

# Comparison between nadimide and 1,2,3,6-tetrahydrophthal-imide end-capped resins, preparation and thermal behaviour

Véronique Bounor-Legare, Pierre Mison and Bernard Sillion\*

Laboratoire des Matériaux Organiques à Propriétés Spécifiques (CNRS-UPR 9031) BP 24-69390 Vernaison, France

(Received 17 January 1997; revised 14 July 1997)

Nadimide and tetrahydrophthalimide end-capped oligomers have been synthesized from a mixture of para- and meta-phenylenediamine, 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (HFDA) and nadic or tetrahydrophthalic anhydride. Several percentages (25 to 50%) of metaphenylenediamine were used to obtain end-capped oligomers soluble in N-methylpyrrolidone. The tetrahydrophthalimide end-capped resins were characterized by <sup>1</sup>H nuclear magnetic resonance and size exclusion chromatography; their rheological behaviour was compared to their nadimide analogues. As expected from statistics both nadimide and tetrahydrophthalimide end-capped oligomers exhibit similar polydispersity ratios, with a high proportion of diimides which do not contain the HFDA moiety. However, their thermal treatments lead to different behaviours. Bis-nadimides gave crosslinked insoluble materials and bis-tetrahydrophthalimides gave soluble materials in spite of the disappearance of their olefinic protons. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: 1,2,3,6-tetrahydrophthalimide; nadimide; para- and meta-phenylenediamine (mPDA and pPDA))

## INTRODUCTION

Some 30 years ago, polymer matrix composites have been developed due to their good mechanical properties associated with their great lightness, made them able to compete with metallic alloys. However to be fully accepted by aerospace industries, these components need to withstand temperature up to 300°C<sup>1,2</sup>.

In 1972, the NASA proposed the PMR (polymerization of monomeric reactants) concept and more particularly the PMR-15 resin development<sup>3</sup>, which changed the composite matrix world. The PMR-15 resin ( $\bar{M}_n = 1500 \text{ g mol}^{-1}$ ) is a benzophenonetetracarboxylic acid dimethyl ester (BTDE)/methylene dianiline (MDA) oligomer nadimide end-capped; it presents a relatively easy processability (Scheme 1). Nowadays commercially available, this matrix however suffered numerous disadvantages such as its aromatic diamine toxicity, the need to store its monomers alcoholic solution at -18°C<sup>4</sup> and a susceptibility to microcracking during its final treatment, which affect its application field and market expansion. Several industries are looking for a PMR-15 substitute which would have improved thermal and mechanical properties and less drawbacks.

Vanucci showed that a modified resin called PMR-II<sup>5</sup> where the MDA is replaced by the pPDA and the BTDA moiety (benzophenonetetracarboxylic acid dianhydride) by HFDA one (4,4'-(hexafluoroisopropylidene)diphthalic anhydride), presents a better thermo-oxidative stability. However, the HFDA high cost is a barrier to a large scale manufacture of this PMR-15 substitute and it was also shown that the polymerized nadimide end-group was responsible for the limited stability at 300°C.

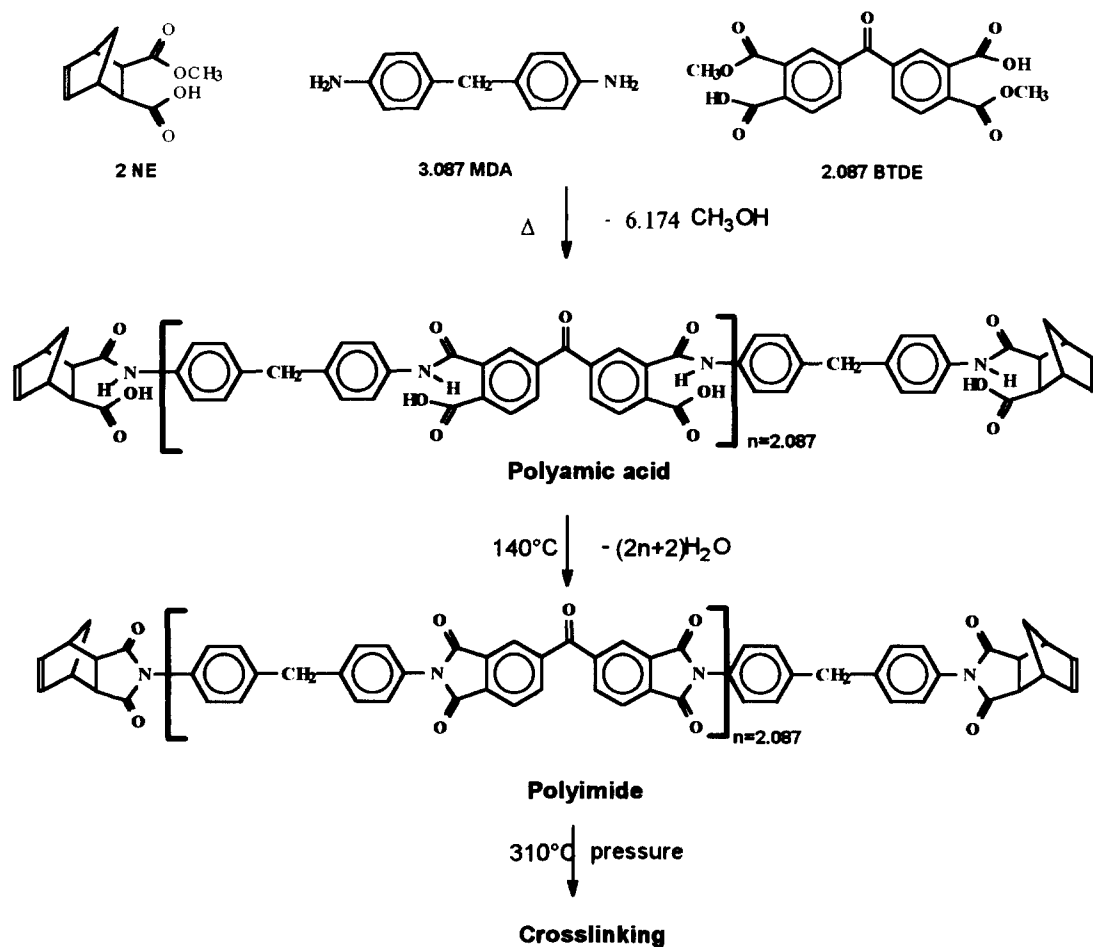
Another way to overcome some drawbacks encountered with the PMR-15 resin such as the storage of its monomers

alcoholic solution or MDA toxicity was proposed by our research group<sup>6,7</sup>. Indeed, the PMR methodology was abandoned in favour of a return to a totally imidized oligomer. The BBN-1500 (Benzhydrol methylene dianiline oligoimide BisNadimide end-capped) (Scheme 2) is prepared from the same PMR-15 elements but replacing the BTDA by the BHTDA (benzhydroltetracarboxylic acid dianhydride). This change provides the diglyme or N-methylpyrrolidone (NMP) resin solubility, but does not solve the oxidation problem.

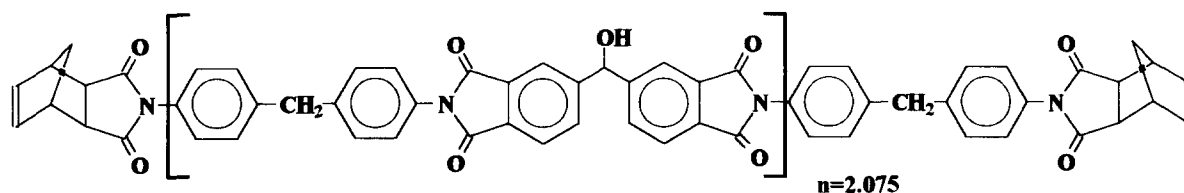
On the other hand, some problems of mechanical stress are still observed. This could be due, at least partially, to reverse Diels–Alder reaction (rDA) which the nadimide group undergoes as soon as 160°C is reached. The cyclic strain of the nadic moiety could be the origin of this observation<sup>8</sup> (Scheme 3).

In this study, the advantages of each of the previous works were combined to find a 'composite picture' of the ideal thermoset resin which would possess better thermo-oxidative stability and a low toxicity, which presents no more microcracking, an easy processability and of course good mechanical and thermal performances. The fully cyclized oligomer methodology was used; a mixture of less toxicity mPDA and pPDA was employed as the diamine agent and the tetrahydrophthalic anhydride (THPA) as the end-capping one. In fact, the choice of this anhydride is based on its reduced cyclic strain compared with the nadic ring (NA) (a bicyclic skeleton compared with a monocyclic one), so the rDA reaction should be of higher activation energy<sup>9,10</sup>. The bridge-head positions of the nadimide group which constitute a possible oxidation site<sup>11</sup>, were also eliminated. So theoretically, the nadimide replacement by tetrahydrophthalimide should enhance the thermo-oxidative stability and should present a simpler polymerization mechanism without volatile evolution.

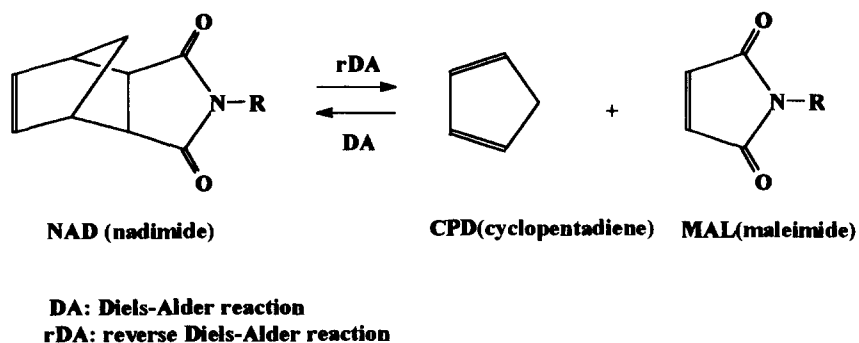
\* To whom correspondence should be addressed



Scheme 1



Scheme 2



Scheme 3

This paper deals with the synthesis of some tetrahydrophthalimide end-capped oligomers prepared from a mixture of pPDA and mPDA with HFDA. These resins were characterized by <sup>1</sup>H and <sup>13</sup>C n.m.r., size exclusion chromatography (s.e.c.) and their rheological behaviour was compared to their nadimide end-capped analogues.

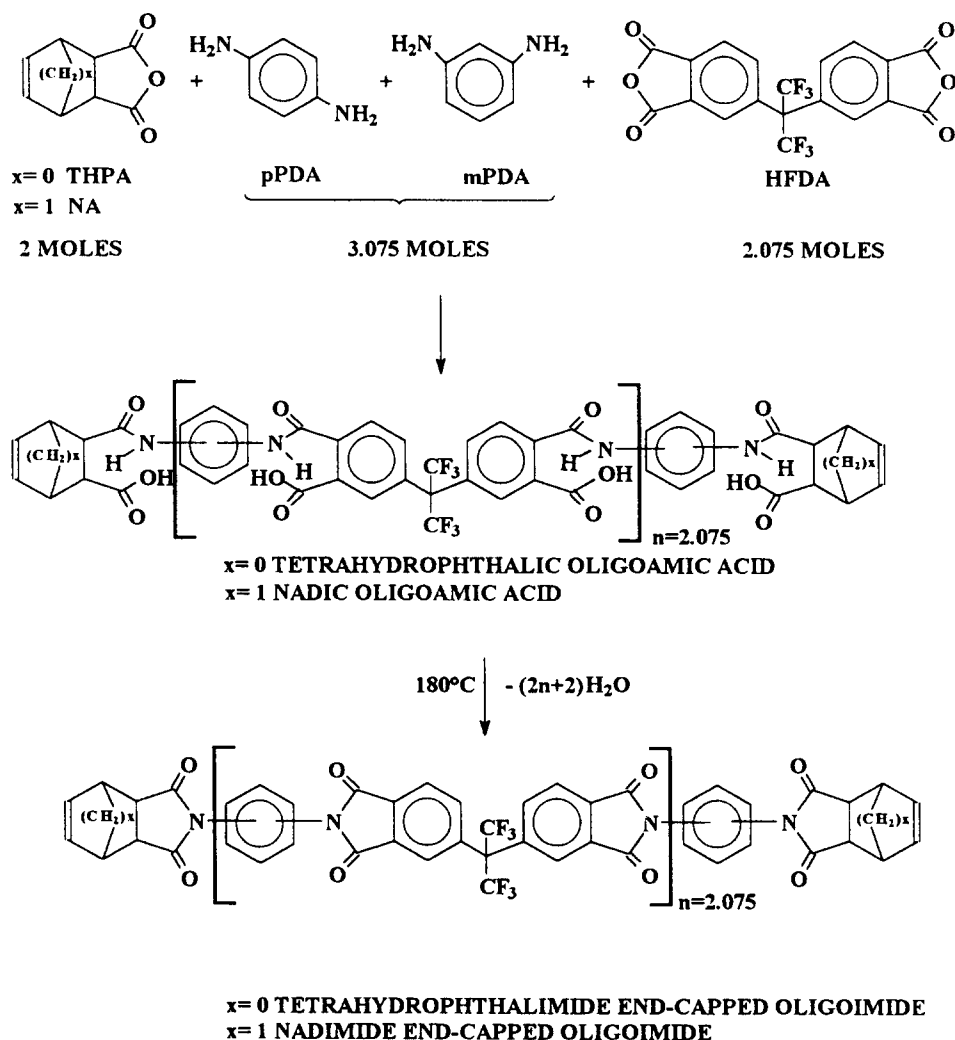
## EXPERIMENTAL

### Instrumentation

<sup>1</sup>H and <sup>13</sup>C n.m.r. spectra were recorded as solution in DMSO-d<sub>6</sub> with a Bruker AC250 spectrometer (the analysis frequency was 250 MHz for the proton and

**Table 1** Reagent quantities [g, (mmol)] used to carry out the preparation of tetrahydrophthalimide (THPI) and nadimide (NAD) end-capped oligoimides

Resin	HFDA	mPDA + pPDA	NA	THPA	NMP
THPI	30.42 (68.51)	10.82 (100.19)	0 (0)	10.00 (65.79)	51.41
NAD	31.52 (70.99)	11.36 (105.19)	11.17 (68.11)	0 (0)	42.88

**Scheme 4**

62.9 MHz for the carbon). The internal reference was tetramethylsilane (TMS).

The s.e.c. was performed in DMF with a Waters apparatus. The pump system was a Waters model 510 connected to four columns (two HR05 and two HR1). The differential refractometer was a Waters model 484.

Complex shear modulus ( $G^* = G' + iG''$ ) and complex viscosity ( $\eta^*$ ) on resin powders were determined with a Rheometrics RMS 800 viscoelastometer equipped with two parallel plates (rate =  $10 \text{ rad s}^{-1}$ ).

**Preparation**

In a 250 ml three necked flask fitted with a mechanical stirrer, a nitrogen inlet tube and a thermometer, the first reagents (HFDA, mPDA, pPDA) and the solvent were introduced (Table 1). The reaction mixture was stirred for 3 or 4 hours at room temperature and then the required quantity of end-capping anhydride was added (THPA or NA). After 2 additional hours of stirring, the temperature was slowly raised to  $180^{\circ}\text{C}$  and left at this temperature for

4 hours in order to complete the cyclization. After cooling down to room temperature, the mixture was poured into cold water, filtered and dried in an oven ( $150^{\circ}\text{C}$ ) under vacuum. In both cases around 50 g of dry product were obtained.

**RESULTS AND DISCUSSION****Preparation of resins**

The mPDA/pPDA/HFDA oligomers nadimide (NAD) and tetrahydrophthalimide (THPI) end-capped were prepared similarly to the BBN-1500 oligoimide. It is a one-pot preparation but a two-step process (Scheme 4): the first consists of preparing an amic-acid oligomer; the amic-acid oligomer is then cyclized to oligoimide by simply heating the reaction mixture at  $180^{\circ}\text{C}$  for 4 hours.

It was demonstrated in the case of the PMR-15 that the best balance between the targetted thermomechanical properties and a good processability is obtained with a theoretical molecular weight of  $1500 \text{ g mol}^{-1}$ .<sup>11,3,12</sup> This corresponds to an average polymerization degree of

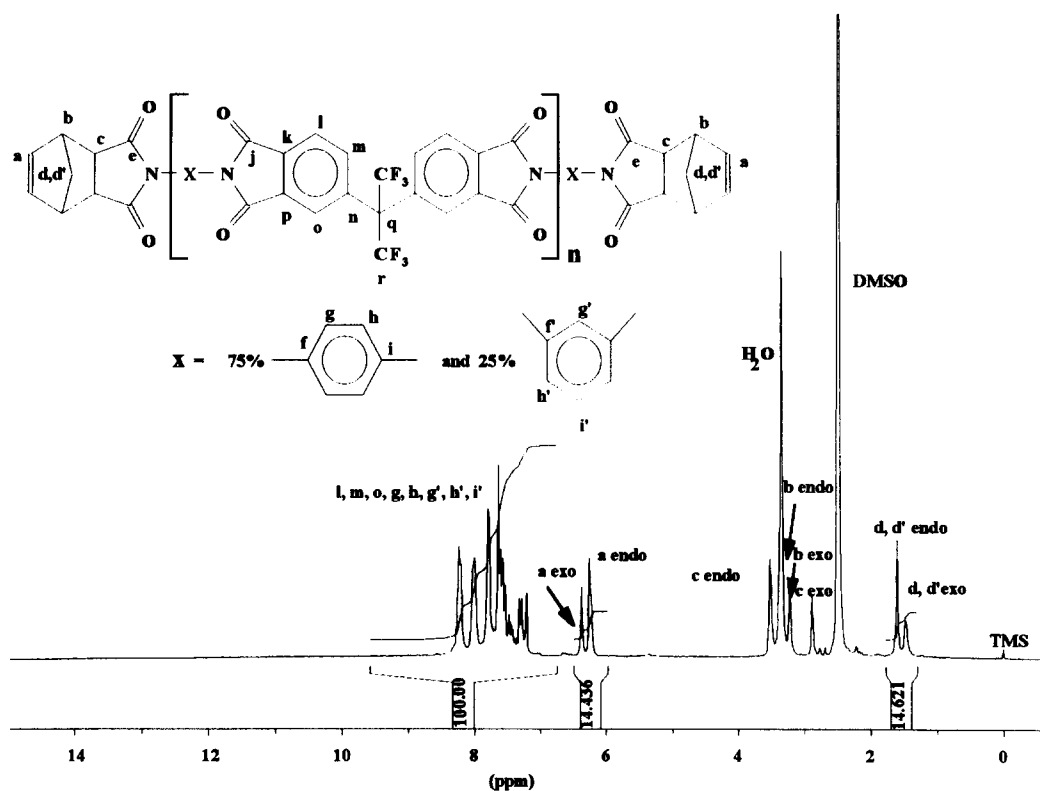


Figure 1 <sup>1</sup>H n.m.r. (250 MHz) spectrum of NAD-25

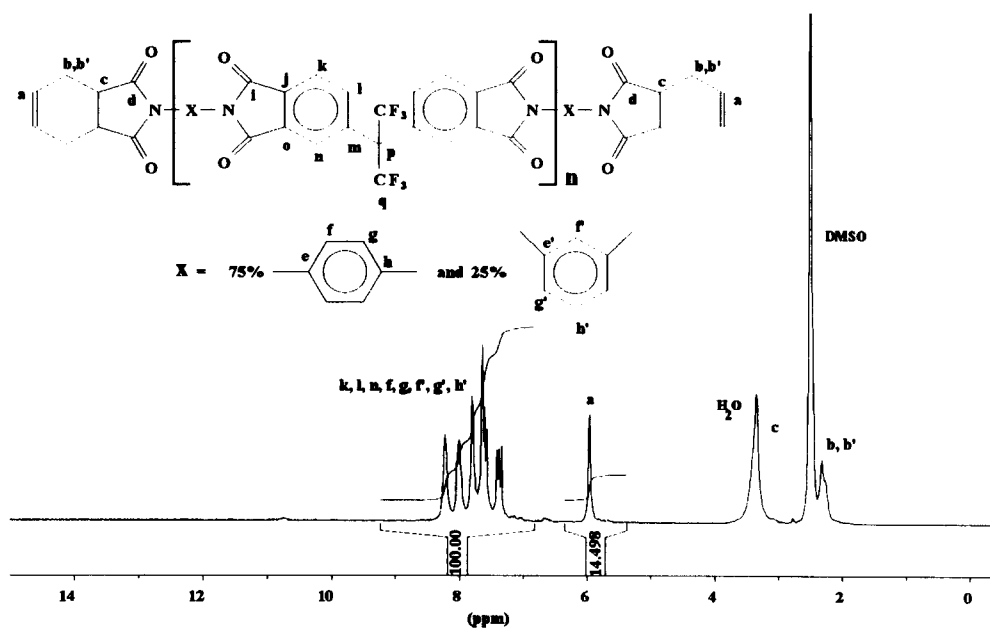


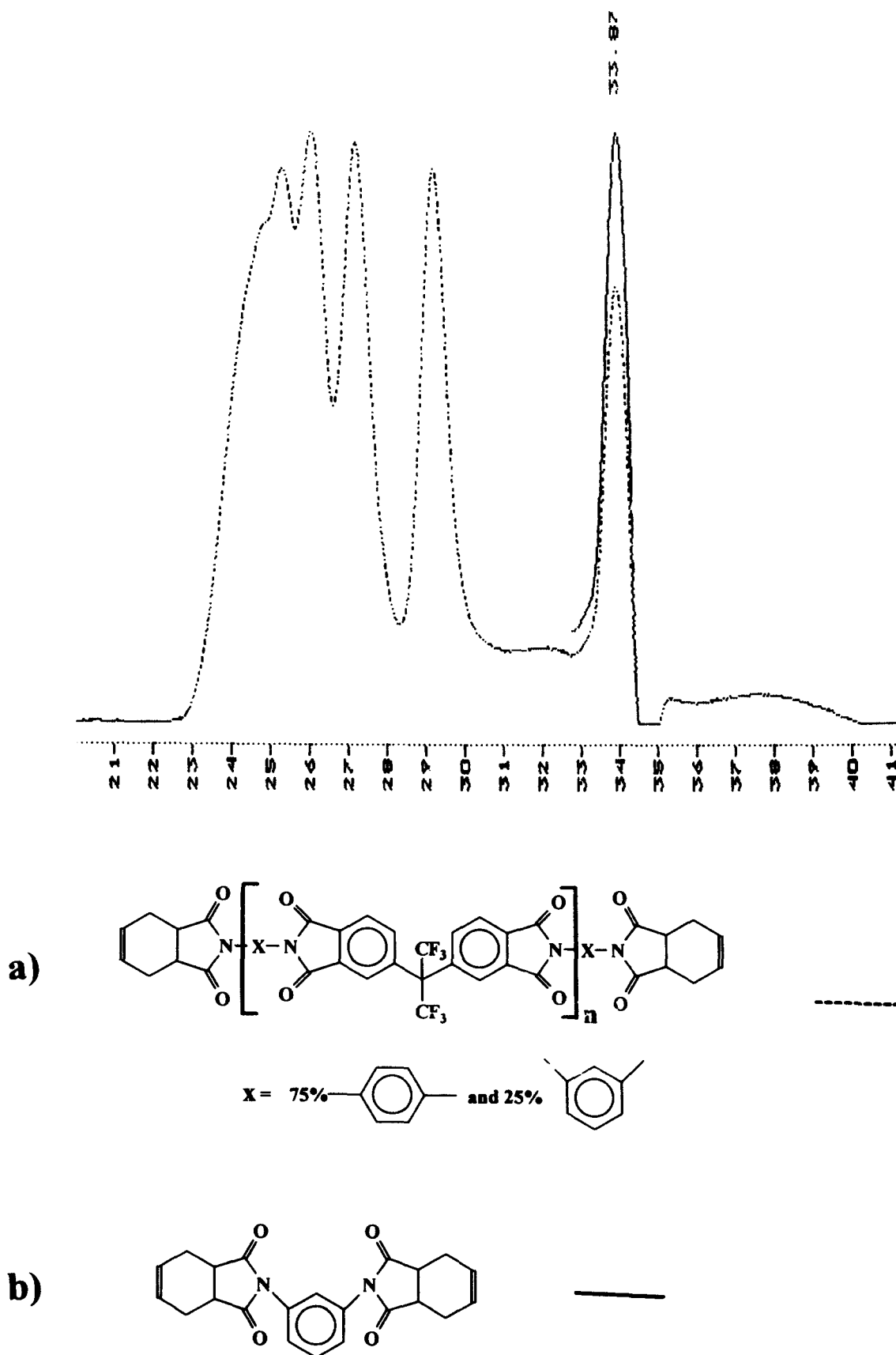
Figure 2 <sup>1</sup>H n.m.r. (250 MHz) spectrum of THPI-25

Table 2 <sup>1</sup>H n.m.r. chemical shifts (ppm) of the endo and exo nadimide end-capping groups

	Protons	ppm	Protons	ppm
	d, d' endo	1.60	d, d' exo	1.50
	b endo	3.40	c exo	2.90
	c endo	3.50	b exo	3.25
	a endo	6.25	a exo	6.40

Table 3 <sup>1</sup>H n.m.r. chemical shifts (ppm) of the tetrahydrophthalimide end-capping group

	Protons	ppm
	b, b'	2.10–2.60
	c	3.35
	a	5.95



**Figure 3** A s.e.c. diagram of the THPI-25 (a) and of the bistetrahydrophthalimide of the meta-phenylenediamine (b)

$n = 2.087$  for the PMR-15 and  $n = 2.075$  for the BBN-1500. This latter average polymerization degree was kept. So the theoretical average molecular weight is  $1470 \text{ g mol}^{-1}$  for the nadimide end-capped oligomers and  $1450 \text{ g mol}^{-1}$  for the tetrahydrophthalimide ones.

The stoichiometry used for the synthesis is:

mPDA + pPDA = 3.075 mol;

NA = 2 mol or THPA = 2 mol according to the desired terminal function.

Research of the minimal ratio of mPDA

During the different syntheses, we tried to determinate the minimal mPDA proportion to introduce in the diamine mixture in order to obtain an imidized oligomer soluble in NMP. Moreover, if this meta-substituted fraction is too

great, it can be anticipated that the glass transition temperature ( $T_g$ ) will be decreased.

Several tests with various ratios of mPDA/pPDA were carried out. The tetrahydrophthalimide and nadimide end-capped oligomers are respectively named THPI-X and NAD-X where X corresponds to the mPDA percentage

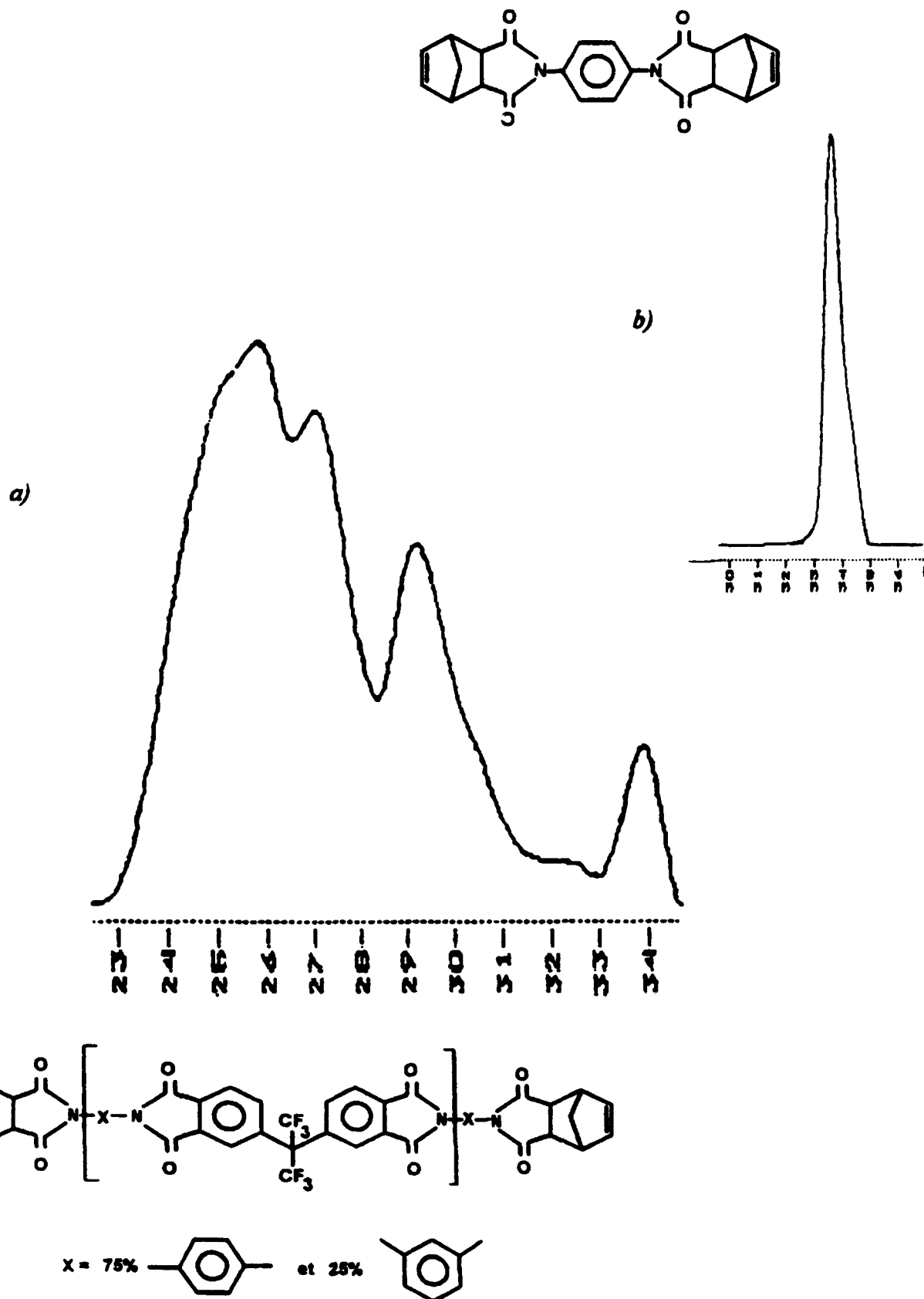


Figure 4 A s.e.c. diagram of the NAD-25 (a) and of the bisnadimide of the paraphenylenediamine (b)

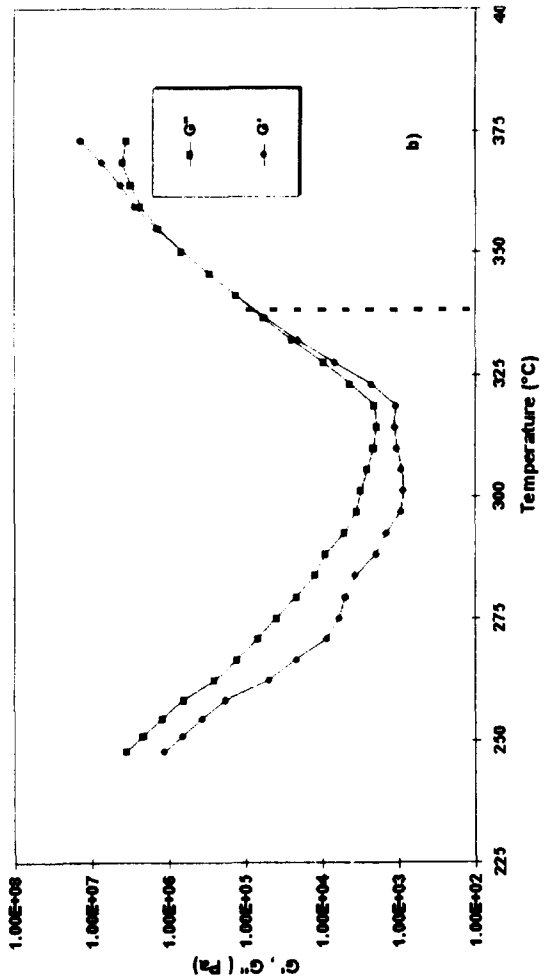


Figure 5 Viscoelastic behaviour of NAD-25:  $\eta^*$  (a),  $G'$  and  $G''$  (b) versus temperature

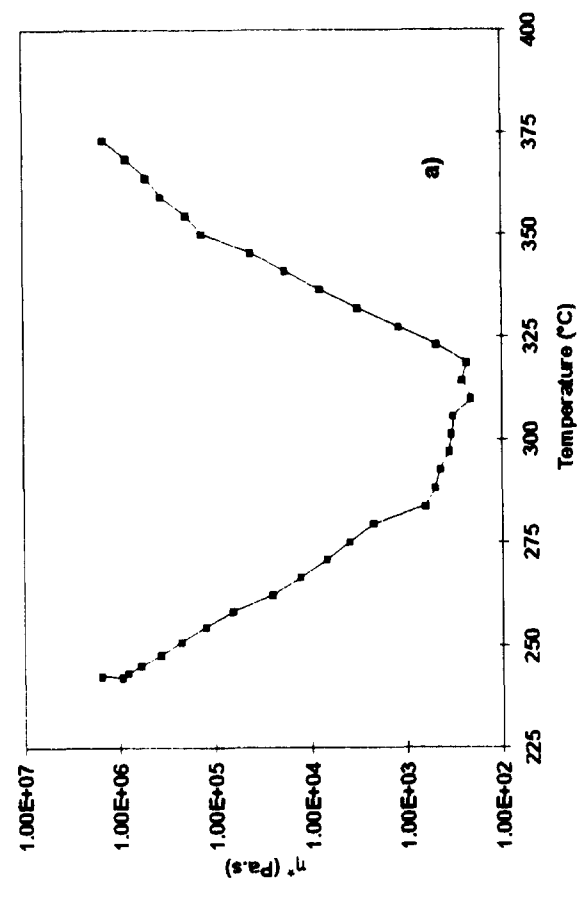
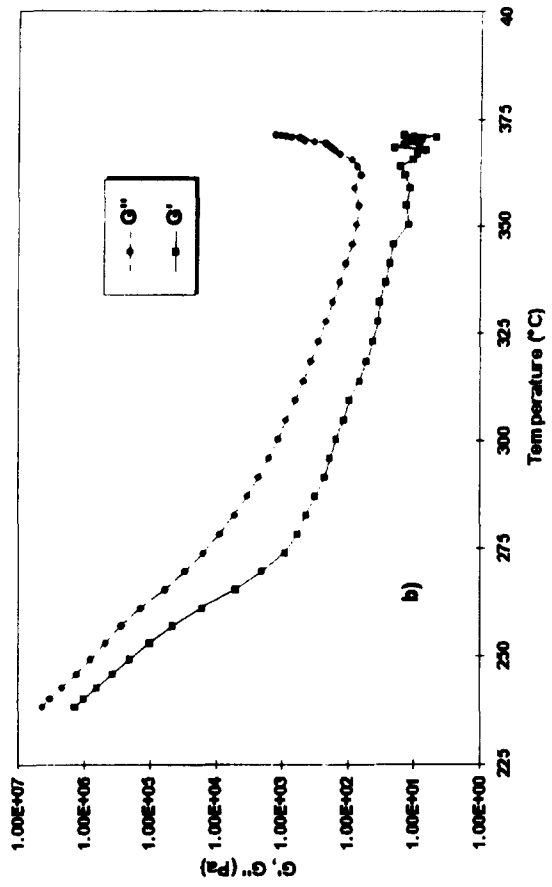
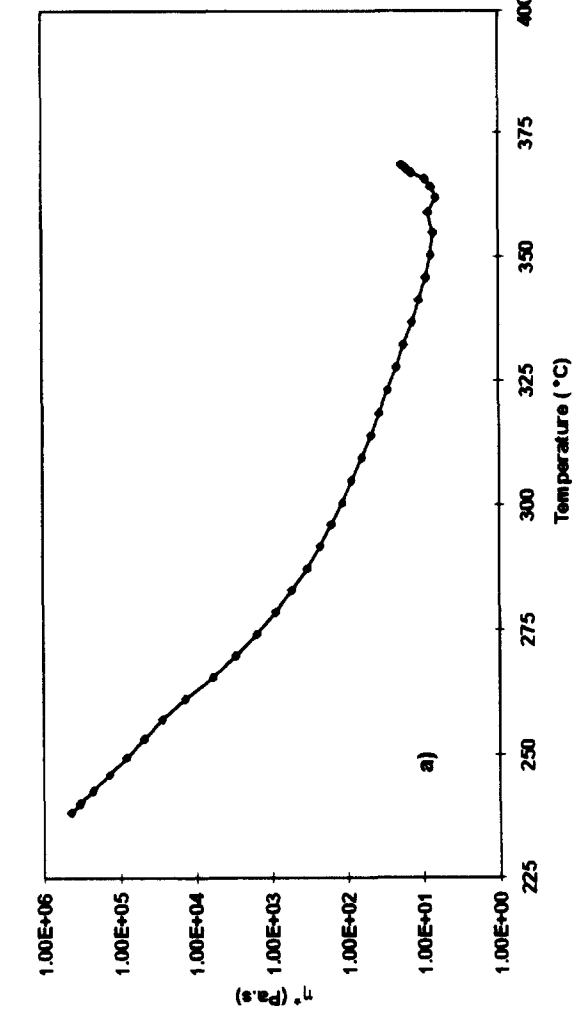


Figure 6 Viscoelastic behaviour of THPI-25:  $\eta^*$  (a),  $G'$  and  $G''$  (b) versus temperature



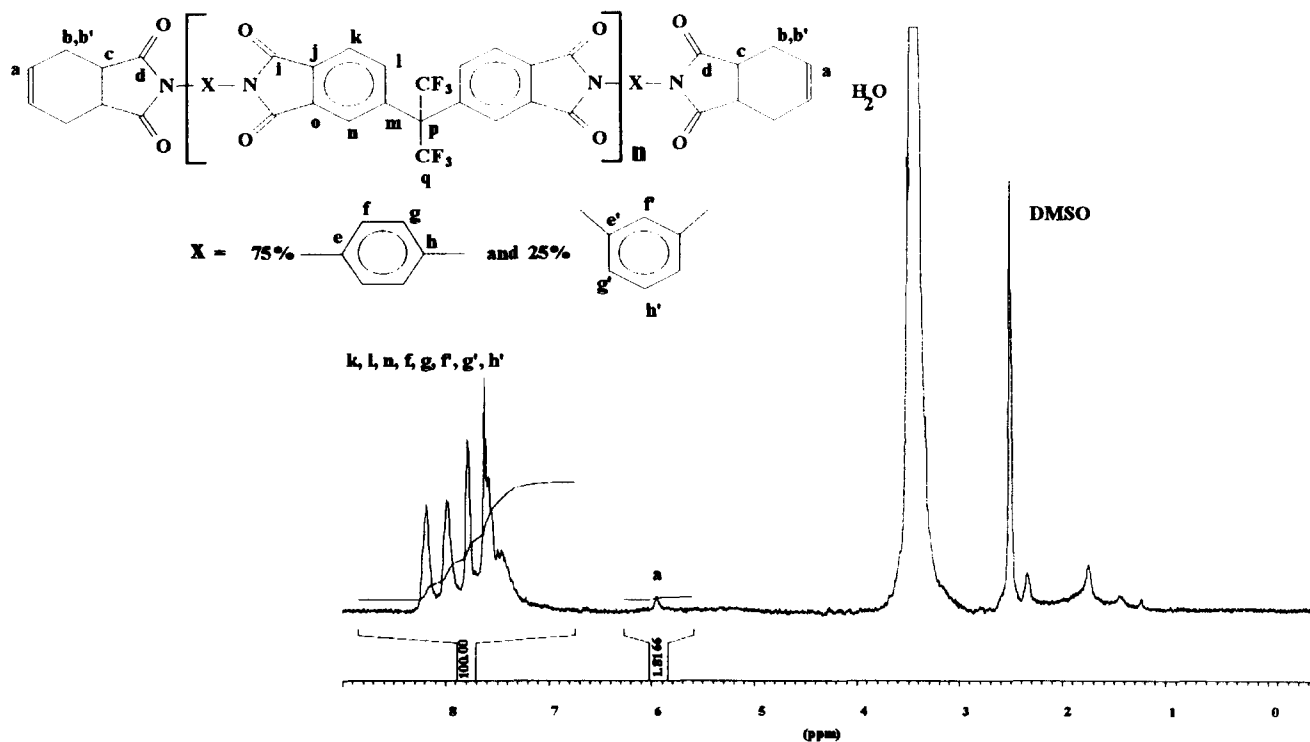


Figure 7  $^1\text{H}$  n.m.r. spectrum of THPI-25 after its viscoelastometer analysis

Table 4 Average molecular weights ( $\bar{M}_n$ ) and polymerization degrees ( $n$ ) obtained from  $^1\text{H}$  n.m.r. spectra and from stoichiometry (th)

Oligomer	$\bar{M}_{\text{th}}$	$\bar{M}^1\text{H n.m.r.}$	$n_{\text{th}}$	$n^1\text{H n.m.r.}$
THPI-25	1450	1594	2.075	2.36
NAD-25	1470	1618	2.075	2.35

introduced. Concerning the tetrahydrophthalimide end-capped oligomers, when the percentage of mPDA ranged from 25 to 50% a good solubility of the reaction medium was not achieved as it was for the nadimide one. Tests with a mPDA percentage higher than 50% were not undertaken for the reasons states above. On the other hand, results of tests performed with the nadic anhydride showed that the minimal mPDA proportion necessary to obtain a good solubility is 25%. Thus the characterization of both oligomers were performed with a mPDA percentage of 25%.

#### Characterization

$^1\text{H}$  n.m.r.. Each oligomer was characterized by  $^1\text{H}$  n.m.r. (Figures 1 and 2). The chemical shifts of nadimide and tetrahydrophthalimide end-capping groups were assigned as shown in Tables 2 and 3. Both endo and exo isomers of nadimide units are present. This is a consequence of reaction temperature as reported earlier<sup>3,8</sup>.

The mPDA, pPDA and HFDA aromatic proton resonances are located between 7.10 and 8.40 ppm. These spectra do not exhibit NH signal at around 10.8 ppm showing that the imidization of amic-acid oligomers to oligoimides is complete.

From resonance integrations, the oligoimide average molecular weight and the average polymerization degree can be determined. This weight is calculated from the integration ratio of the end-capping nadimide or tetrahydrophthalimide ethylenic protons to oligomer aromatic ones. These measurements are quite easy to perform because these kinds of protons resonate far away from the aromatic ones.

With each oligomer being bifunctionalized, four ethylenic protons are to be considered for THPI-25 (5.95 ppm) and for NAD-25 (6.25 and 6.40 ppm: endo/exo configuration of nadimide moieties).  $(10n + 4)$  protons are to be considered for the aromatic moieties. The results of the calculation are listed in Table 4. Good agreements are observed between the theoretical and the experimental values.

*Size exclusion chromatography.* The THPI-25 (Figure 3) and NAD-25 (Figure 4) analyses were performed in DMF. In both cases, the molecular weight distribution is relatively wide. As expected from a statistical point of view, these analyses show the presence of a large amount of low molecular weight species and particularly the diimides which do not contain HFDA ( $n = 0$ ). This had seen supported in the case of THPI-25 by analysing the bistetrahydrophthalimide of the meta-phenylenediamine which presents a 34 minute elution time (the bistetrahydrophthalimide of the paraphenylenediamine was not sufficiently soluble in DMF to be s.e.c. analyzed). The peak corresponding to this elution time is found in the s.e.c. diagram of THPI-25 (Figure 3). The presence of this low molecular weight species ( $n = 0$ ) and of several others peaks on the s.e.c. diagram indicate a high polydispersity. The same kind of observation can be done from the s.e.c. diagram of NAD-25 where the bisnadimide of para-phenylene diamine peak appears at 34 minutes (Figure 4). The bisnadimide of metaphenylene diamine presented the same retention time.



*Comparison of the thermal behaviour by rheological analysis*

The rheological study (complex viscosity and complex shear modulus) was performed in order to obtain information about polymerization of the end-capping groups.

The temperature has been stabilized at 230°C in order to obtain a total sample softening and then experimental measurements were recorded every 5°C until 380°C (°C min<sup>-1</sup>).

The results for NAD-25 are shown in *Figure 5*.

The resulting rheological characteristics show a minimum complex viscosity ( $\eta^*$ ) of 200 Pa s<sup>-1</sup> at 310°C; the gel point ( $G' = G''$ ) is observed at around 338°C. All these data support the occurrence of a crosslinking of the end-capping nadimide group.

The THPI-25 rheological behaviour (*Figure 6*) is very different of the NAD-25 one. We observe a large viscosity decrease until 360°C and no increase after this temperature which should correspond to a crosslinking of the end-capping tetrahydrophthalimide groups. This appears to be confirmed by the non observation of a gel point (no cross-over of the  $G'$  and  $G''$  curves). It shows that the THPI-25 does not exhibit a thermal polymerization advancement. In addition, the cured product of THPI-25 is wholly soluble in DMSO, allowing a n.m.r. analysis. The <sup>1</sup>H n.m.r. spectrum of THPI-25 after curing (*Figure 7*) shows a drastic decrease in the intensity of the ethylenic protons ( $\delta = 5.9$  ppm) relatively to aromatic protons ( $\delta = 7.0$ – $8.3$  ppm) and to protons attached to sp<sup>3</sup> hybridized carbon atoms ( $\delta = 2.0$ – $2.5$  ppm). On the other hand, new signals appear at around  $\delta = 1.3$ – $1.7$  ppm which could be assigned to cyclohexanic protons. Thus, it is clear that thermal activation modifies the tetrahydrophthalimide end-capping groups but not towards a polymerization reaction alone.

The driving force of the thermal polymerization of nadimide end-capped oligomers seems to be the reverse Diels–Alder reaction (*Scheme 3*) which is the lowest activation energy process for unsubstituted nadimide moieties<sup>8</sup>. Thus, when the reaction temperature reaches about 200°C the initiation of the crosslinking by the in situ generated maleimide units competes with the Diels–Alder reaction. In the case of tetrahydrophthalimide end-caps the reverse Diels–Alder reaction is a highest activation energy reaction and another radical initiation is probably followed by competitive reaction processes.

CONCLUSION

Nadimide and tetrahydrophthalimide end-capped oligomers showed very similar analytical characteristic (molecular weight, polydispersity). However, their thermal behaviours are very different. The bis nadimide oligomers crosslinked whereas under the same experimental conditions the bis tetrahydrophthalimide did not. In the meantime other chemical pathways were taking place as evidenced by the disappearance of the olefinic protons during thermal treatment. In order to identify these competitive reaction pathways, a study on model compounds was undertaken. It is presented in the following paper<sup>13</sup>.

ACKNOWLEDGEMENTS

The authors would like to thank the DGA (Délégation Générale pour l'Armement) and the SNECMA for financial support and their permission to publish this work.

REFERENCES

1. Delvigs, P., Serafini, T. T. and Lightsey, G. R., *Materials Review for '72'*, SAMPE, Azusa, (CA), 1972.
2. Serafini, T. T., Delvigs, P. and Lightsey, G. R., *J. Appl. Polym. Sci.*, 1972, **16**, 905–915.
3. Serafini, T. T., in *Polyimides: Synthesis, Characterization and Applications*, ed. K. L. Mittal. Plenum Press, New York, 1982, Vol. 2, pp. 957–975.
4. Grenier-Loustalot, M. F. and Grenier, P., *High Perform Polym.*, 1991, **3**, 113–116.
5. Vannucci, R.D., *Sampe Quarterly*, 1987, **19**, 31–36.
6. Malinge, J., Rabilloud, G. and Sillion, B., Patent Fr. no. 8701983, 1987, US A4987218, 1991.
7. Malinge, J., Rabilloud, G., Sillion, B., Garcin, C., Bardin, I. and Berthier, J. M., in *Looking Ahead for Materials and Processes*, eds. J. de Bossu, B. Briens and P. Lissas. Elsevier Science, Amsterdam, 1987, pp. 455–465.
8. Bertholio, F., Mison, P., Pascal, T. and Sillion, B., *High Perform. Polym.*, 1993, **5**, 47–57.
9. Scola, D.A. and Stevens, M.P., *J. Appl. Polym. Sci.*, 1981, **26**, 231–247.
10. Galia, M., Ronda, J. C., Mantecom, A., Serra, A. and Cadiz, V., *Eur. Polym. J.*, 1992, **28**, 175–181.
11. Wilson, D., *High Perform. Polym.*, 1993, **5**, 77–95.
12. Serafini, T.T. and Delvigs, P., *Appl. Polym. Symp.*, 1973, **22**, 89–100.
13. Bounor-Legaré, V., Mison, P. and Sillion, B., *Polymer*, 1998, **39**, 2825–2833.