The Strategy of Chlorophthalic Anhydride for Polyimides

Mengxian Ding, Lianxun Gao, Changlu Gao, Jingling Yan
Changchun Institute of Applied Chemistry,
Chinese Academy of Sciences

1. Chlorophthalic anhydride can be produced in large scale via chlorination of o-xylene then oxidized by oxygen, finally distilled to separate the isomers,3- and 4-chlorophthalic anhydride in high purity.
2. Chlorophthalic anhydrides are inexpensive starting materials for preparation of isomers of BPDA, ODPA, TDPA, DSDA and diether dianhydrides.
3. Various polyimides can be synthesized directly from chlorophthalic anhydrides in one-pot procedure.
4. The relative reactivity of 4- and 3-chlorine in N-phenylphthalimide for nucleophilic substitution and coupling reaction is 1.82:1 and 3.64:1, respectively. The hydrolysis of N-phenyl chlorophthalimides in nucleophilic substitution is depended on temperature, water content and the nucleophilic reagent used, in DMAC containing 500ppm of water, a system which using K_2CO_3 and phenol as reagent hydrolysis is 11 times more than that using phenoxide as the reagent.
5. The comparation between chlorophthalic anhydride route and nitrophthalic anhydride route.

   A. Chlorophthalic anhydride: The whole yield for gas phase oxidation is >65%, for liquid phase is >80%; easily to obtain 3- and 4- chlorophthalic anhydrides in a purity as high as 99%; hydrochloric acid is the main by-product; bis(chlorophthalimide)s are easily prepared from chlorophthalic anhydrides; chlorophthalic anhydride or chlorophthalimides has the reactivity high enough in nucleophilic substitution to synthesize dianhydrides or polyimides; can be used in coupling reaction to obtain BPDA or polyimides containing byphenyl unit.

   B. Nitrophthali anhydride: Nitrophthali anhydride is difficulty to be prepared in high yield and high purity. In nitrogination of phthalic anhydride or phthalimide, large amount of waste acids can hardly be reused and the product most be purified by recrystallization. Their is high reactivity in nucleophilic substitution. It is not easy to obtain bis(nitrophthalimide)s due to hard to prepare pure nitrophthalic anhydrides. Nitrophthalimide can not be used in coupling reaction.References.

References

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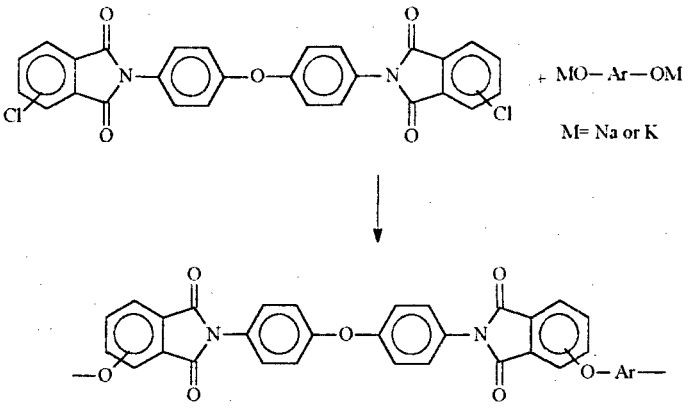
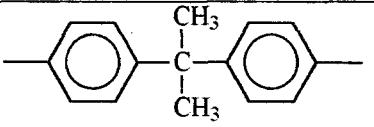
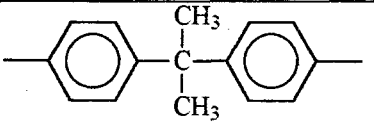
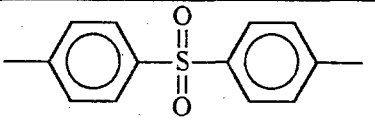
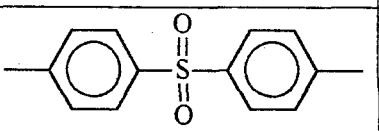
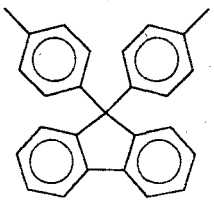
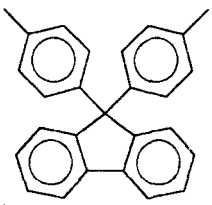
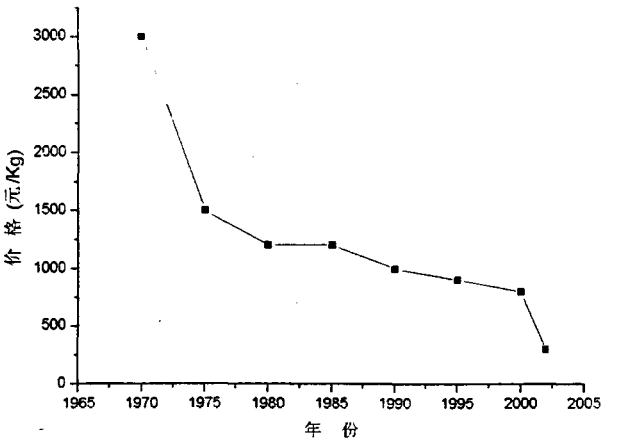
[4] Mengxian Ding, Changlu Gao, Suobo Zhang, Lianxun Gao, Polyimides from Chlorophthalic anhydrides, in Recent Progress in Polycondenzation, Ed. By Toshihiko Matsumoto, Research Signpost, pp. 257-263, (2002).



Scheme 1 Synthesis of polyetherimides by one-pot procedure

Table 1 Polyetherimides prepared by one-pot procedure

Cl	Ar	ηinh dL/g	Tg °C	$T_{5\%}$ °C	Film
3		0.65	238	462	Flexible
4		0.56	217	456	Flexible
3		0.20	269	475	Brittle
4		0.55	260	493	Flexible
3		0.63	294	495	Flexible
4		0.54	277	487	Flexible



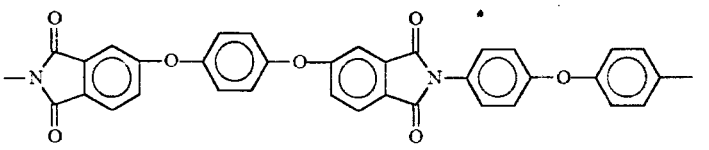


Fig. 1 The cost lowering of a commercialized polyetherimide by using of chlorophthalic anhydride as the starting material and direct synthesis procedure.

聚酰亚胺的氯代苯酐战略

丁孟贤，高连勋，高昌录，阎敬灵

中国科学院长春应用化学研究所

一、 氯代苯酐是能够大规模生产的化工原料：由邻二甲苯氯代，然后用空气气相氧化，最后进行 3-和 4-氯代苯酐异构体的分离是合成高纯度氯代苯酐最经济的合成路线，而且是目前获得 3-氯代苯酐唯一具有工业化价值的路线。

二、 氯代苯酐是合成多种二酐和聚酰亚胺的廉价原料：由氯代苯酐出发可以合成联苯二酐、二苯醚二酐、二苯硫醚二酐及多种二醚二酐的各种异构体。

三、 由氯代苯酐直接合成聚酰亚胺：由氯代苯酐出发可以用“一锅煮”的方法合成高分子量的多种聚酰亚胺，大大降低了聚酰亚胺的成本。

四、 在酞酰亚胺 3-位和 4-位氯的相对活性及氯代酞酰亚胺在亲核取代反应中的水解行为：在亲核取代反应中 4-位和 3-位氯原子的相对活性为 1:1.82；在偶联反应中为 3.64:1。在亲核取代反应中酞酰亚胺的水解行为取决于温度，体系中的水含量和亲核试剂，在含水 500ppm 的体系中，以碳酸钾和酚为原料所引起的酞酰亚胺环的水解为比以酚盐为原料时高 11 倍。

五、 氯代苯酐路线与硝基苯酐路线的比较：

1. 氯代苯酐：气相氧化和液相氧化总收率相应为>65%及>80%,；容易得到高纯度（99%）的两个异构体；副产物为盐酸；容易制备双（氯代酞酰亚胺）；在亲核取代反应中有足够高的活性；可以进行偶联反应得到联苯二酐或联苯型聚酰亚胺。
2. 硝基苯酐：难以得到高收率高纯度的硝基苯酐，所以多以硝基酞酰亚胺为原料，通常只能得到 4-硝基酞酰亚胺；硝化副产物废酸量大而且难以再用；不易得到双（硝基酞酰亚胺）；在亲核取代反应中活性高，但不能用于合成联苯结构的偶联反应。

所以可以认为，氯代苯酐是合成异构二酐和异构聚酰亚胺并得到低成本聚酰亚胺的理想原料。

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