Polymer Bulletin 35, 285–290 (1995)

Polymer Bulletin

A novel route to polyimides via polyamic aryl amides

Part 1. A study on model compounds

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Received: 22 February 1995/Revised version: 4 April 1995/Accepted: 7 April 1995

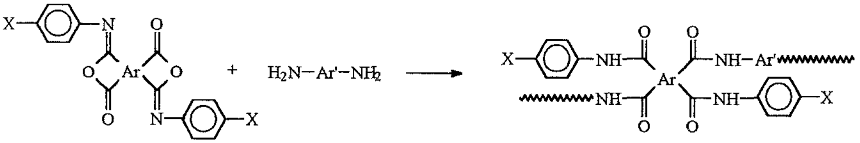
Summary

A new synthetic route to polyimides was studied on monofunctional model compounds by the reaction of various 4-substituted phenyl-phthalisoimides with paratoluidine to form asymmetrically substituted diphthalamides followed by thermal cyclization to phthalimide. Both steps of the preparation pathway were kinetically explored. It was determined that the first step is governed by second order constants directly dependent upon the pK_a of the amine used to prepare the beginning isoimide as well as the regioselectivity of the last step.

Introduction

The preparation of polyimides from dianhydrides and primary diamines proceeds commonly through a two step process: an addition to form first a polyamic acid which can then be cyclized by means of thermal or chemical treatment (1). The presence of water can deplace the equilibrium between polyamic acid and monomers to form diacids, lowering the overall molecular weight of the polyimides (2). In order to prevent this polymer degradation, attempts to modify the chemical structure of the polyamic acid lead to the preparation of polyamic alkyl esters (3) and polyamic alkyl amides (4) through acyl chlorides. However, evolution of chlorhydric acid is observed during the cyclization step.

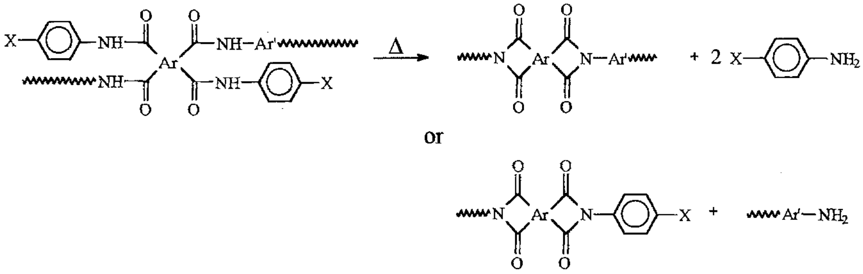
To circumvent these difficulties, our idea was to prepare a polyamic aryl amide from a bisisoimide and a diamine as follows:



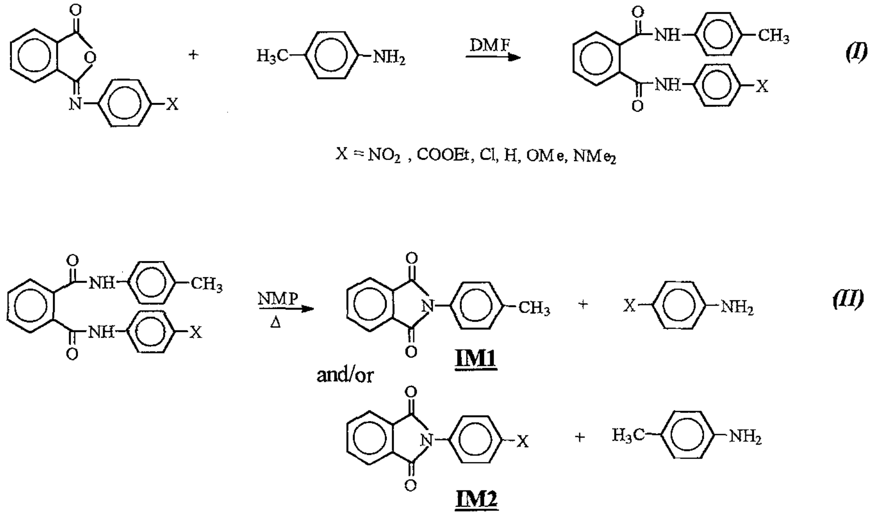
Scheme 1. Reaction of a bisisoimide with a diamine

The reaction with a secondary amine is well described (5,6), however the peculiar case of a primary amine reaction is only described for a low viscosity polymer (7). During the imidization process, two possible competitive routes can arise: a normal polyimidization producing a paraphenyl substituted monoamine and a second one leading to chain cleavage (scheme 2).

The present paper tries to investigate the role of the X substituent on phthalic models by studying the kinetics of the reaction between an isoimide and paratoluidine and then the selectivity of thermal imidization (scheme 3).



Scheme 2. Cyclisation of a polyamic amide



Scheme 3. Two step reaction on phthalic models

Experimental

Materials: Phthalic anhydride was sublimed just prior to use. All the amines used were commercial and used as received. Dimethylformamide (DMF) was twice distilled over phosphoric anhydride and stored over 3Å molecular sieves. N-methylpyrrolidone (NMP) was distilled and also stored over 3Å molecular sieves.

Isoimide preparation: Phthalic anhydride (0.1 mole) was added to a solution of a selected parasubstituted aniline (0.1 mole) in NMP (20% w/v) at room temperature. The formation of the amic acid was followed by thin layer chromatography. The solution can be heated up to 60°C depending on the amine reactivity. Then, it was cooled to -15°C, and 1.3 molar equivalent of trifluoracetic anhydride was added dropwise. After one hour, the solution was precipitated in cold saturated sodium carbonate water, washed with ice water and dried at 40°C. The crude product yielded 80 to 93% and was not recrystallized.

Diamide preparation: Paratoluidine (0.01 mol) was added to a solution of the selected 4-phenyl substituted phthalisoimide in DMF (0.01 mol, 20% w/v) at room temperature. After reaction (monitored by reverse phase chromatography), DMF was removed and the phthaldiamide was crystallized from water, filtered, washed with toluene and then dried at 40°C. Quantitative yields were obtained.

Imide preparation from diamide: A solution of the above phthaldiamide was heated at NMP reflux (20% w/v) for two hours, cooled to 0°C, precipitated into water, washed with ether, and dried at 100°C. Quantitative yields were obtained.

Kinetics and characterization: The kinetics were carried out on an HP 1050 reverse phase chromatograph with acetonitrile/water elution gradient at a 254 nm UV detection. A Spherisorb ODS II column was chosen. Spectroscopic characteristics were determined by ^{13}C NMR ($CDCl_3$) on a Bruker AC 250 MHz spectrometer and by FTIR on a Bio-Rad FTS-155 spectrometer (KBr pellets). Melting points were observed on a Kofler hot bench.

Results and discussion

I. Phthalic diamide preparation (scheme 3, equation I)

The preparation of isoimides is based upon the selective dehydration of amic acids by reagents such as trifluoracetic anhydride (8) or N,N'-dicyclohexylcarbodiimide (9). Due to their instability, only phthalic, maleic and camphoric isoimides are isolable (10). Kurita et al. (11) have recently described the preparation of N-benzyloxyisoimides carried out with acetic anhydride with a perceptible enhancement of stability. The reaction of isoimides with water or with nucleophilic agents according to the pH is well established (12). Due to its asymmetry, a phthalisoimide can be easily distinguished from the corresponding phthalimide with ^{13}C NMR and a confirmation is achieved with infrared spectroscopy (13). In addition compared with imide, the isoimide exhibits a weak absorption in 320-400 nm U.V. zone (14) and at last, a lowering of the melting points (M.p.) as given in table 1.

Table 1. *Compared melting points of isoimide and imide structures*

X	isoimide M.p., °C	imide M.p., °C (8)
NO_2	143 (^{a}) (litt. 172)	268
$COOC_2H_5$	136	153
Cl	161 (litt.160)	197
H	120 (litt.116)	211
OCH_3	134 (litt.134)	162

(^{a}) decomposition

The reaction was performed in DMF. Due to its nucleophilic impurities, undistilled DMF initiates a rapid transformation of the isoimide into imide. Two successive distillations of the DMF over P_2O_5 are necessary. The kinetic study of this reaction was monitored with reverse phase chromatography and all the data were established owing to an internal standard i.e. 4,4'-dimethylbenzophenone. For example, in the case of the nitro derivative (figure 1), the reaction is completed in 3 hours.

The expected second order is confirmed by plotting the diamide concentration as a function of time according to the second order equation (figure 2):

$$\frac{1}{[diamide]} = \frac{1}{k[isoimide]_0^2 t} + \frac{1}{[isoimide]_0}$$

and

$$t_{\frac{1}{2}} = \frac{1}{k[isoimide]_0}$$

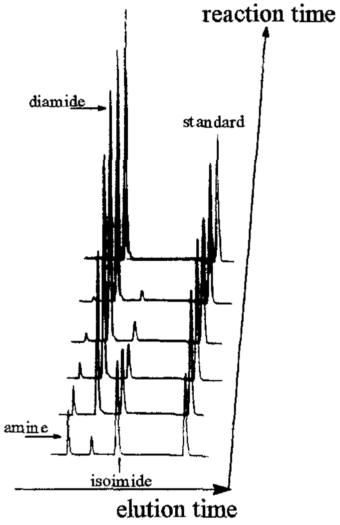


Figure 1. HPLC graphs of the nitro diamide formation

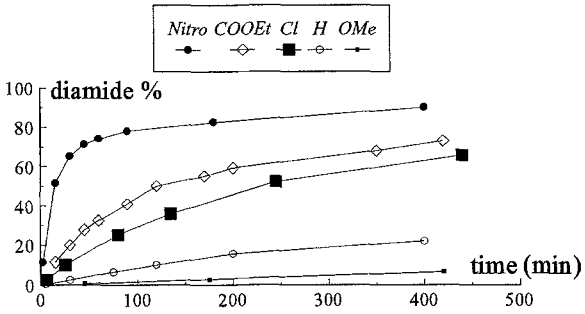


Figure 2. Evolution of the diamide concentration with time

Constant rates and half-reaction times can then be calculated using the slope (table 2).

Table 2. Reaction of the 4-phenyl substituted phthalisoimides with paratoluidine: kinetic data of the diamide formation and correlation with the pK_a of the parasubtituted anilines

X	k ($mol^{-2}.l^{2}.s^{-1}$)	$t_{1/2}$	pK_a
NO_2	$1.12.10^{-2}$	15 min	1
$COOC_2H_5$	$1.71.10^{-3}$	1 h 45	2,3
Cl	$7.51.10^{-4}$	4 h 05	2,9
H	$1.31.10^{-4}$	19 h 40	4,6
OCH_3	$2.76.10^{-5}$	100 h	5,3

These data can be compared to the dissociation constant of the parent amines used to prepare isoimides with a good correlation between ln k and pK_a (figure 3).

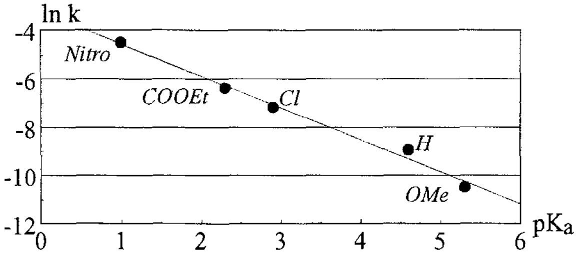


Figure 3. *Relation between constant rate of the phthaldiamide formation and pK_a of the parent amine*

In all the cases studied, a small amount (<2%) of imide is also detected coming from isomerisation during HPLC analysis.

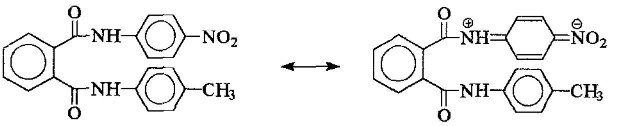
II. Phthalic diamide cyclization (scheme 3, equation II)

When a phthaldiamide is heated at NMP reflux, cyclization occurs in general with the formation of both N-(p-tolyl)-phthalimide (IM1) and parasubstituted phenyl-phthalimide (IM2) with the corresponding by-product amines (table 3).

Table 3. *Selectivity of the thermal phthaldiamide cyclization*

X	% IM1	% IM2
NO_2	100	0
$COOC_2H_5$	43	57
Cl	57	43
H	55	45
OCH_3	50	50

This selectivity is determined by measuring the imide yield with the chromatographic technique indicated above. The electron withdrawing character of the nitro group decreases the electronic density of the carbonyl site. So the nucleophilic attack of the adjacent amide group is predominant:



This result is confirmed by the disappearance of the 1340 cm^{-1} nitro band (figure 4). This effect rapidly decreases with the others substituents so that a complete regioselectivity is observed only with the nitro substituent.

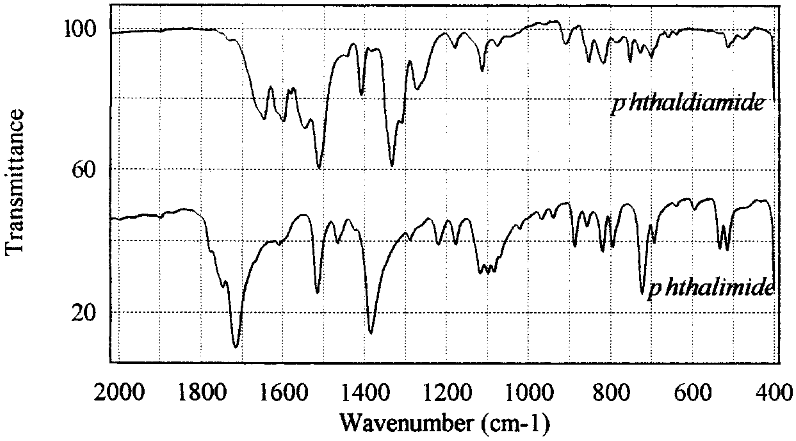


Figure 4. *Compared IR spectra of nitro-phenyl-phthalimide and nitro-phenyl-phthaldiamide*

Conclusion

A possible pathway to polyimide preparation via polyamic aryl amide precursors has been investigated on model compounds. The reaction between isoimide and paratoluidine leads to this precursor and is governed by a second order rate constant which is directly dependent upon the pK_a of the parent amine used to prepare the isoimide. The thermal imidization of the precursor does not obey to the same scale except for one amic amide which is regioselective. The synthesis of a nitro-arylisoimide and the polycondensation with an aromatic diamine are in progress.

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