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# Stability study of sulfonated phthalic and naphthalenic polyimide structures in aqueous medium

C. Genies[a], R. Mercier[a,*], B. Sillion[a], R. Petiaud[b], N. Cornet[c], G. Gebel[c], M. Pineri[d]

[a]Laboratoire des Matériaux Organiques à Propriétés Spécifiques, UMR 5041, CNRS, BP 24, 69 390 Vernaison, France
[b]Service RMN, Réseau des Polyméristes Lyonnais, Laboratoire des Matériaux Organiques à Propriétés Spécifiques, UMR 5041, CNRS, BP 24, 69 390 Vernaison, France
[c]CEA/Département de Recherche Fondamentale sur la Matiére Condensée, SI3m-Groupe Polymères Conducteurs Ioniques, 17 rue des Martyrs, 38 054 Grenoble cedex 9, France
[d]CEA/Département d'Etudes des Matériaux, SPCM, 17 rue des Martyrs, 38 054 Grenoble cedex 9, France

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**Abstract**

The purpose of this paper is to evaluate the respective hydrolysis stability of phthalic and naphthalenic imide structures through the study of model compounds. The NMR and IR spectroscopic analyses of model compounds, before and after aging in water, at temperature representative of fuel cell working temperature, indicated structural modifications according to imide ring structure. The phthalic model stability was inferior to 1 h at 80°C whereas the confirmed naphthalenic model one was superior to 100 h in the same conditions. Moreover, a limited hydrolysis of naphthalenic imide cycle was also shown. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Sulfonated polyimides; Phthalic Naphthalenic model compounds; Hydrolysis stability

## 1. Introduction

In a previous study we have shown that sulphonated polyimides could be used as fuel cell membranes [1]. Experiments were performed both with phthalic and naphthalenic sulfonated polyimides at 60°C, at a 3 bar pressure for $H_2$ and $O_2$ and under a constant current density of 250 mA $cm^{-2}$. Some differences in terms of stability were observed depending on the polyimide structure concerned. The phthalic structure quickly degraded and became brittle within a few days, while naphthalenic polyimides were shown to be significantly more stable in the same conditions. Indeed, one experiment was carried out for 3000 h in order to study the membrane aging. A slow decrease in the fuel cell performances during the experiment was observed, which could be attributed to a loss of ionic conductivity related to either a continuous dehydration or polymer degradation. One speculative explanation to account for the sulphonated polyimide membrane degradation is the hydrolysis leading to polymer chain scissions. Such a decrease in the molecular weight could also explain the brittleness of the observed membrane.

The objective of this study was to underline the possible imide cycle hydrolysis connected with $SO_3H$ presence since the hydrolysis stability of imide cycle is well known [2]. In order to obtain as clear information as possible about structural modifications from NMR and IR analyses, we have performed our investigations using model compounds. The structures of sulfonated phthalic and naphthalenic compounds presented in Fig. 1 are similar to the repetition unit of ionic sequence of phthalic and naphthalenic sulphonated polyimides, respectively, which were studied in our laboratory [1]. These two compounds were prepared and characterized by NMR and IR spectroscopy. Then, they were placed in a water environment at a chosen temperature. The aging products were finally analyzed by NMR and IR spectroscopy.

## 2. Experimental part

### 2.1. Materials

Metanilic acid, triethylamine, aniline, benzoyl chlorine, *m*-cresol and dimethylsulfoxide (DMSO) were purchased from commercial source and used as received. Oxydiphthalic anhydride (ODPA) and 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) are commercial products.

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* Corresponding author. Tel.: +33-0478-02-22-72; fax: +33-0478-02-77-38.

*E-mail address:* regis.mercier@lmops.cnrs.fr (R. Mercier).

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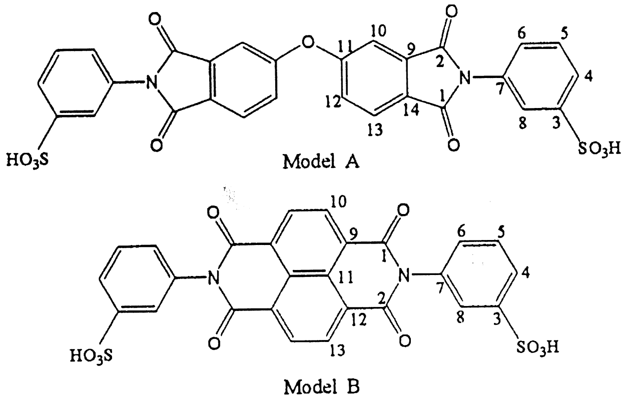


Fig. 1. Structures of phthalic model A and naphthalenic model B.

Prior to being used, ODPA was purified by sublimation, and NTDA was dried at 160°C under vacuum.

## 2.2. Model compound synthesis

### 2.2.1. Phthalic compound A (see Fig. 1)

In a three-necked round bottom flask fitted with a magnetic stirrer, a nitrogen pad and a thermometer, 6.69 g ($3.9 \times 10^{-2}$ mol) of metanilic acid and 4.70 g ($4.6 \times 10^{-2}$ mol) of triethylamine were introduced along with 100 ml of *m*-cresol. This mixture was stirred at room temperature allowing the solubilization of metanilic acid by acid–soda exchange. Then, 6.00 g ($1.9 \times 10^{-2}$ mol) of ODPA were added. The reaction mixture was stirred at room temperature for 10 min, and then heated at 160°C for 8 h. After cooling, the reaction solution was precipitated into an ether/ethanol mixture. The precipitated white powder was filtered out, washed with ether and dried at 120°C. The yield of the phthalic model A was 12.49 g (72.5%).

This model A under triethylammonium sulfonate form (4.00 g) was dissolved in 25 ml of DMSO. The solution was treated on a high acid ion exchange resin (Amberlyst 15). The recovered solution was precipitated in ether/methanol mixture. The white powder was filtered out and dried under vacuum at 120°C. The yield of the phthalic model in acid form was 1.87 g (61.9%). The global yield of phthalic model A was 44.9%.

NMR $^1$H (DMSO-d6): $\delta$ (ppm) = 7.41 (d, $J = 7.9$ Hz, 2H, $H_{4\ \mathrm{or}\ 6}$); 7.51 (dd, $J = 7.9$ Hz, 2H, $H_5$); 7.69 (m, 6H, $H_{6\ \mathrm{or}\ 4,12,10}$); 7.71 (s, 2H, $H_8$); 8.07 (d, $J = 8.87$ Hz, 2H, $H_{13}$); 8.07 (s, 2H, H acid).

NMR $^{13}$C (d6-DMSO): $\delta$ (ppm) = 114.25 (2C, $C_{10}$); 125.01 (2C, $C_8$); 125.42 (2C, $C_{12}$); 125.84 (2C, $C_{6\ \mathrm{or}\ 4}$); 126. 58 (2C, $C_{13}$); 127.74 (2C, $C_{14}$); 128.11 (2C, $C_{4\ \mathrm{or}\ 6}$); 128.92 (2C, $C_5$); 131.85 (2C, $C_7$); 135.05 (2C, $C_9$); 149.32 (2C, $C_3$), 161.33 (2C, $C_{11}$); 166.59 (2C, $C_2$); 166.76 (2C, $C_1$).

### 2.2.2. Model naphthalenic B (see Fig. 1)

In a three-necked round bottom flask fitted with a magnetic stirrer, a nitrogen pad and a thermometer, 7.75 g ($4.5 \times 10^{-2}$ mol) of metanilic acid and 5.43 g ($5.4 \times 10^{-2}$ mol) of triethylamine were introduced along with 130 ml of *m*-cresol. This mixture was stirred at room temperature to allow the solubilization of metanilic acid by acid–soda exchange. Then, 6.00 g ($2.24 \times 10^{-2}$ mol) of naphthalenic dianhydride and 3.82 g ($3.13 \times 10^{-2}$ mol) of benzoic acid were added. The reaction mixture was stirred at room temperature for 10 min, and then heated at 160°C for 8 h. After cooling, the reaction solution was precipitated into ethyl acetate. The precipitated white powder was filtered out, washed with ether and dried at 120°C. The yield of the naphthalenic model B was 18.30 g (59.8%).

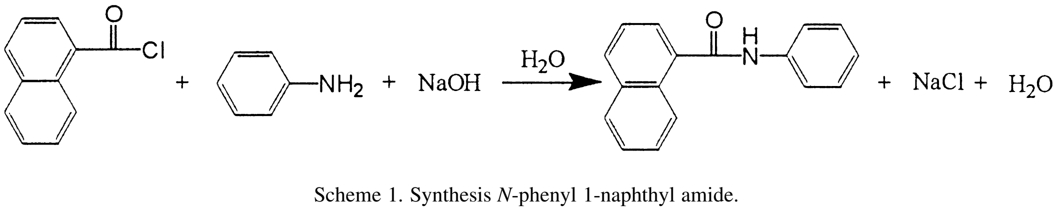
This model B in triethylammonium sulphonate form (1.00 g) was dissolved in 10 ml of DMSO. The solution was treated on a high acid ion exchange resin (Amberlyst 15). The recovered solution was precipitated in ether. The white powder was filtered out and dried under vacuum at 120°C. The yield of the naphthalenic model B in acid form was 0.69 g (93.1%). The global yield of naphthalenic model B was 55.7%.

NMR $^1$H (d6-DMSO): $\delta$ (ppm) = 7.42 (d, $J = 8.0$ Hz, 2H, $H_{4\ \mathrm{or}\ 6}$); 7.53 (dd, $J = 8.0$ Hz, 2H, $H_5$); 7.71 (m, 4H, $H_{6\ \mathrm{or}\ 4,8}$); 7.93 (sl, 2H, $H_{\mathrm{acide}}$); 8.72 (s, 4H, $H_{10,13}$).

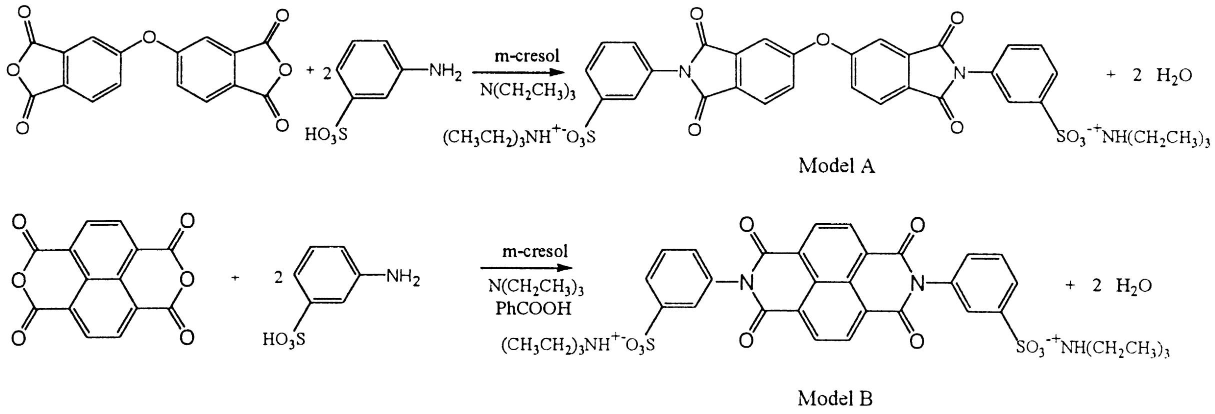
NMR $^{13}$C (d6-DMSO): $\delta$ (ppm) = 125.99 (2C, $C_8$); 126.58 (2C, $C_{4\ \mathrm{or}\ 6}$); 126.99 (2C, $C_{11}$); 127.35 (4C, $C_{9,12}$); 128.75 (2C, $C_{6\ \mathrm{or4}}$); 129.61 (2C, $C_5$); 130.60 (4C, $C_{10,13}$); 135.38 (2C, $C_7$); 149.11 (2C, $C_3$); 163.29 (4C, $C_{1,2}$).

### 2.2.3. N-phenyl 1-naphthyl amide synthesis (see Scheme 1)

In a flask, 2.44 g ($2.63 \times 10^{-2}$ mol) of aniline were mixed in 20 ml of distilled water with sodium hydroxide in excess of 15% (1.21 g of NaOH ($3.02 \times 10^{-2}$ mol). 5.50 g ($2.9 \times 10^{-2}$ mol) of benzoyl chlorine were slowly added to the reaction mixture under stirring. A white product precipitated in solution. The precipitated amide formed was filtered out, washed three times with water, and then dried under vacuum at 80°C. The product was purified by recrystallization in methanol. After filtration and drying



Scheme 1. Synthesis *N*-phenyl 1-naphthyl amide.



Scheme 2. Synthesis of models A and B.

under vacuum at 80°C, 5.76 g of amide were obtained with a yield of 88.8%.

### 2.2.4. Experimental conditions for aging

The model compound was put in a glass tube along with a known quantity of water before sealing the tube. The tube was then put into an oven at a temperature representative of the fuel cell working temperature. After aging, the sample was isolated using a lyophilization technique to prevent any further degradation of the compound.

### 2.3. Measurements

Both $^{1}H$ and $^{13}C$-NMR spectra were recorded on a Bruker spectrometer (AC250). Products were dissolved in DMSO-d6 working at 250 MHz for $^{1}H$ and 62.9 MHz for $^{13}C$. Some attributions were made with 2D-NMR. In these cases, spectra were obtained with a Bruker DRX 400 spectrometer using an inverse-probe with field-gradients for COSY, HMQC and HMBC at 400 MHz. IR spectra were recorded in the 4000–400 $cm^{-1}$ range on Nicolet 20 SX spectrometer.

## 3. Results and discussion

### 3.1. Model synthesis

The synthetic procedures of models A and B are shown in Scheme 2. These compounds were synthesized by condensation of metanilic acid with the ODPA or with the 1,4,5,8-naphthalene tetracarboxylic dianhydride (NTDA) in the presence of triethylamine, respectively, to allow the solubilization of BDSA by formation of its triethylammonium sulphonate. For the synthesis of model B, benzoic acid was added as suggested in literature [3–6]. The acid form was regenerated by the acidic ionic exchange resin treatment. Their structures were confirmed by $^{1}H$ and $^{13}C$-NMR and IR spectroscopic analyses and the results were in good agreement with the proposed structures (see Figs. 2a and 3a for model A and Figs. 9a and 11a for model B).

### 3.2. Stability study of the model compound A

### 3.2.1. Qualitative analysis

The model A was put in distilled water at a concentration of $1.61 \times 10^{-1}$ mol $l^{-1}$. The chosen aging temperature was 80°C. After 1 h at this temperature, a structural modification

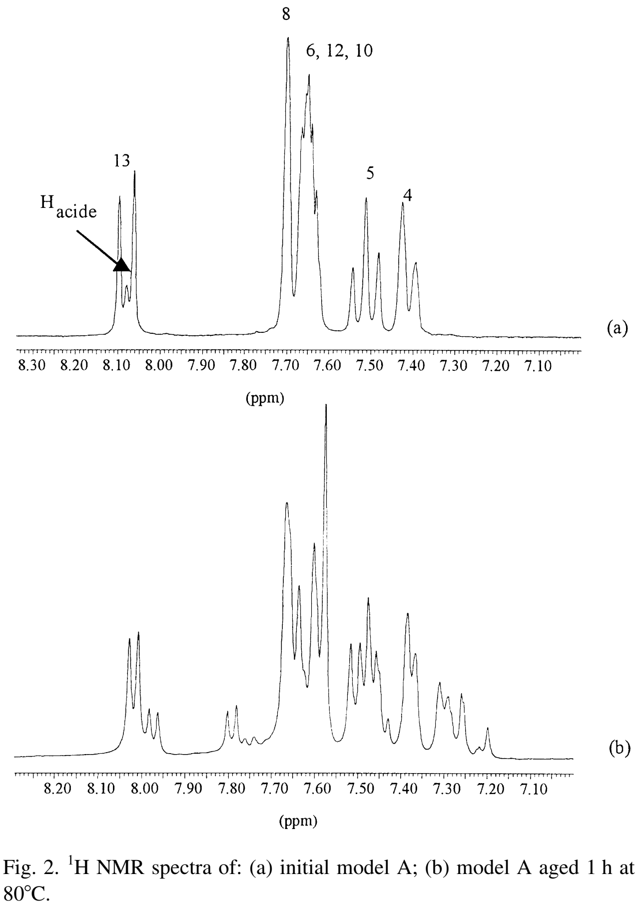


Fig. 2. $^{1}H$ NMR spectra of: (a) initial model A; (b) model A aged 1 h at 80°C.

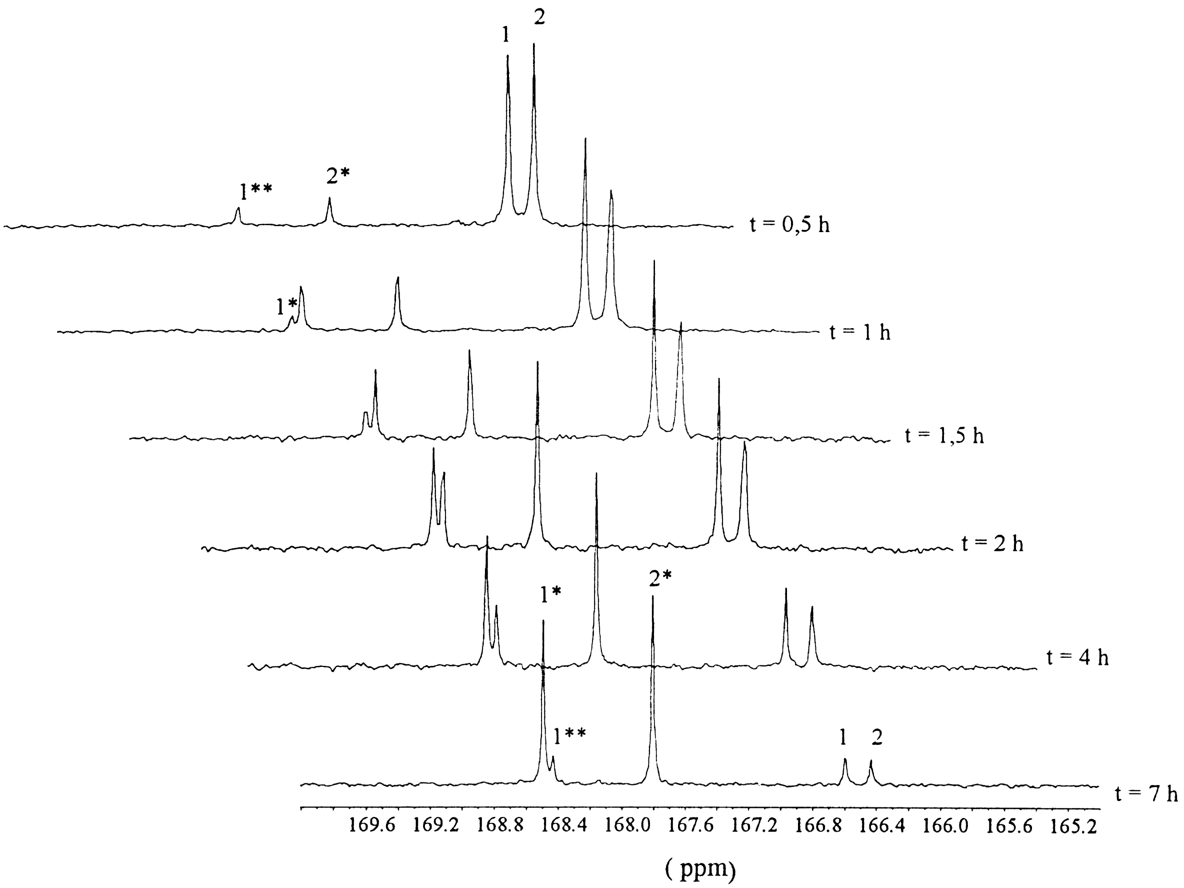


Fig. 3. $^{13}$C NMR spectra of: (a) initial model A; (b) model A aged 1 h at 80°C.

of the compound A was observed by NMR analysis. Indeed, the $^{1}$H and $^{13}$C-NMR spectra in DMSO-d6 solvent of the lyophilized sample were highly modified compared to those of the virgin model (Figs. 2b and 3b). Particularly, on the $^{13}$C NMR spectrum, we could observe many peaks other than the peaks corresponding to the starting product which means a partial transformation of the model A. But, after 10 h of aging, the $^{13}$C NMR spectrum (see Fig. 4) was

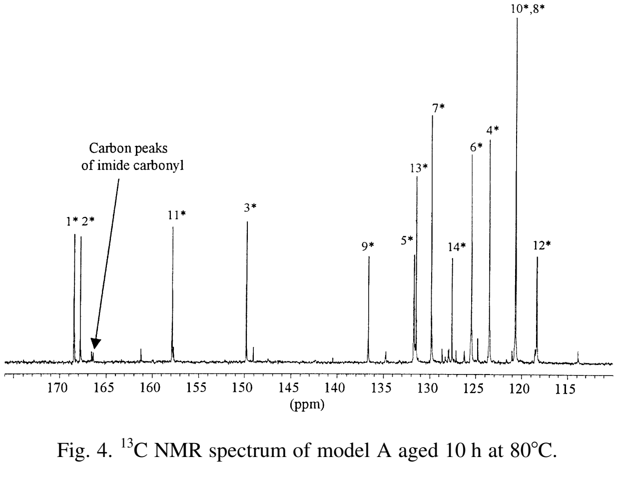
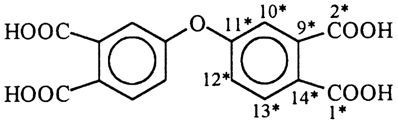
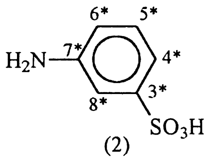


Fig. 4. $^{13}$C NMR spectrum of model A aged 10 h at 80°C.

Table 1
Attributions and chemical shifts of carbons of metanilic and oxydiphthalic acid



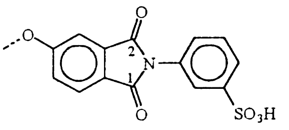
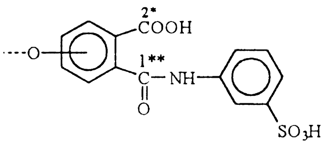
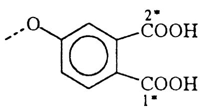
(1)



(2)

| Carbons positions | δ (ppm/TMS) |
|---|---|
| 1* | 168.49 |
| 2* | 167.80 |
| 3* | 149.85 |
| 4* | 123.66 |
| 5* | 131.80 |
| 6* | 125.59 |
| 7* | 129.85 |
| 8* | 120.71 |
| 9* | 136.69 |
| 10* | 120.79 |
| 11* | 157.89 |
| 12* | 118.42 |
| 13* | 131.40 |
| 14* | 127.62 |

Table 2
Attributions and chemical shifts of carbonyl carbons of hydrolysis compounds

| Imide (model A) | | Acid-amid | | Carboxylic diacid | |
|---|---|---|---|---|---|
|  | |  | |  | |
| Positions | δ (ppm/TMS) | Positions | δ (ppm/TMS) | Positions | δ (ppm/TMS) |
| 1 | 166.56 | $1^{**}$ | 168.41 | $1^{*}$ | 168.49 |
| 2 | 166.40 | $2^{*}$ | 167.79 | $2^{*}$ | 167.79 |

greatly simplified and showed a complete disappearance of the starting product peaks, whereas we observed two peaks at 168.49 and 167.80 ppm corresponding to carbons of carboxylic acid function. The peaks corresponding to carbons of model A and probably of amid acid were practically lost to benefit of those of carbons of the oxydiphthalic and the metanilic acid. Table 1 summarizes the carbons attributions and the δ values of metanilic and oxydiphthalic acid. This degradation was confirmed by IR spectroscopy. Indeed, IR spectrum showed the disappearance of characteristic imide bands ($\nu_{sym}$(C=O):1772 cm$^{-1}$, $\nu_{asym}$(C=O):1718 cm$^{-1}$ and $\nu$(CN):1375 cm$^{-1}$).

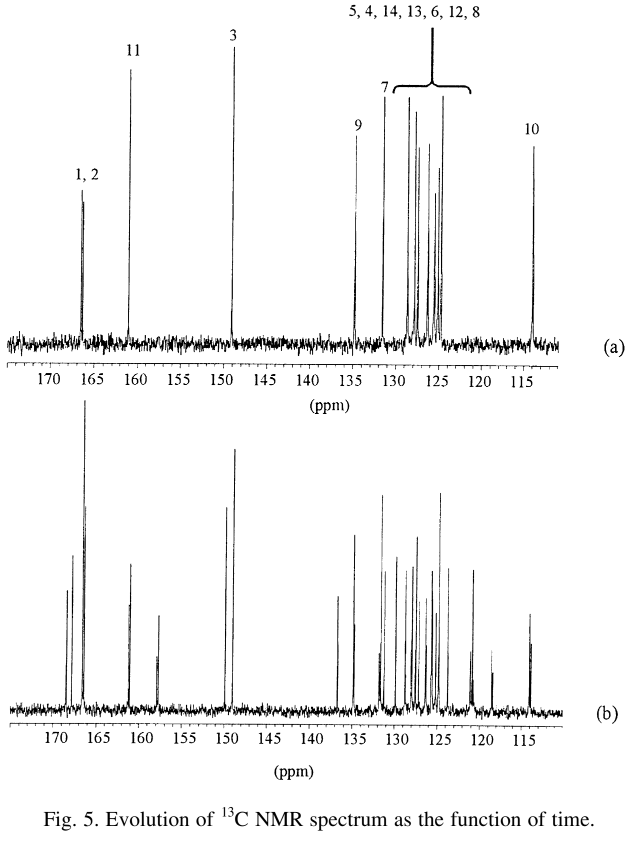


Fig. 5. Evolution of $^{13}$C NMR spectrum as the function of time.

### 3.2.2. *Quantitative analysis*

Based on our qualitative analysis showing hydrolysis reactions, a quantitative evaluation of this phenomenon was undertaken using quantitative $^{13}$C NMR analysis (see Fig. 5). The disappearance of both non equivalent imide carbonyl carbons peaks at 166.40 and 166.58 ppm are observed as well as the increasing peaks at 167.79 and 168.41 ppm corresponding to carboxylic acid carbons. Another peak at 168.41 ppm corresponding to acid-amid carbonyl carbon was also noticed. The chemical shift values of the carbonyl carbons of different compounds are gathered in Table 2.

The molar percentage of each compound was calculated from integral ratio after peak deconvolution. Concentration variations of each compound during hydrolysis are shown in Fig. 6. It is surprising to observe, at the beginning of the hydrolysis (before 2 h), an accumulation of acid-amid structure, which is normally easily hydrolyzed in aqueous medium. Concerning the structure of this amid-acid, three structures shown in Fig. 7 could be obtained in function of imide cycle opening. By 2D NMR, it was defined that hydrolysis specifically led to the isomer $I_2$. The attributions and δ values are summarized Table 3. We can explain this

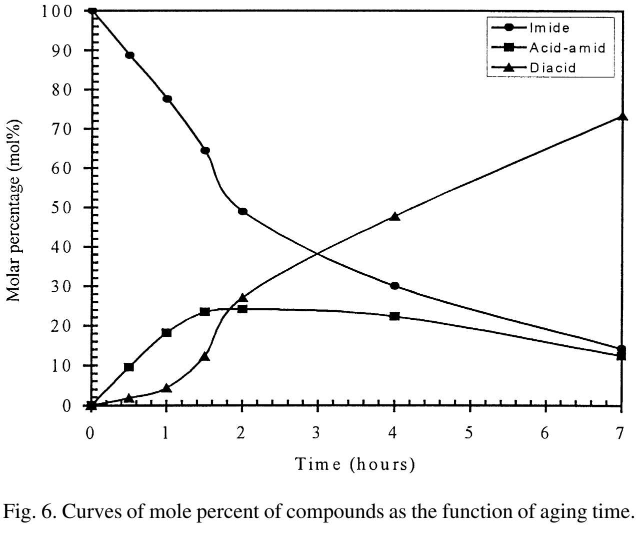


Fig. 6. Curves of mole percent of compounds as the function of aging time.

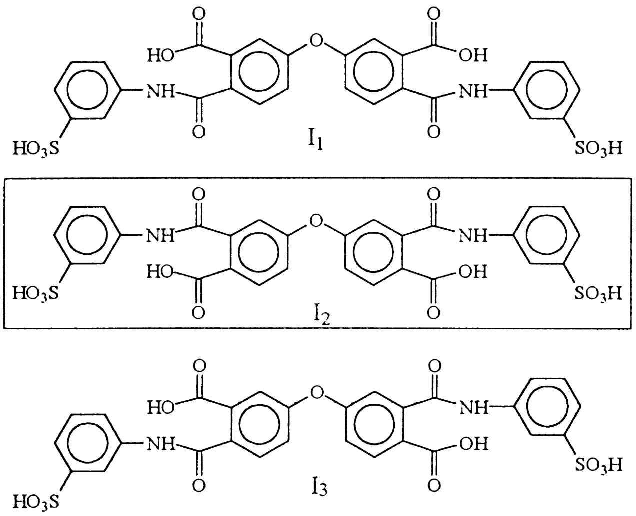
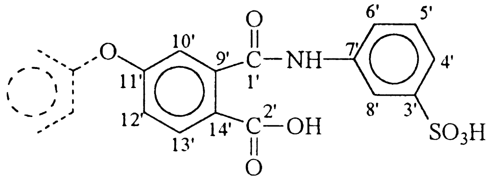


Fig. 7. Structures of amid-acid (model A degradation).

Table 3
Attributions and chemical shifts of carbons of acid-amid $I_2$



| Positions | δ (ppm/TMS) | |
|---|---|---|
| | $^1$H | $^{13}$C |
| 1′ | – | 168.62 |
| 2′ | – | 168.05 |
| 3′ | – | 148.64 |
| 4′ | 7.49 | – |
| 5′ | 7.35 | – |
| 6′ | 7.67 | – |
| 7′ | – | 127.38(?) |
| 8′ | 7.56 | 114.23 |
| 9′ | – | 136.95 |
| 10′ | 7.30 | 118.96 |
| 11′ | – | 157.95 |
| 12′ | 7.35 | 121.50 |
| 13′ | 7.84 | 132.20 |
| 14′ | – | 128.47(?) |

behavior according to the classical electronic effect as shown in Fig. 8.

### *3.3. Stability study of the model compound B*

#### *3.3.1. Qualitative analysis*

As for model A, model B in distilled water ($1.73 \times 10^{-1}$ mol $l^{-1}$) was aged at 80°C. Structural modifications of this compound were not observed by NMR spectroscopy before 120 h of aging (see Figs. 9b and 11b). Indeed, the $^1$H spectrum (see Fig. 9b) of the lyophilized sample showed two doublets at 8.22 and 8.57 ppm and a modification of the protons of sulphonated phenyl groups multiplet (indicated by * on the spectrum). These peaks at 8.22 and 8.57 ppm could be attributed to non equivalent naphthalenic protons of asymmetric compounds resulting from an hydrolysis. In order to explain these two additional peaks, three hypotheses were proposed (Fig. 10). The first was to consider the formation of totally or partially opened acid-amid ($B_1$ and $B_2$ structures). The second one implied a complete imide hydrolysis into carboxylic diacid. In this case, two asymmetric compounds could be formed ($B_3$ and $B_4$). The last hypothesis was to consider the anhydride formation ($B_5$, $B_6$ and $B_7$). Based on these different hypotheses, seven structures could explain the appearance of the proton peaks. The $B_1$, $B_4$ and $B_6$ structures can be excluded, they are unsuitable because all naphthalenic protons are non-equivalent and theoretically give four distinct protons.

Different syntheses were performed in order to verify

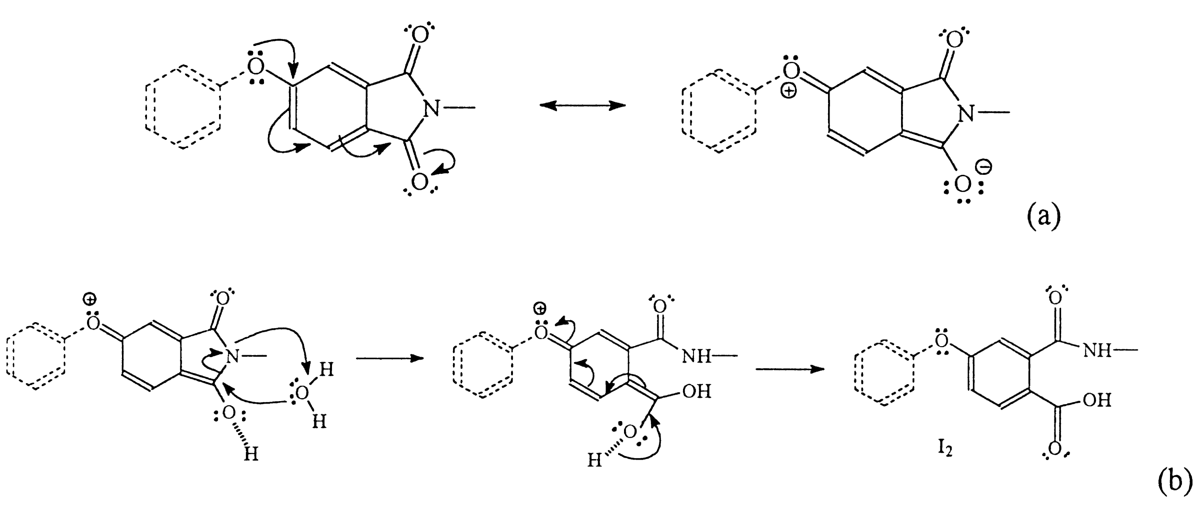


Fig. 8. Possible resonance structures of: (a) model A; (b) Imide cycle opening mechanism.

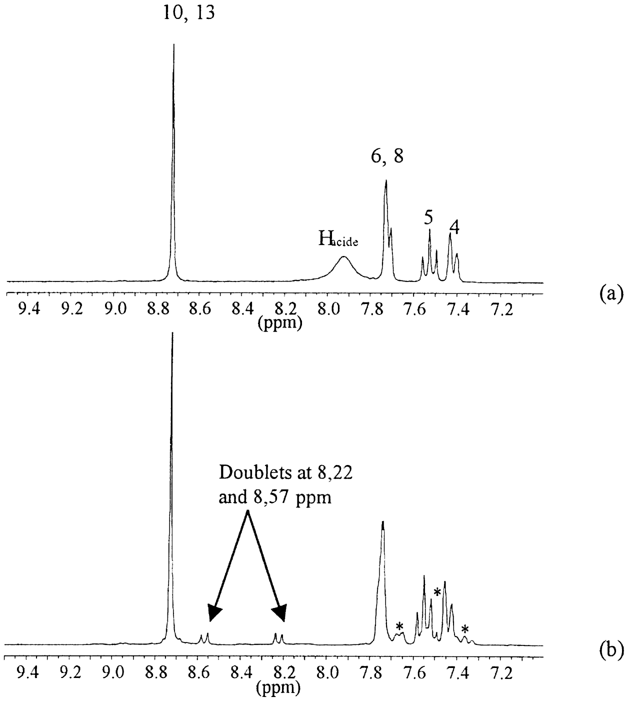


Fig. 9. $^1$H NMR spectra of: (a) initial model B; (b) model B aged 120 h at 80°C.

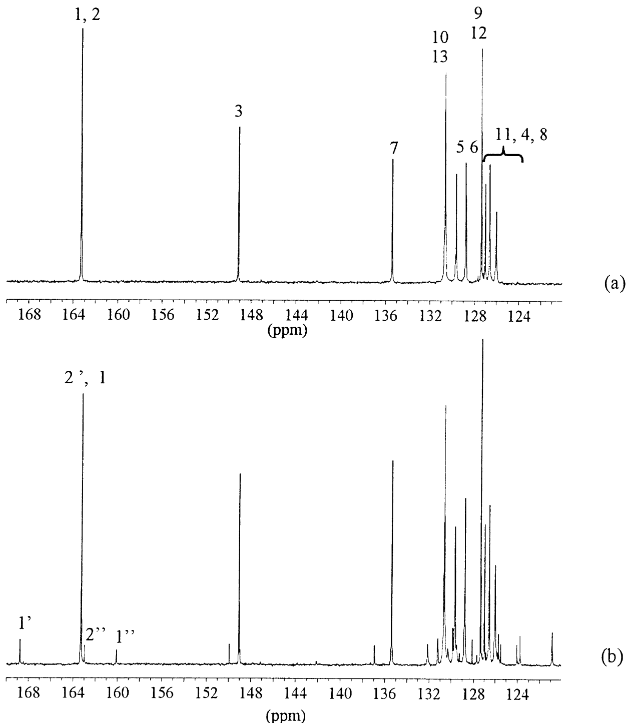


Fig. 11. $^{13}$C NMR spectra of: (a) model B; (b) model B aged 120 h at 80°C.

one of these hypotheses. To be close to naphthalenic acid-amid structure, *N*-phenyl, 1-naphthyl amid were synthesized, and the NMR analysis showed that the $\delta$ value of carbon of amid function was located at 167.52 ppm. No peak presents this chemical shift on the $^{13}$C NMR spectrum of model B aged 120 h at 80°C (see Fig. 11b), hence we can say that the amid-acid structure was not formed during the aging in distilled water. We have also determinated the $\delta$ values of carbonyl carbons and naphthalenic protons of semi-hydrolyzed dianhydride (Table 4). We observed that the proton 3$^*$ of semi-hydrolyzed dianhydride presents the same chemical shift (8.21 ppm) as one of the doublet observed on the $^1$H NMR spectrum of the model B aged 120 h. Then, the hydrolysis product of model B is probably the compound B$_3$. The imide presence in this hydrolysis product of model B has been confirmed by IR spectroscopy. The $^{13}$C NMR spectrum

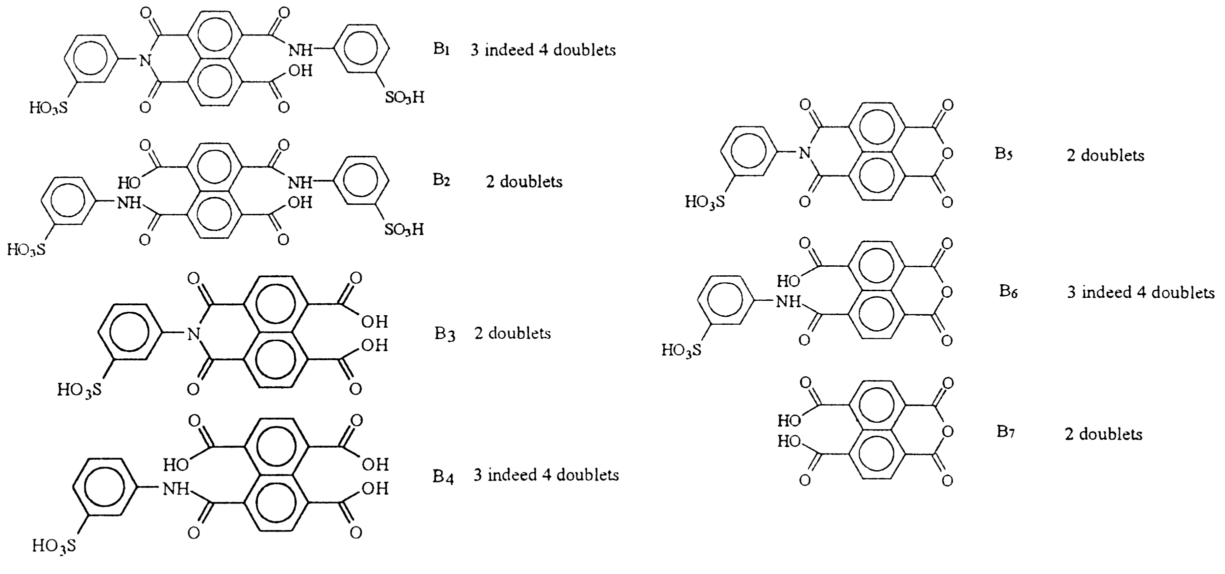


Fig. 10. Possible asymmetric hydrolyzed molecules from model B.

Table 4
Attributions and chemical shifts of carbonyl carbons and naphthalenic protons of semi-hydrolyzed and totally hydrolyzed dianhydride NTDA

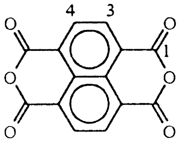
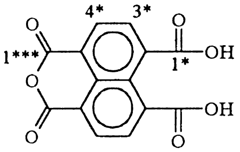
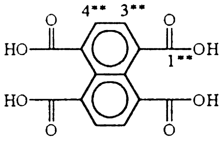
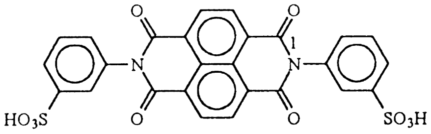
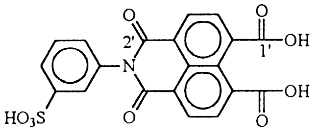
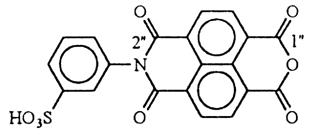
| Compounds | | Proton positions | $\delta$ values (ppm/TMS) | Carbon positions | $\delta$ values (ppm/TMS) |
|---|---|---|---|---|---|
|  | B | 3,4 | s (8.71) | 1 | 159.95 |
|  | $B_7$ | $3^*$<br>$4^*$ | d (8.21)<br>d (8.60) | $1^*$<br>$1^{***}$ | 168.42<br>160.30 |
|  | | $3^{**}$, $4^{**}$ | s (8.03) | $1^{**}$ | 169.67 |

Table 5
Attributions and chemical shifts of carbonyl carbons of model B and hydrolysis products

| Compounds | | Carbon positions | $\delta$ (ppm/TMS) |
|---|---|---|---|
|  | B | 1 | 163.28 |
|  | $B_3$ | $1'$<br>$2'$ | 168.77<br>163.36 |
|  | $B_5$ | $1''$<br>$2''$ | 160.07<br>162.99 |

(see Fig. 11b) also confirmed the presence of this molecule. On this spectrum, two peaks located at 168.77 and 162.99 ppm correspond to $1'$ and $1'$ carbons of compound $B_3$, respectively. Moreover, an additional peak could be observed with $\delta$ of 160.07 ppm relative to carbon of anhydride carbonyl. The carbon attributions of model B and its hydrolysis products between 140 and 180 ppm were summarized in Table 5.

### 3.3.2. Quantitative analysis

Based on our previous qualitative analysis, the evolution of doublets at 8.22 and 8.27 ppm corresponding to non equivalent naphthalenic protons of the product $B_3$ was studied. The initial model was aged during 1200 h at

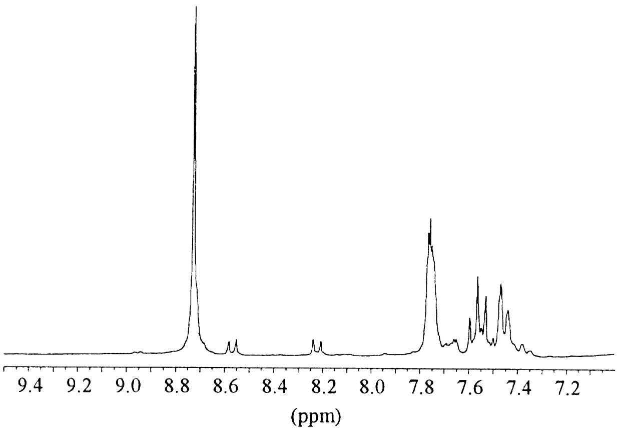


Fig. 12. $^1H$ NMR spectra of model B aged 1200 h at 80°C.

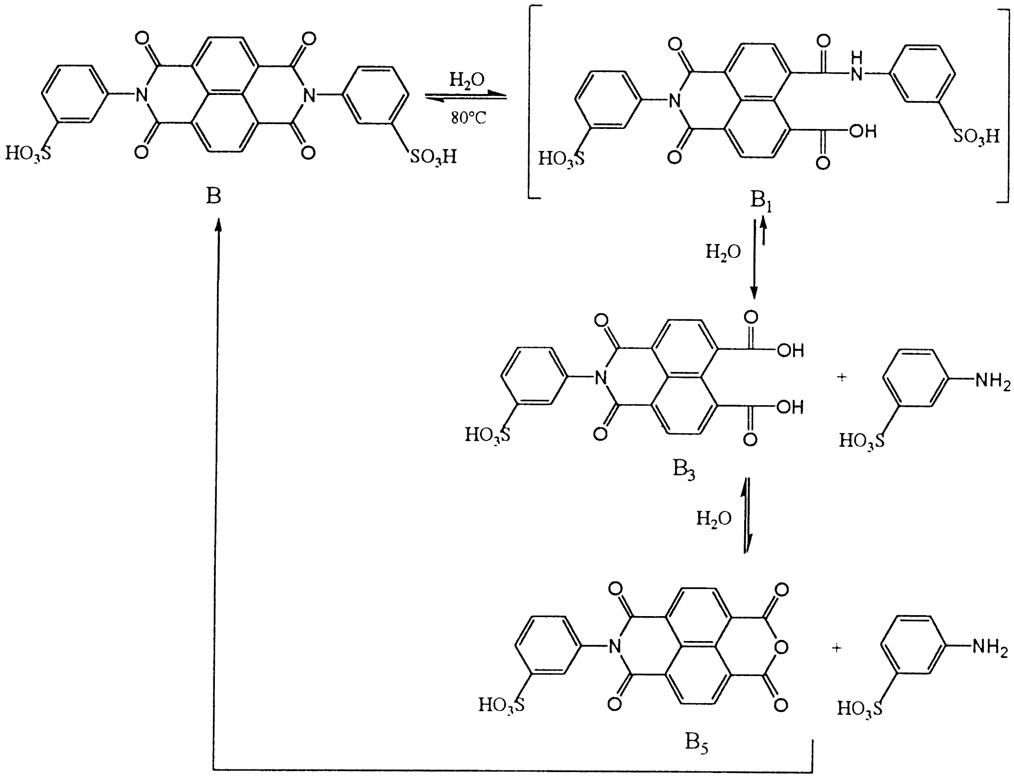


Fig. 13. Equilibrium between the products formed during hydrolysis of model B.

80°C. The $^1$H NMR spectrum is shown in Fig. 12. It is worth noting that the intensity of doublets remains constant as function of time. We could explain this behavior by the presence of an equilibrium between the products formed from model B (see Fig. 13). The cyclization of carboxylic diacid is possible through the reaction with the metanilic acid freed in the medium at the time of the $B_3$ formation, and leading to the regeneration of the starting product. The conversion was then limited to about 12%.

## 4. Conclusions

The NMR and IR spectroscopic analyses of model compounds, before and after aging in water, at different temperatures, allowed to show some structural modifications strongly depending on imide ring structures. The weakest stability of the phthalic model compound was confirmed in comparison with the naphthalenic one. This stability could be explained by several equilibria allowing the regeneration of the imide structure.

## Acknowledgements

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