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Thermal reaction of *N*-(4′-benzyl)phenyl-1,2,3,6-tetrahydrophthalimide: a model for the behaviour of tetrahydrophthalimide end-capped oligomers

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N-(4′-benzyl)phenyl-1,2,3,6-tetrahydrophthalimide model compound has been synthesized and its thermal reaction mechanism studied. The products of the *N*-(4′-benzyl)phenyl-1,2,3,6-tetrahydrophthalimide (THPI) thermal treatment have been analysed by ^{1}H nuclear magnetic resonance, size exclusion chromatography and liquid secondary ion mass spectrometry. According to quantitative analysis (column chromatography), only 50% of the reaction products are oligomerization products. Competitive isomerization (20%) and disproportionation (5%) reactions were evidenced. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: tetrahydrophthalimide; isomerization; disproportionation)

INTRODUCTION

In a previous paper[1] we have compared the reactivity of two similar oligomers obtained by reaction of 4,4′-(hexafluoroisopropylidene)dipthalic anhydride with a mixture of meta phenylene diamine (25% molar) and para phenylene diamine (75% molar). The first one (NAD 25) was end-capped by nadic anhydride and the second one (THPI 25) by tetrahydrophthalic anhydride (*Scheme 1*).

The results obtained showed a very low degree of thermal polymerization of the tetrahydrophthalimide end-caps. However, the disappearance of the cyclohexene double bond (^{1}H n.m.r. spectroscopy determination) showed that the tetrahydrophthalimide moiety did not stay inert to the thermal treatment. In order to understand what happens to the tetrahydrophthalimide units, a study on model compounds was undertaken as was done for other telechelic oligomers[2–12]. This paper deals with the syntheses of model compounds and the study of their thermal behaviour using classical analytical methods such as ^{1}H and ^{13}C nuclear magnetic resonance (n.m.r.) and size exclusion chromatography (SEC).

EXPERIMENTAL

Instrumentation

^{1}H and ^{13}C n.m.r. spectra were recorded as solution in DMSO-d_6 or CD_2Cl_2 with a Bruker AC250 spectrometer (the analysis frequency was 250 MHz for the proton and 62.9 MHz for the carbon). The chemical shifts are given in ppm relative to tetramethylsilane (TMS) used as an internal reference.

SEC was performed in THF with a Waters device. The pump was a Waters model 510 connected to PSS gel mixed B columns. The differential refractometer was a Waters model 410.

LSIMS (Liquid secondary ion mass spectrometry) analyses were carried on a mass spectrometer, equipped with a double electron focusing in inversed geometry (ZAQ-SEQ) fitted with a cesium ion gun. This method involves a sample ionization and a detection of molecular ions of all the components, with a generally very low level of fragmentation processes.

Syntheses

N-[4′-benzyl]phenyl-1,2,3,6-tetrahydrophthalimide (THPI) (Figure 1). In a 100 ml three necked flask fitted with a magnetic stirrer, a nitrogen inlet tube and a thermometer, 3.60 g (24 mmol) of 1,2,3,6-tetrahydrophthalic anhydride, 4.10 g (20 mmol) of para-benzylaniline and 30 ml of N-methylpyrrolidone (NMP) were introduced. The mixture was heated at 60°C for 1 h and at 180°C for 5 h. Then the solution was cooled down to room temperature and poured into an excess of ice-water. The obtained precipitate was filtered, washed with water and recrystallised in ethanol. Pure product of the order of 4.24 g (13 mmol, 65%) was obtained mp=120°C.

^{1}H n.m.r. (250 MHz) (CD_2Cl_2). 2.25 and 2.65 (2bd, ^2J = 15 Hz, 4 H, $H_{b,b'}$); 3.20 (bs, 2H, H_c); 4.00 (s, 2 H, H_i); 5.95 (bs, 2H, H_a); 7.05–7.40 (m, 9 H, $H_{f,g,k,l,m}$)

^{13}C n.m.r. (62.9 MHz) (CD_2Cl_2). 24.1 (2C, C_b); 39.6 (2C, C_c); 41.8 (1C, C_i); 126.6 (1C, Cm); 127.0 (2C, C_f*); 128.2 (2C, C_g*); 128.9 (2C, C_k*); 129.3 (2C, C_l*); 129.7 (2C, C_a*); 130.8 (1C, C_e); 141.0 (1C, C_h+); 142.3 (1C, C_j+); 179.5 (2C, Cd). *, + : assignments which can be reversed.

Elemental analysis. ($C_{21}H_{19}NO_2$): C 79,47%, H 6.03%, N 4.41%, O 10.08% (calculated); C 79.81%, H 6.05%, N 4.28%, O 10.10% (found).

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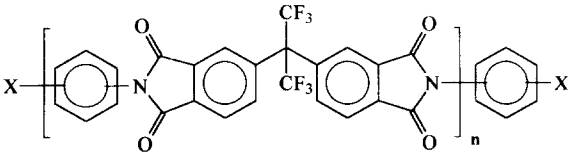
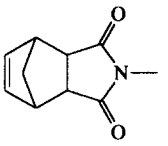
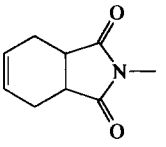


NAD 25 X = 

THPI 25 X = 

Scheme 1

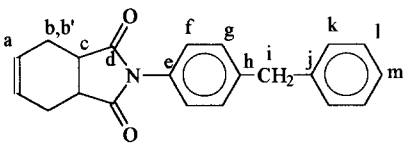


Figure 1 N-(4'-benzyl)phenyl-1,2,3,6-tetrahydrophthalimide structure

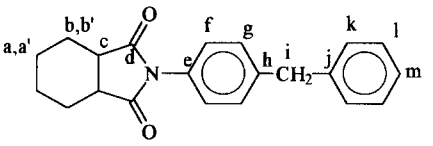


Figure 4 N-(4'-benzyl)phenyl cis-1,2-cyclohexanedicarboximide structure

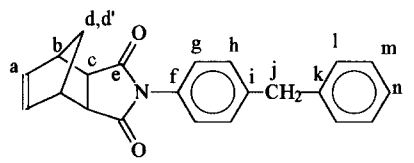


Figure 2 N-(4'-benzyl)phenyl nadimide structure

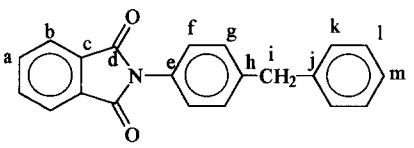


Figure 3 N-(4'-benzyl)phenyl phthalimide structure

N-(4'-benzyl)phenyl nadimide (NAD) (Figure 2)

This compound had been prepared according to the method described by V. Damerval *et al.*[12] (endo isomer) mp = 128°C.

^1H n.m.r. (250 MHz) (DMSO-d_6). 1.62 (bs, 2H, $H_{d,d'}$); 3.33 (bs, 2H, H_b); 3.48 (bs, 2H, H_c); 3.98 (s, 2H, H_j); 6.20 (bs, 2H, H_a); 7.01 (d, J = 8 Hz, 2H, H_g); 7.23 (d, J = 8 Hz, 2H, H_h); 7.10–7.30 (m, 5H, $H_{l,m,n}$)

^{13}C n.m.r. (62.9 MHz) (DMSO-d_6). 40.8 (1C, C_j); 44.9 (2C, C_b*); 45.4 (2C, C_c*); 51.8 (1C, C_d); 126.2 (1C, C_n); 127.2 (2C, C_g); 128.6 (2C, C_h +); 128.8 (2C, C_l +); 129.2 (2C, C_m); 130.3 (1C, C_f); 134.6 (2C, C_a); 141.0 (1C, C_i**); 141.7 (1C, C_k**); 176.9 (2C, C_e). + , *, **: assignments which can be reversed.

N-(4'-benzyl)phenyl phthalimide (PHTA) (Figure 3)

This synthesis was performed by using the conditions previously described for THPI from: 1.54g (8.4 mmol) of para-benzylaniline, 1.37 g (9.3 mmol) of phthalic anhydride and 10 ml of DMF. The reaction mixture was stirred at room temperature for 2 h and at 120°C for 5 h. Then the cold solution was poured into an excess of ice-water, filtered and the solid residue was dried. Raw product (2.5 g; 8 mmol, 95%) was obtained and then column chromatographed on silica gel with a solvent mixture prepared from 80% of dichloromethane and 20% of ethyl acetate. Pure para-benzylaniline phthalimide (2.3 g; 7.3 mmol, 86%) was obtained. mp = 137°C.

^1H n.m.r. (250 MHz) (CD_2Cl_2). 4.05 (s, 2H, H_i); 7.10–7.40 (m, 9H, $H_{f,g,k,l,m}$); 7.75–7.90 (2m, 4H, $H_{a,b}$).

^{13}C n.m.r. (62.9 MHz) (CD_2Cl_2). 41.8 (1C, C_i); 123.8 (2C, C_b); 126.6 (1C, C_m); 127.1 (2C, C_f +); 128.9 (2C, C_g +); 129.3 (2C, C_k +); 129.7 (2C, C_l +); 130.2 (1C, C_e); 132.1 (2C, C_c); 134.7 (2C, C_a), 141.1 (1C, C_h*), 142.0 (1C, C_j*); 167.6 (2C, C_d). *, + : assignments which can be reversed.

Elemental analysis. ($C_{21}H_{15}NO_2$): C 80.49%, H 4.83%, N 4.47%, O 10.21% (calculated); C 80.68%, H 4.87%, N 4.28%, O 10.24% (found).

N-(4'-benzYl)phenyl cis-1,2-cyclohexanedicarboximide (CYCLO) (Figure 4)

The same experimental conditions were used as previously with 1.70 g (9.3 mmol) para-benzylaniline, 1.45 g (9.4 mmol) cis-1,2-cyclohexane dicarboxylic anhydride and 10 ml DMF. The mixture was stirred for 3 h at room temperature, 20 h at 120°C, then cooled down and poured into an excess of ice-water. The precipitate was filtered, washed with petroleum ether and dried. Raw product (2.44 g; 7.6 mmol 82%) was obtained and column chromatographed on silica gel with a solvent mixture prepared from 80% of dichloromethane and 20% of ethyl acetate. 2.3 g (7.2 mol, 77%) of pure CYCLO were obtained mp=152°C.

^1H n.m.r. (250 MHz) (CD_2Cl_2). 1.45 (bs, 4H, $H_{a,a'}$); 1.85 (bs, 4H, $H_{b,b'}$); 2.95 (bs, 2H, H_c); 4.00 (s, 2H, H_i); 7.05–7.35 (m, 9H, $H_{f,g,k,l,m}$).

^{13}C n.m.r. (62.9 MHz) (CD_2Cl_2). 22.2 (2C, C_a*), 24.3 (2C, C_b*); 40.5 (2C, C_c); 41.8 (1C,C_i); 126.6 (1C, C_m); 126.8 (2C, C_f +); 128.9 (2C, C_g +); 129.3 (2C, C_k +); 129.7 (2C, C_l +); 130.8 (1C, C_e); 141.1 (1C, C_h''), 142.1

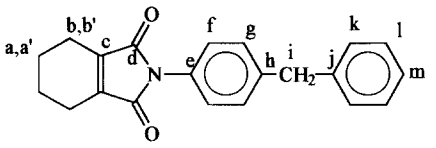


Figure 5 N-(4'-benzyl)phenyl cis-3,4,5,6-tetrahydrophthalimide structure

(1C, C_j''); 179.0 (2C, C_d). *, +, '': assignments which can be reversed.

Elemental analysis. ($C_{21}H_{21}NO_2$): C 78.97%, H 6.63%, N 4.39%, O 10.04% (calculated); C 79.53%, H 6.66%, N 4.21%, O 9.82% (found).

N-(4'-benzyl)phenyl cis-3,4,5,6-tetrahydrophthalimide (ISOM-3) (Figure 5)

Same reaction conditions as previously described with 2.5 g (13 mmol) of para-benzylaniline, 2.0 g (13 mmol) of cis-3,4,5,6-tetrahydrophthalic anhydride and 10 ml of DMF. The mixture was stirred at room temperature for 5 h and 18 h at 170°C, then cooled down and poured into ice-water, filtered and dried. Raw product (3.8 g; 12 mmol, 86%) was obtained and column chromatographed on silica gel with a solvent mixture prepared from 80% of dichloromethane and 20% of petroleum ether. ISOM-3 (2.8 g; 9 mmol, 64%) was obtained mp=136°C.

^{1}H n.m.r. (250 MHz) (CD_2Cl_2). 1.75 (bs, 4H, $H_{a,a'}$); 2.35 (bs, 4H, $H_{b,b'}$); 3.95 (s, 2H, H_i); 7.05–7.45 (m, 9 H, $H_{f,g,k,l,m}$).

Elemental analysis. ($C_{21}H_{19}NO_2$): C 79.47%, H 6.03%, N 4.41%, O 10.08% (calculated); C 79.62%, H 6.09%, N 4.13%, O 9.79% (found).

PREPARATION OF SAMPLES FOR THERMAL REACTION

Thermal treatments were performed in pyrex tubes containing around 60–100 mg of product. They were sealed under inert atmosphere to prevent interaction with air oxygen and put in a regulated oven for the required time and temperature. After cooling down, each tube content was ^{1}H n.m.r. analysed. Some of them were also studied by SEC and by LSIMS. THPI samples were heated separately at four different temperatures: 210°C/24 h, 250°C/7 h, 280°C/24 h and finally 310°C/24 h. Some experiments were also performed on the NAD model compound in order to compare its behaviour to the THPI one. Then to obtain more information about the THPI thermal reaction mechanism, a silica gel column chromatography separation was carried out in order to identify each component of the reaction mixture of THPI and ISOM-3 thermal treatment. These latter studies were performed on 350–500 mg of samples resulting from the thermal treatments at 310°C/24 h. Yields of these chromatographies were almost quantitative (98–100%).

RESULTS AND DISCUSSION

Comparison between the thermal polymerization of THPI and NAD

This study was conducted on THPI (*Figure 1*). The choice of the 4-benzylphenyl substituent was used to obtain an internal standard for ^{1}H n.m.r. reaction monitorings. Thus, the integration of the methylenic proton signal is not dependent on the chemical changes in the cyclohexenyl moiety. It is not the case of the integration of the aromatic, ethylenic and cycloalkyl proton signals.

The products of the thermal reactions were investigated using several analysis techniques and the results are presented in the following sections.

Table 1 THPI and NAD ethylenic protons: disappearance percentages versus reaction time and temperature (NMR measurements)

Temperature and time of heating	Ethylenic proton disappearance (%)	
	THPI	NAD
210°C/24 h	0	9
250°C/7 h	12	–
250°C/16 h	–	46
280°C/24 h	40	–
310°C/2 h	–	97
310°C/4 h	–	100
310°C/24 h	90	–

Table 2 Number average molecular weight ($\overline{Mn}$), polymerization degree ($\overline{PD_n}$) and polydispersity (Ip) of thermal treatment products of THPI and NAD model compounds

Model compound	Mn	PDn	Ip
THPI M = 317	506	1.6	1.22
NAD M = 329	1322	4.0	1.44

^{1}H n.m.r.. The resonance of ethylenic protons (δ = 5.9 ppm) was considered to follow the reaction extent as it was generally done for the nadimide resin studies. The intensity decrease of this signal can be estimated relative to the methylene ones δ = 4.0 ppm (*Figure 6*). Listed in *Table 1* are ethylenic proton disappearing percentages versus reaction time and temperature. The corresponding nadimide model NAD (*Figure 2*), reacts more rapidly towards thermal treatments (*Figure 7*). Firstly, it starts to react at 210°C; under the same reaction conditions the THPI is recovered unchanged. In addition to the overall double bond disappearance (provided by the ratio of the integrations of ethylenic versus methylenic protons), the n.m.r. spectrum (*Figure 7*) shows the endo-exo isomerization (δ = 6.20 ppm for the endo isomer and δ = 6.35 ppm for the exo isomer for the ethylenic protons) and the formation of cycloadducts of cyclopentadiene with NAD (ethylenic protons δ = 6.05 ppm)[6,13,14].

Secondly, at 250°C, the thermal reaction of NAD has almost reached the same conversion degree (46%) than the THPI at 280°C (40%) (*Table 1*). Finally, after 4 h at 310°C, there is no ethylenic proton left for NAD whereas 10% of THPI ones are still present after 24 h of reaction. Moreover, the shape of the signals of THPI (*Figure 6*), are particularly affected in the range of aromatic proton resonances (7–8 ppm) and in the range of aliphatic proton one (1–3.5 ppm). This clearly evidences a sequence of chemical changes other than the expected polymerization during thermal treatment. It is worth noting that by the end of thermal treatments the ^{1}H n.m.r. resonance signal broadening is more important for NAD than for THPI.

SEC. THPI and NAD after thermal treatment at 310°C for 24h and 6h respectively were analysed by SEC. Results

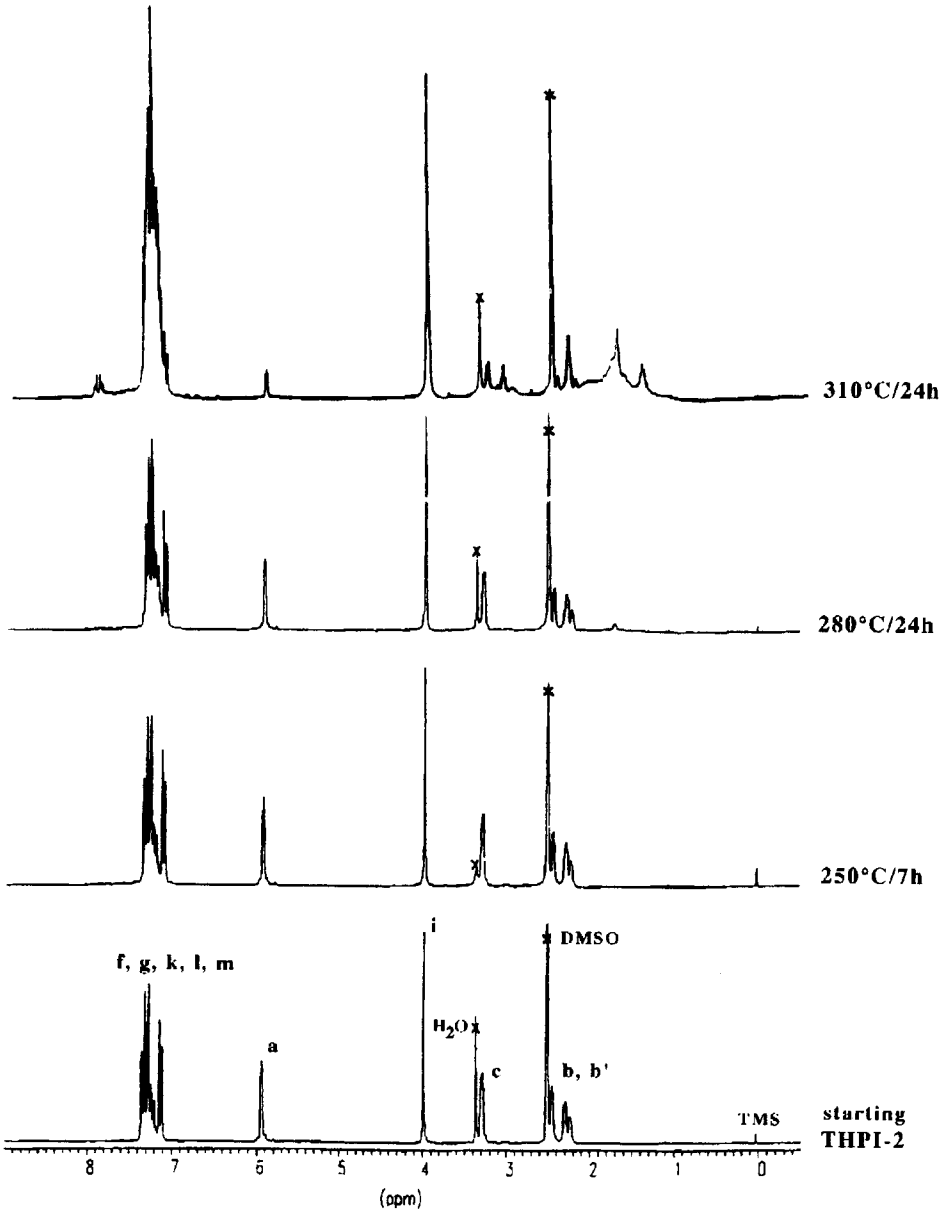


Figure 6 ^{1}H NMR (250 MHz) analyses of THPI evolution versus reaction time and temperature (for alphabetical indexations, see *Figure 1*)

Table 3 THPI cure product: molecular ions observed by LSIMS

Ion structure	Molecular weight (m/z)
Monomer (THPI)	318 $[M + 1]^{\cdot+}$
Dimer	635 $[2M + 1]^{\cdot+}$
Trimer	952 $[3M + 1]^{\cdot+}$
Tetramer	1269 $[4M + 1]^{\cdot+}$

are compiled in *Table 2*. The $\overline{Mn}$ values are relative to polystyrene calibrations.

In terms of polymerization degree ($\overline{PD_n}$), a low THPI reaction progress is observed if compared to the NAD one even though the thermal treatment time of THPI had been longer. So the THPI thermal polymerization inertness detected from the n.m.r. analyses is confirmed by this SEC study.

LSIMS (liquid secondary ion mass spectrometry). For polymers, the LSIMS method allows a qualitative approach to the molecular weight distribution. Interaction between a matrix and the sample is at the origin of the preferential formation of the molecular ions relatively to the fragment ones. The same thermal product (THPI after 24 h at 310°C) as in the SEC analysis was then LSIMS studied. Molecular ions from monomer (317) to tetramer (1269) are observed (*Figure 8, Table 3*). Though the LSIMS spectrum of thermal product of NAD after 4 h at 310°C is more complex[12] molecular ions until 2500 atomic mass unity was observed. Once again, a very low polymerization degree of THPI is evidenced.

Characterization of the low molecular weight products after heating THPI at 310°C

In order to analyse each species present in the reaction product, a column chromatography on silica gel was performed on 500 mg of cured THPI. The ^{1}H n.m.r. spectrum of the raw product was recorded previously (*Figure 9*); it is roughly identical to the spectrum of the test experiment (*Figure 6*, upper trace). However, it shows that around 22% of starting materials are unreacted (δ = 5.9 ppm, ethylenic proton) instead of 10% observed on an analytical scale (*Table 1* and *Figure 6*).

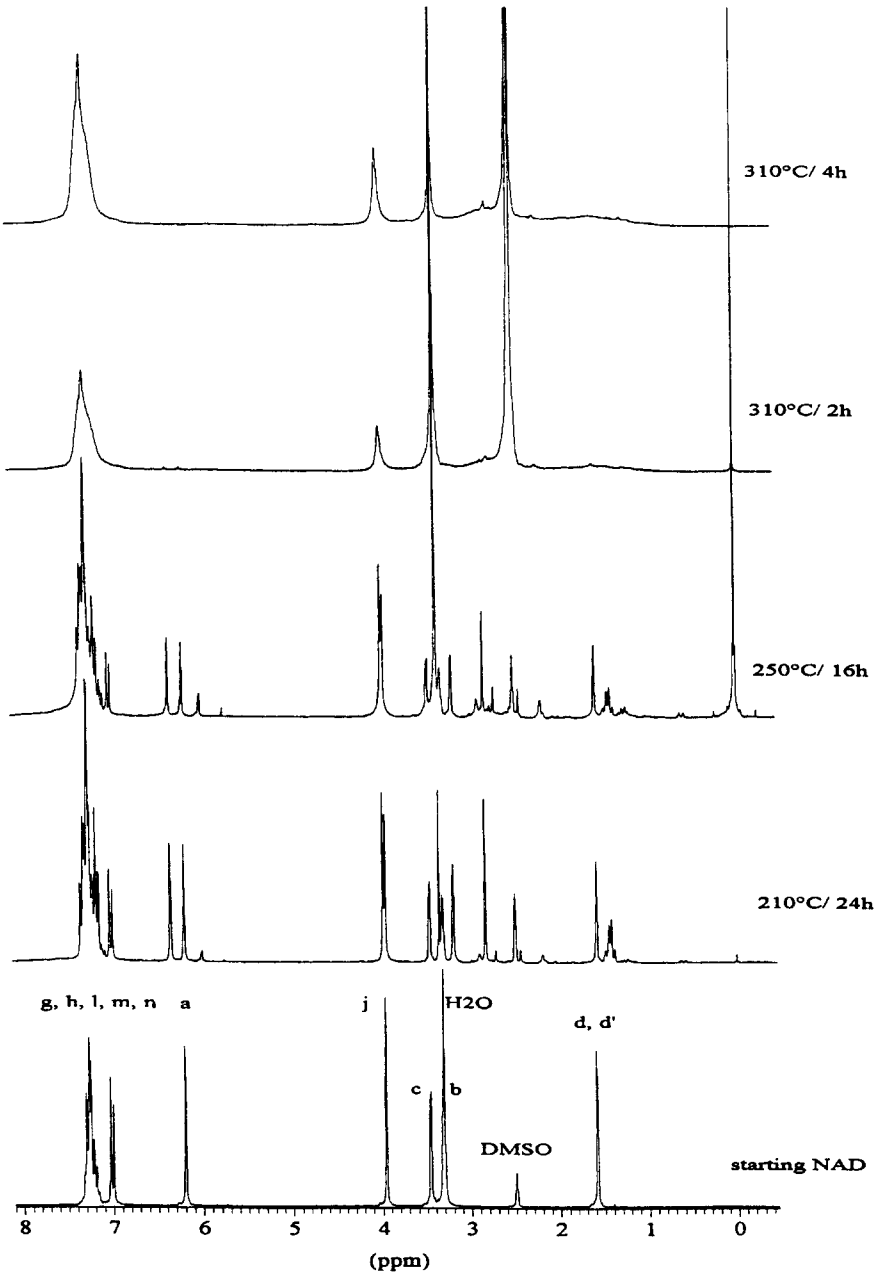


Figure 7 ^{1}H NMR (250 MHz) analyses of NAD evolution versus reaction time and temperature (for alphabetical indexations, see *Figure 2*)

The column chromatography was then performed using a solvent mixture of cyclohexane (70%) and ethyl acetate (30%) as eluent. Each chromatography fraction was identified by ^{1}H n.m.r. and compared to authentical compounds when it was possible. For example the ^{1}H n.m.r. spectrum (*Figure 10*) of the first fraction shows clearly the characteristics of the cis-3,4,5,6-tetrahydrophthalimide ISOM-3 (*Figure 5*). The second fraction was a mixture of ISOM-3 and the N-(4'benzyl) phenylphthalimide (PHTA) which was identified from ^{1}H and ^{13}C n.m.r. spectra by comparison with the ones of a synthesized authentical sample (*Figure 3*). The aromatic imide can be easily quantified (1.2%) from the ^{1}H n.m.r. spectrum of the thermal reaction product (*Figure 9*) through the relative integration of the aromatic proton resonances (the symmetrical signal centered at 7.8 ppm relative to the one of the nitrogen atom substituent located at 7.2 ppm or to the one of methylenic protons at 4.2 ppm).

Table 4 Column chromatography balance sheet of cured THPI product

✱	15% of ISOM-3
✱	1% of PHTA;
✱	3% of CYCLO
✱	4% of ISOM-1
⊕	25% of starting material (THPI)
⊕	52% of oligomers

The next fraction was a mixture of N-(4'-benzyl)phenyl-1,2,5,6-tetrahydrophthalimide (ISOM-1, *Figure 11*), N-(4'-benzyl)phenyl cis-1,2-cyclohexanedicarboxyimide (CYCLO, *Figure 4*) and some of unreacted starting material. CYCLO (3%) was identified by comparison with a synthesized authentical sample. ISOM-1 structure was assigned to the second main component of this fraction on the basis of an AB

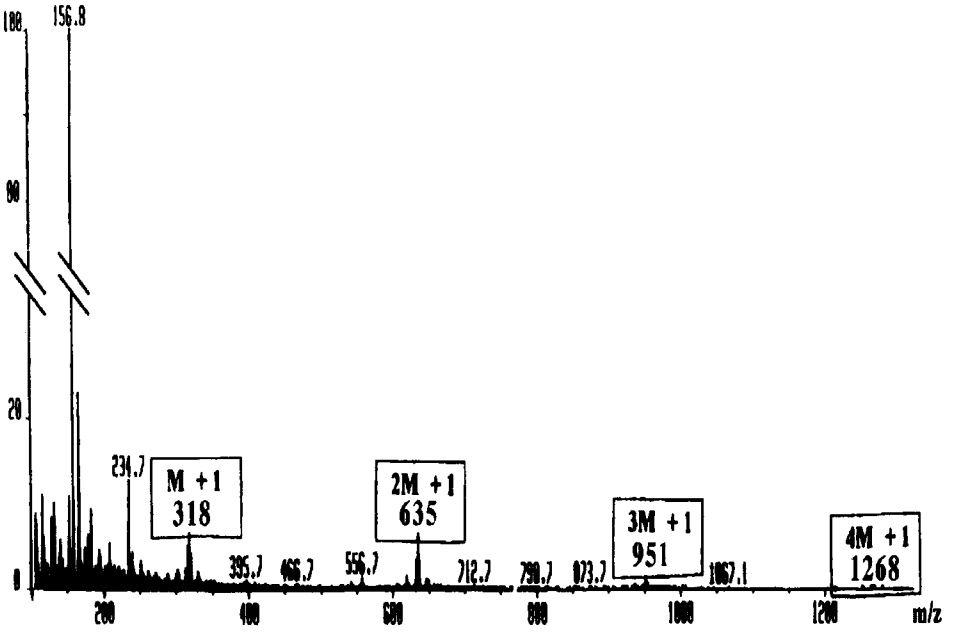


Figure 8 LSIMS spectrum of THPJ (M=317 g mol^{-1}) after curing at 310°C/24 h

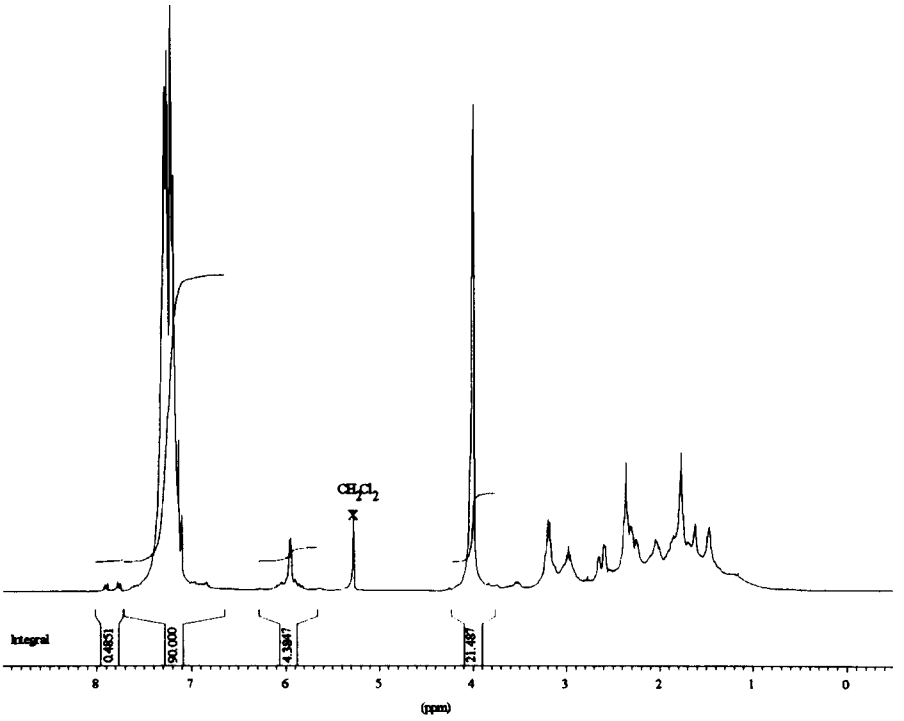


Figure 9 ^{1}H NMR spectrum of the raw product of the thermolysis of 500 mg of THPI at 310°C/24 h (CD_2Cl_2)

part (centered at 6.0 ppm) of a complex signal in the ^{1}H n.m.r. spectrum, indicating a structure with two ethylenic protons.

The last two fractions were respectively starting THPI (25%) and oligomers (52%). The balance sheet of this column chromatography is listed in *Table 4*.

It appears that three competitive reaction pathways are appearing (*Scheme 2*):

(1) the expected oligomerization reaction;
(2) a disproportionation, leading to cyclohexane and benzene derivatives (it is interesting to point out that the molecular ratio of PHTA over CYCLO is in agreement with the theoretical yield);
(3) an isomerization reaction 'displacing' the double bond all around the cyclohexene ring from THPI to ISOM-3 through probably the formation of ISOM-1 and ISOM-2.

Thermal polymerization of ISOM-3. ISOM-3 is a maleimide derivative which could polymerise faster than THPI. So a question arises: is THPI or ISOM-3 the initiator of the oligomer formation? Thus, the thermolysis product (310°C/24 h) of ISOM-3 was ^{1}H n.m.r. and LSIMS investigated. It was also column chromatographed for identification of its components.

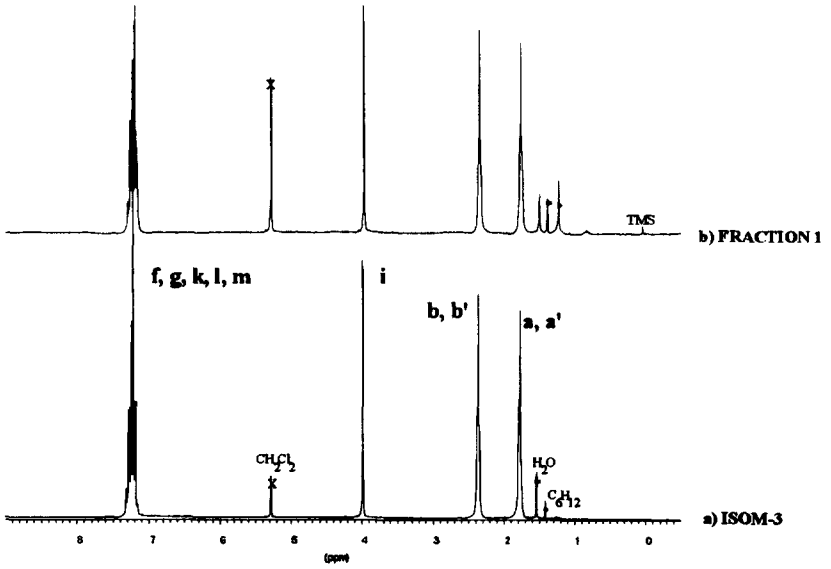


Figure 10 ^{1}H NMR spectra of the first fraction (*b*) and of ISOM-3 (*a*) (CD_2Cl_2)

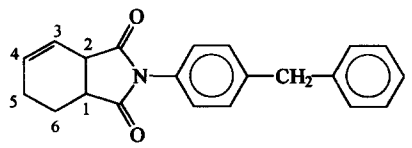


Figure 11 N-(4'-benzyl)phenyl-1,2,5,6-tetrahydrophthalimide (ISOM-1) structure

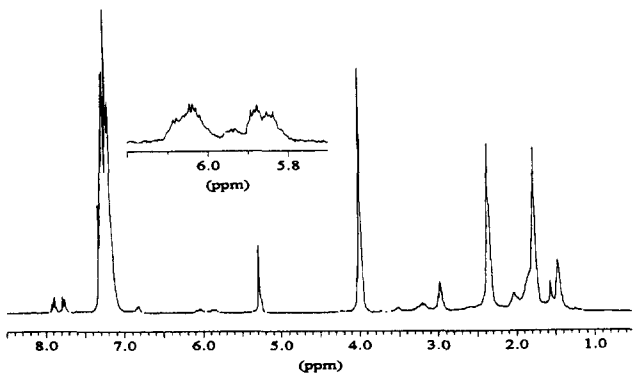


Figure 12 ^{1}H NMR spectrum of the product obtained after ISOM-3 thermolysis at 310°C/24 h (CD_2Cl_2)

^{1}H n.m.r.. The ^{1}H n.m.r. spectrum (*Figure 12*) of the cured product shows a 8% contribution of PHTA (δ = 7.7–8.0 ppm) and we also observe the resonance signals of THPI and ISOM-1 ethylenic protons (δ = 5.9 and δ = 5.8 and 6.1 ppm, respectively) as well as the cyclohexyl ring proton resonance of CYCLO at 3.0 ppm.

LSIMS. The thermolysis product was studied as a THF solution. A four member family (from monomer to tetramer) is observed (*Table 5* and *Figure 13*). These results compared with the THPI ones (*Table 3*, *Figure 8*) indicate, once again, a very low polymerization degree.

Column chromatography on silica gel. As for the THPI cure product, the elution was performed with a mixture of cyclohexane and ethyl acetate; each obtained fraction is ^{1}H n.m.r. analysed and compared to authentical compound

Table 5 ISOM-3 cure product: molecular ions observed by LSIMS

Ion structure	Molecular weight (m/z)
Monomer	318 $[M + 1]^{\cdot+}$
Dimer	635 $[2M + 1]^{\cdot+}$
Trimer	952 $[3M + 1]^{\cdot+}$
Tetramer	1269 $[4M + 1]^{\cdot+}$

Table 6 Column chromatography balance sheet of cured ISOM-3 product

★	42% of starting material (ISOM-3)
✸	7% of PHTA
✹	18% of CYCLO
✹	6% of ISOM-1
↯	2% of THPI
⊕	25% of oligomers

spectra. The balance sheet of this chromatography is listed in *Table 6*.

ISOM-3 undergoes the same kind of reactions as THPI: polymerization, disproportionation and isomerization which give back some ISOM-1 and THPI; only 25% of oligomers are obtained in the case of ISOM-3 versus 52% for THPI. Indeed, concerning the formation of oligomers, it seems that they come from THPI and not from the ISOM-3 one. The low reactivity of the maleimide double bond of ISOM-3 towards thermal polymerization is related to steric factors; generally substituted maleimides are less reactive than unsubstituted ones[15]. Moreover, due to the highest substitution of its double bond, ISOM-3 seems to be less reactive than THPI and probably for this reason the disproportionation reaction is rather taking place from ISOM-3 than from THPI.

CONCLUSION

Monofunctional model compound studies elucidates several reaction typical features about the behaviour of tetrahydrophthalimide during thermal treatment.

First of all, these studies demonstrate that the polymerization of tetrahydrophthalimide species cannot be

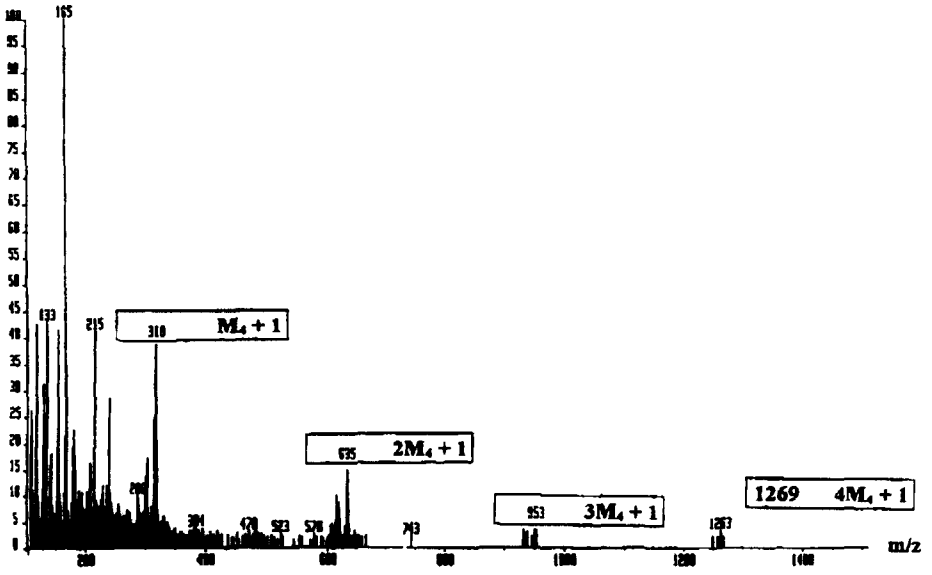
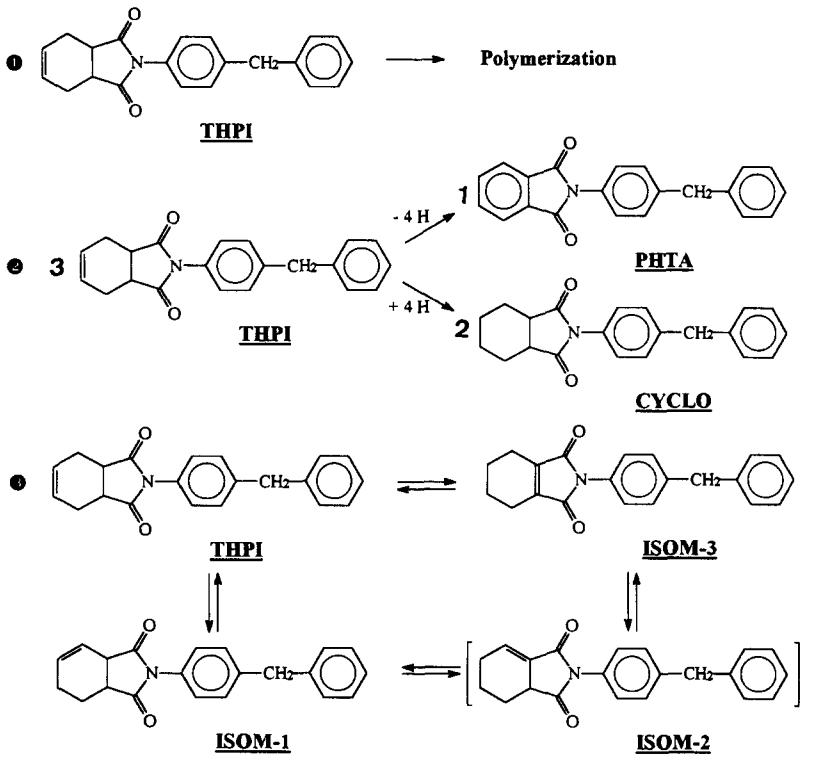


Figure 13 LSIMS spectrum of ISOM-3 (M = 317 g.mol^{-1}) after curing at 310°C/24 h



Scheme 2

monitored only by the disappearance of the double bond protons.

A low selectivity in polymerization (50%) and low polymerization degrees of the tetrabydophthalimide function were evidenced. This is the result of a strong intervention of competitive isomerization and disproportionation reactions; this latter gives rise to aromatic and saturated species which cannot participitate in the polymerization processes. The very low polymerization degrees partly explain the theological behaviour (air atmosphere) observed for the tetrahydrophthalimide end-capped oligomers[1]. Finally, the main thermal polymerization difference between nadimide and tetrahydrophthalimide end-capped oligomers is due to the nadimide best ability to give a reverse Diels-Alder process. Such a process forms maleimide entities which initiate the thermal polymerization[12]. In the case of tetrahydrophthalimide, the activation energy of the reverse Diels-Alder reaction is higher than for nadimide. Thus, other reaction processes (isomerization, disproportionation) can take place.

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