

Novel approach to the mechanism of the high-temperature formation of naphthalimides

Danuta Sek*, Andrzej Wanic and Ewa Schab-Balcerzak

*Institute of Polymer Chemistry, Polish Academy of Sciences, Zabrze, Poland
(Received 18 August 1992; revised 5 October 1992)*

A series of model compounds has been synthesized from 4-benzoylnaphthalic anhydride and oxydianiline in various solvents (aprotic, protic), with or without catalyst at 180°C. A mechanism of the reaction is proposed.

(Keywords: amic acid; isoimide; imide)

Introduction

Polyimides with six-membered imide rings are of interest because of their higher thermal stability than those with five-membered rings. But six-membered ring anhydrides are less reactive towards aromatic amines, therefore in this case high temperature polycondensation is usually used. In our previous work¹ we investigated the relationship between the structure of diamines and bisnaphthalic dianhydrides and also the influence of high-temperature process conditions on the reduced viscosity of new polynaphthalimides. The results obtained, especially the influence of the rate and method of catalyst addition, prompted us to look for an explanation of the observed relations from the point of view of the reaction mechanism. In this communication we report the results of investigations of a series of model compounds from 4-benzoylnaphthalic anhydride and oxydianiline, with the reaction carried out in aprotic and protic solvents with or without catalyst.

Experimental

Materials. Acenaphthene (Sojuzchim) was used as laboratory grade chemical. Oxydianiline (Fluka) was sublimed before use. Solvents were dried and distilled in the usual manner.

Anhydride. 4-Benzoylnaphthalic anhydride was prepared by Friedel-Crafts acylation of acenaphthene to 4-benzoylacenaphthene followed by oxidation to diacid and cyclization to anhydride. The anhydride was crystallized from acetic anhydride before use. M.p. 202°C.

Model compounds. Anhydride (2 mmol) and oxydianiline (1 mmol) in solvent (20 ml) were placed in a container equipped with a stirrer and an air condenser and heated at 180°C for 18 h under argon atmosphere. For reactions carried out in the presence of catalysts, 2 mmol of catalyst was used. Products were precipitated with 120 ml of methanol.

Measurements. I.r. spectra were recorded on a Specord M 80 spectrometer. For elemental analysis a 240 C Perkin

Elmer analyser was used. Melting points were determined on DSC Du Pont 1090 B apparatus. N.m.r. spectra were recorded on a Varian VXR 300 spectrometer. Molecular masses were determined on a SSQ 700 Finnigan MAT spectrometer.

Results and discussion

The first part of the work was to determine whether amic acid is formed at high temperature in the reaction of anhydride and amine groups, as it is generally supposed². To achieve this, reactions were carried in aprotic solvents, which should prefer the formation of amic acid, such as tetraglyme, NMP and HMPT, with or without catalysts, i.e. benzoic acid and isoquinoline. The same product, having m.p. 325°C and soluble in chloroform, was obtained independent of the reaction conditions. I.r. spectra of the product did not show the absorption band characteristic of the acid group. Also, in ¹H n.m.r. spectra no signal was observed in the range for acid protons. Elemental analyses (C 77.90%, H 3.60%, N 3.55%) and mass analyses (mol. peak 768) gave data corresponding to imide or isoimide structure.

To determine the structure of the compound, the i.r. and ¹³C n.m.r. analyses were resolved. In the i.r. spectrum, absorption bands at 1712 cm⁻¹, characteristic of isoimide C=O stretching vibrations, and at 1672 cm⁻¹, characteristic of C=N stretching vibrations, were present. In the ¹³C n.m.r. spectrum the most important feature for differentiation of imide and isoimide structures is the position of signals of carbon atoms in the phenylene ring of oxydianiline. For theoretical calculations the isocyanate (O=C=N-) and tertiary amine ((CH₃)₂N-) groups were used as a pattern for isoimide and imide structures, respectively. Table 1 shows calculated and obtained values of chemical shifts³. As can be seen, the observed shifts of the carbon signals fit quite well with the isoimide structure.

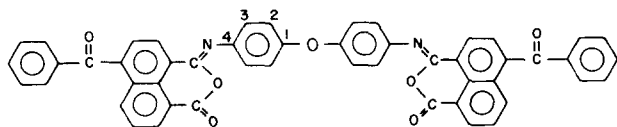
In the next step, the model compounds were synthesized in protic solvents, i.e. *m*-cresol, *p*-chlorphenol. When reactions were carried out in *m*-cresol with or without benzoic acid, the product was soluble in chloroform and had the same properties as that obtained in aprotic solvents. But when isoquinoline was added to the reaction mixture in *m*-cresol with benzoic acid as catalyst after

* To whom correspondence should be addressed

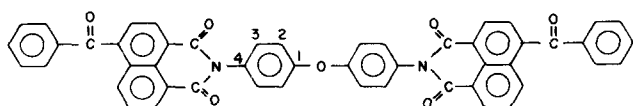
Table 1 Calculated and observed signals in ^{13}C n.m.r. spectra

Number of carbon atoms	Calculated values for		Values observed in spectra
	Isoimide	Imide	
1	154.9	142.0	156.0
2	120.3	119.9	118.8
3	126.5	114.4	129.1
4	129.1	145.8	129.3

Isoimide structure:



Imide structure:



9 h of heating, and heating was continued for another 9 h, two different products were obtained. One product was soluble in chloroform and its properties were the same as the models obtained before, having isoimide structure. The second product (yield about 1%), was black and crystalline, completely insoluble in chloroform and

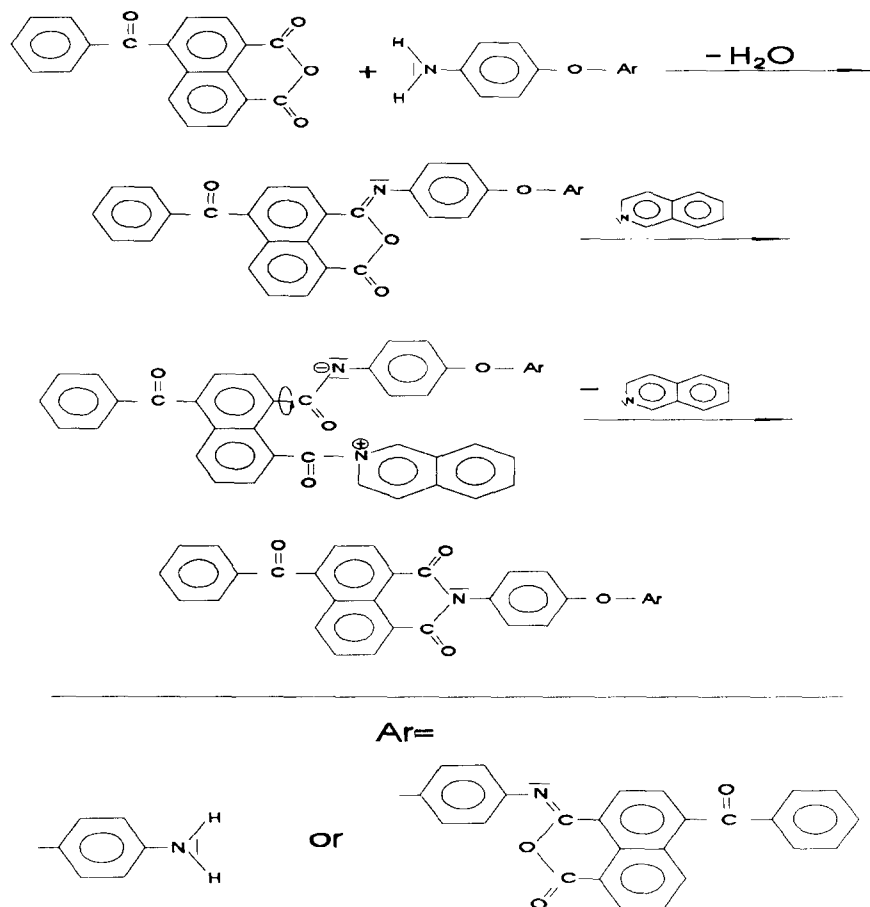
most other organic solvents, and did not melt up to 450°C (mol. mass 768, elemental analysis C 77.6%, H 3.5%, N 3.6%). When the reaction was carried out in *p*-chlorophenol in the presence of benzoic acid and isoquinoline, two products were also obtained, one soluble and the other insoluble in chloroform, but their weight ratio was about 1:1. It seems that the more acidic the solvent used as reaction medium, the higher the yield of the insoluble product. Elemental analysis and mol. mass of the black product were similar to those of the soluble product, but in the i.r. spectrum absorption bands at 1640 cm^{-1} , characteristic of a six-membered imide ring, were observed.

Conclusions

In the reaction of six-membered ring anhydride with aromatic amine in a high-temperature condensation process in aprotic solvents, only a product with isoimide structure was obtained, independent of the presence or absence of catalyst (benzoic acid and isoquinoline). Amic acid was not observed to be present.

In protic phenolic type solvents, the formation of isoimide structure only was observed when reactions were carried out without catalyst or in presence of benzoic acid. Addition of isoquinoline to the reaction mixture caused the formation of the imide structure as well. The amount of imide compound increased if the reaction was carried out in a more acidic solvent.

So it seems that, in the high-temperature condensation process of a six-membered anhydride ring with aromatic amine, the imide structure is formed by isomerization of

**Figure 1** Scheme of the reaction mechanism

the isoimide structure in suitable conditions, i.e. correct acidity of the solvent and the presence of acid catalyst (benzoic acid) and tertiary amine (isoquinoline). These facts led us to propose the following mechanism for the high-temperature polycondensation (see *Figure 1*):

1. Nucleophilic addition of amine to carbonyl group followed by dehydration leading to isoimide structure without opening anhydride ring. The anhydride ring, especially the six-membered ring, being a product of dehydration of two carboxylic groups, should be stabilized by high temperature.
2. Isomerization of isoimide to imide in the presence of benzoic acid and isoquinoline.

Our preliminary work seems to confirm that the mechanism presented is common and is probably also valid for high-temperature condensation of five-membered ring anhydrides with aromatic amines and benzimidazoles. Work is in progress and more detailed results will be published in the near future.

References

- 1 Sek, D., Pijet, P. and Wanic, A. *Polymer* 1992, **33**, 190
- 2 Wilson, D., Stenzenberger, H. D. and Hergenrother, P. M. (Eds) 'Polyimides', Blackie, Glasgow, 1990
- 3 Atta-ur-Rahman, 'Nuclear Magnetic Resonance', Springer-Verlag, New York, 1986