	573.7	592.3	555.2	568.1	16	280	6.46
75/25	2.66	452.5	548.3	578.5	552.7	581.6	9.1	185	3.81

References

[1] C. E. Sroog, Prog. Polym. Sci., 16, 561(1991).

[2] Mihailov, G.M., Korzawin, L.N., Lebejeva, M.F. and Baklagina, Yu.G., J. Pract. Chem., (Russ.). 71(12), 2040(1998).

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[4] Mihailov, G.M., Lebejeva, M.F., Baklagina, Yu.G., and Maricheva, T.A., J. Pract.Chem.,(Russ.), 73(3), 472(2000).

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