A soluble nadimide end-capped fluorinated resin

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Two methods were studied for synthesizing nadimide end-capped fluorinated oligomers with different theoretical molecular weights from 4,4′-methylenedianiline (MDA), 4,4′-hexafluoroisopropylidenebis-(phthalic anhydride) and nadic anhydride. They were a one-step process involving the simultaneous condensation of the three starting reactants and a two-step process involving the formation of an intermediary amine end-capped oligoimide. A comparison between the products obtained from these two routes was based on ^{1}H nuclear magnetic resonance (n.m.r.) determination and confirmed by size exclusion chromatography analysis. ^{1}H n.m.r. was very efficient to investigate the molecular distribution because the chemical shift of the protons belonging to MDA methylene groups was strongly dependent on the chemical environment of the two neighbouring imidic groups. The rheological behaviour of precipitated resin powder (theoretical molecular weight = 1750) was then studied with a viscoelastic spectrometer. The viscosity minimum was about 450 Pa s at 260°C and the gel point was observed at 315°C with a 2°C min^{-1} heating rate. Thermomechanical and thermogravimetric analyses of the corresponding polynadimide network (cure schedule: 100°C for 3 h, 300°C for 1 h and 340°C for 1 h) showed a T_g near 315°C and the onset of degradation near 400°C under a nitrogen atmosphere. Four-ply laminates were finally made from graphite-fibre-reinforced prepreg and characterized by dynamic mechanical analysis. The storage modulus G' was 5.2 GPa at room temperature and showed good constancy up to 300°C.

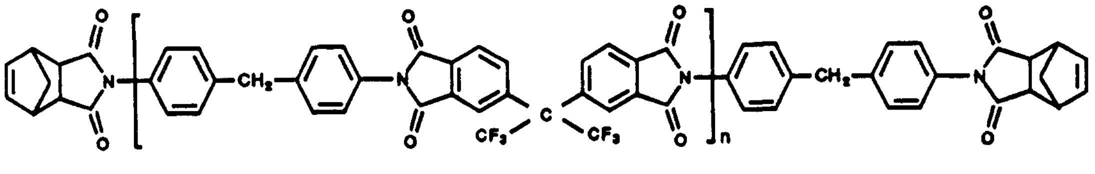
(Keywords: 4,4′-hexafluoroisopropylidenebis(phthalic anhydride); polyimide; nadimide; thermosetting oligomer)

INTRODUCTION

There is an expanding demand for high-performance graphite-fibre-reinforced composite materials for civil and military aerospace applications. High-temperature capability, low toxicity, and improved storage and processing properties are important for any relevant new composite matrix. Among the resins that can withstand a 300°C continuous service temperature, the American PMR (polymerization of monomer reactant) and particularly PMR 15[1] have now reached the stage of industrial development. However, PMR 15 (which is an alcoholic solution of three monomers) is unstable, even at room temperature[2,3], and therefore both the solution and the prepregs must be stored at low temperature (−18°C). Another problem is the toxicity of the resin, since the basic solution contains a large quantity (about 17 wt%) of carcinogenic aromatic amine. Moreover, the processing of the graphite-fibre-reinforced laminates needs thermal condensation and imidization stages, which complicate the cure cycle. In order to avoid these difficulties, we have decided to study a new family of resins based on fully imidized nadimide end-capped oligoimides.

The first product of this family is IP 960 resin, and the graphite-fibre prepregs therefrom: HT 21[4]. The original composition of IP 960 oligomers containing a benzhydrol group in the repeat unit led to the possibility of a highly concentrated solution in diglyme (about 60 wt%). The results of thermomechanical and thermogravimetric investigations have showed that IP 960 is a good matrix candidate for aeronautical applications requiring service temperatures up to 300°C.

Considering the high thermostability and good moisture resistance of PMR systems obtained from monomers containing hexafluoropropylidene linkages[5,6], we have moved our work towards the study of thermosetting nadimide end-capped oligimers obtained by condensation of 4,4′-methylenedianiline (MDA), 4,4′-hexafluoropropylidenebis(phthalic anhydride) (6FBP) and nadic anhydride (NA):



This paper deals with the synthesis of these diglyme-soluble oligoimides by two distinct routes. The resulting products with different molecular weights were characterized by ^{1}H n.m.r. and s.e.c. The thermomechanical behaviour of polymerized films and four-ply laminates were finally examined to study the potential properties of this type of resin as a matrix for composites.

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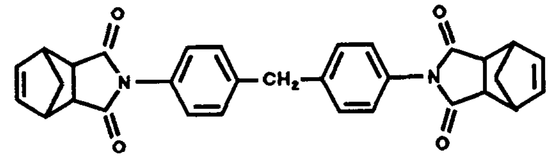
remain stable in diglyme solution after more than four months.

^1H *n.m.r. characterization*

All resin samples were analysed by ^{1}H n.m.r. after precipitation in hexane and drying at 120°C under vacuum for 4 h. The ^{1}H n.m.r. spectrum of the II-17 resin with the attribution of the main peaks is presented in *Figure 1*. The series of peaks corresponding to the protons of the MDA methylene group are reported in *Figure 2*. Four main resonances called H_1, H_2, H_3, H_4 are observed.

A model study involving the short bisnadimide ($n = 0$) **d**:

d



the amine end-capped oligoimides IIa-b and the different nadimide end-capped oligomers allowed these four resonances to be attributed in relation to the chemical environment of the MDA methylene group:

H_1 ($\delta = 4.1$ ppm)	MDA CH_2 located between two 6FBP groups in a nadimide end-capped oligomer.
H_2 ($\delta = 4.04$ ppm)	MDA CH_2 located between one 6FBP group and one NA end-group in a nadimide end-capped oligomer.
H_3 ($\delta = 3.99$ ppm)	MDA CH_2 in the short bisnadimide ($n = 0$) **d** (i.e. located between two NA groups).
H_4 ($\delta = 3.92$ ppm)	MDA CH_2 in a residual amine end-capped oligoimide (position corresponding to the MDA groups at the chain ends).

Using the ratio of the area corresponding to the peaks H_1, H_2, H_3 (denoted H_1, H_2, H_3) the molar concentration $[C_d]$ of compound **d** could be determined. The average polymerization degree $\bar{n}$ of the nadimide end-capped oligomers ($n \geq 1$) could also be calculated.

Taking into account the presence of two MDA methylene groups of H_2 type and $n - 1$ methylene groups

Table 1 Nadimide end-capped oligoimide resins—dynamic viscosity and shelf life

Method	Resin	$\bar{M}_t$	$\bar{n}_t$	η_d (Cp) at $T = 30°C$[a]	Shelf life (days) at $T = 20°C$[b]
One-step	I-15	1500	1.67	–	0
	I-17	1750	2.08	14000	2
Two-step	II-10	1070	0.45	–	0
	II-15	1500	1.67	10000	10
	II-17	1750	2.08	18000	>120
	II-20	2000	2.5	22000	>120

[a] Dynamic viscosity at $T = 30°C$ for a concentration of 58 wt%
[b] Shelf life at room temperature for a concentration of 58 wt%

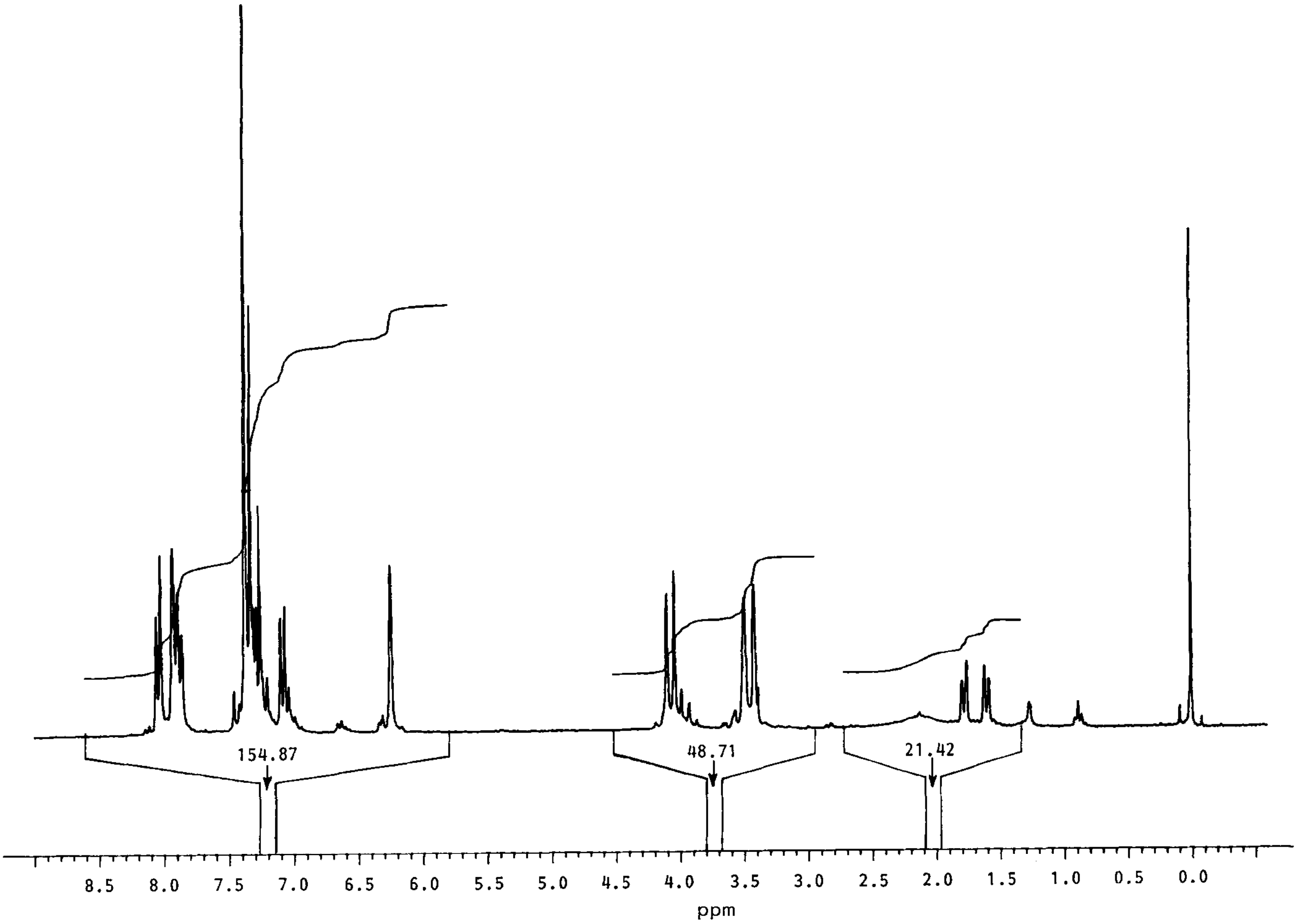


Figure 1 ^{1}H n.m.r. spectra of a nadimide end-capped oligomer: resin II-17

RESULTS AND DISCUSSION

Synthesis

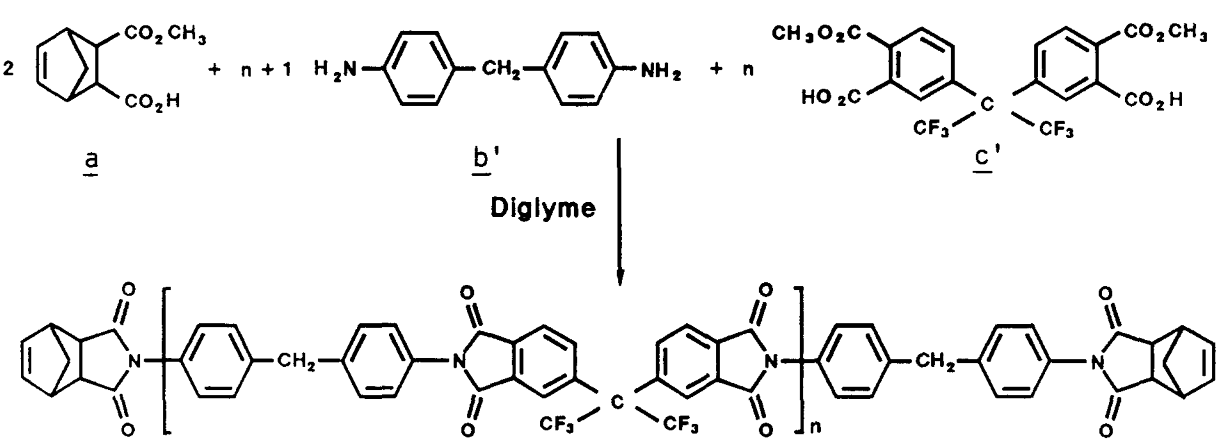
Two synthesis methods were studied to prepare the resins: a one-step process and a two-step process.

In the one-step process (*Scheme 1*), the MDA (**a**) and the bismethyl ester and monomethyl ester (**b**′ and **c**′) respectively derived from 6FBP (**b**) and NA (**c**) were mixed in diglyme solution. The monomers were then condensed and thermally imidized in solution following a thermal schedule up to about 170°C (T(vapour final) = 160°C).

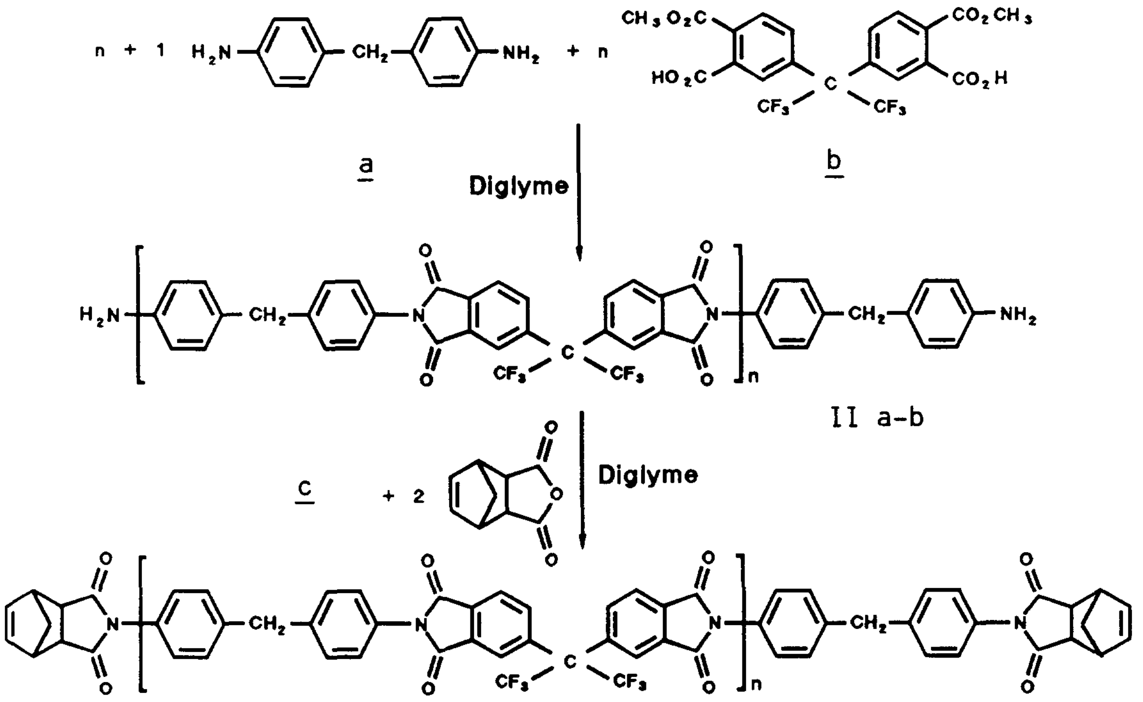
The two-step process involves the preparation of an intermediary amine end-capped oligoimide (*Scheme 2*). In this case, the MDA (**a**) and the 6FBP (**b**) were condensed and thermally imidized in diglyme solution to give the diamine IIa-b. After cooling, the fully cyclized diamine IIa-b is then reacted with the NA (**c**) and a new thermal imidization cycle (T(vapour final) = 160°C) is applied. For all reaction steps, the starting concentration of monomers is 60 wt% in diglyme. The final concentration of resins is thus about 60 wt% in diglyme, which is used as impregnation solvent.

For both methods, the molar proportions of the reactants, respectively **a**, **b**′, **c**′ and **a**, **b**, **c**, were adjusted and nadimide end-capped oligomers with different molecular weights were obtained. The theoretical molecular weights $\bar{M}_t$ of oligomers ranged between 1070 and 2000 and the corresponding polymerization degree $\bar{n}_t$ ranged between 0.45 and 2.5.

Table 1 identifies the characteristics of each of the oligomers investigated. The numbers included in the resin designation correspond to the method of preparation (I, one-step; II, two-step) and the $\bar{M}_t$ (15, 1500). The dynamic viscosity η_d of the resin and the shelf life in diglyme solution were also reported. *Table 1* shows that the shelf life of the resins prepared following the two-step process is longer than the shelf life of the resins prepared from the one-step process. In this latter case, the products precipitated rapidly from the diglyme at room temperature. By contrast, the resins NA II-17 and NA II-20



Scheme 1 One-step process



Scheme 2 Two-step process

remain stable in diglyme solution after more than four months.

^1H n.m.r. characterization

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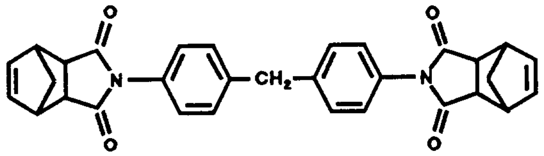

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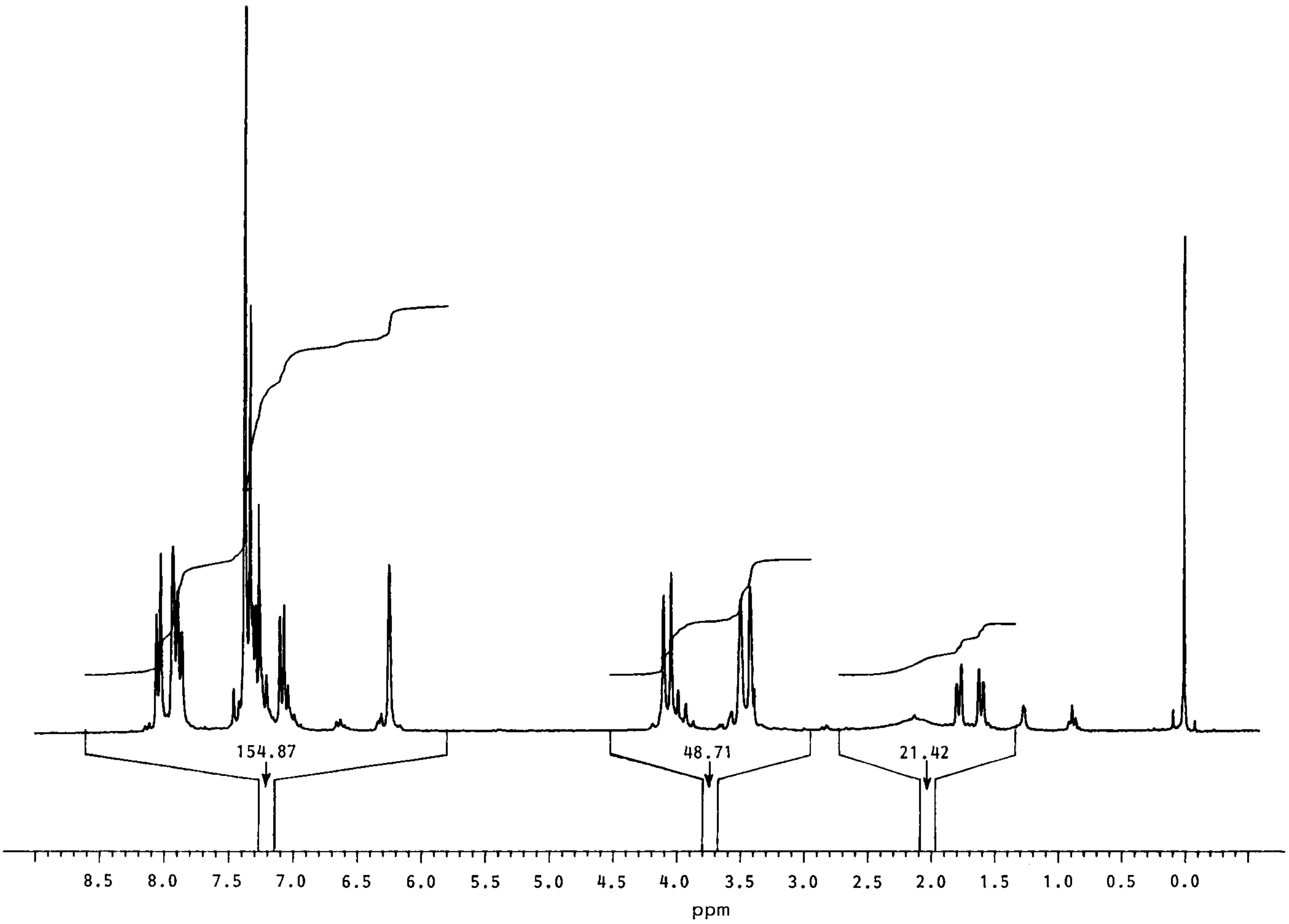

Figure 1 ^{1}H n.m.r. spectra of a nadimide end-capped oligomer: resin II-17

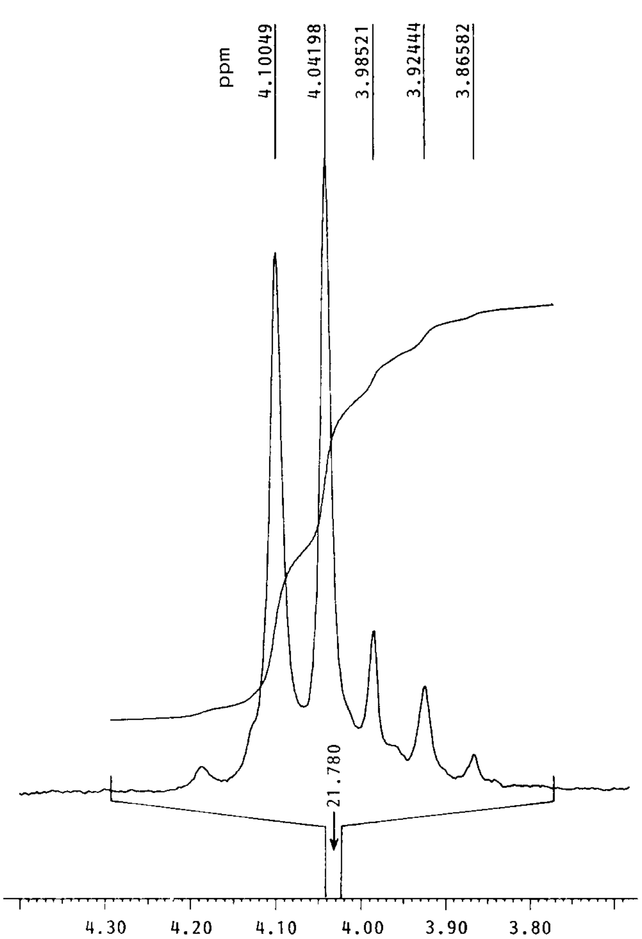

Figure 2 Peaks corresponding to the MDA methylene protons from ^1H n.m.r. spectra of resin II-17

of H_1 type for one nadimide end-capped oligomer, one can write the following two relationships:

$$[C_d] = \frac{H_3}{H_2/2 + H_3} \qquad (1)$$

$$\frac{H_1}{H_2} = \frac{2}{\bar{n} - 1} \qquad (2)$$

These are correct only if the proportion of MDA methylene groups belonging to products different from nadimide end-capped species, for instance residual amine end-capped oligoimide, is neglected.

Considering the existence of only two molecular species, i.e. the compound **d** and the nadimide end-capped oligomer with an average polymerization degree equal to $\bar{n}$ (from expression (2)), we have estimated $\bar{M}_n$ and $\bar{M}_p$ for all resin samples.

Table 2 lists the results of the calculation from the ^1H n.m.r. study. The results show that the concentration $[C_d]$ is lower in the resin samples prepared following the two-step process. As a matter of fact, the formation of an intermediary amine end-capped oligoimide reduces the probability of direct condensation of NA, more reactive than 6FBP, with MDA.

The short bisnadimide compound **d** is weakly soluble in diglyme (less than 1 wt% at room temperature) and can lead to the precipitation of the resin. Its lower concentration in the two-step resins might explain their longer shelf life at room temperature.

Generalizing this reasoning, one can assume that the tendency to precipitate decreases as the polymolecularity of the resin (*IP* factor) is reduced. As seen in *Table 2*, the inclusive effect of the two-step process is a decreasing of the *IP* factor in comparison to the one-step process. Good agreement is noted between the theoretical value $\bar{M}_t$ and the experimental values $\bar{M}_n$ and $\bar{M}_w$. The calculation from the ^1H n.m.r. study thus gives a satisfactory estimate of the average molecular weights.

S.e.c. characterization

All resin specimens were analysed by s.e.c. The s.e.c. diagram of the II-17 resin is presented in *Figure 3*. The oligomeric species with polymerization degree equal to $n = 0$ (compounds **d**), $n = 1$, $n = 2$, $n = 3$ are efficiently separated. The corresponding retention times are respectively 32.20 min ($n = 0$), 38.28 min ($n = 1$), 31.16 min ($n = 2$), 29.92 min ($n = 3$). A calibration curve was obtained from samples containing different concentrations of compound **d**. This allows the determination of $[C_d]$ from s.e.c. in each nadimide resin. The values of $[C_d]$ from s.e.c. and ^1H n.m.r. studies are reported in *Table 3*. Good correlation was observed between both series of data and this confirms the validity of the ^1H n.m.r. investigation.

Table 2 Nadimide end-capped oligomers—determination of $[C_d]$ and average molecular weights from ^1H n.m.r. study

Resin	$\bar{M}_t$	$[C_d]$ (mol%)	$\bar{M}_n$	$\bar{M}_w$	*IP*
I-15	1500	43.0	1280	1660	1.29
I-17	1750	40.0	1370	1750	1.28
II-10	1070	42.6	1130	1410	1.24
II-15	1500	35.1	1370	1680	1.23
II-17	1750	31.0	1710	2080	1.21
II-20	2000	14.0	2220	2500	1.12

Table 3 Nadimide end-capped oligomers—determination of $[C_d]$ from s.e.c. study

Resin	$\bar{M}_t$	$[C_d]$ (mol%) ^1H n.m.r.	$[C_d]$ (mol%) s.e.c.
I-15	1500	43.0	41.9
I-17	1750	40.0	40.1
II-10	1070	42.6	42.4
II-15	1500	35.1	34.2
II-17	1750	31.0	24.9
II-20	2000	14.0	9.6

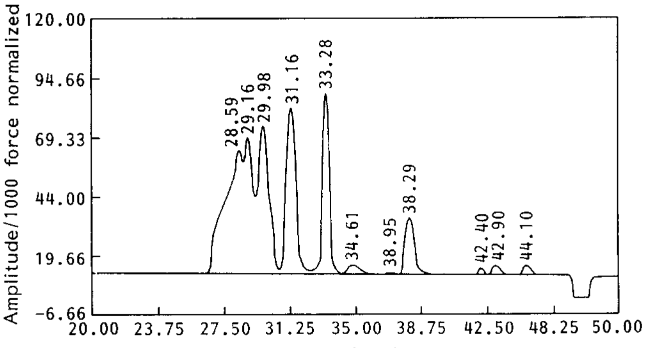

Figure 3 S.e.c. diagram of a nadimide end-capped oligomer: resin II-17

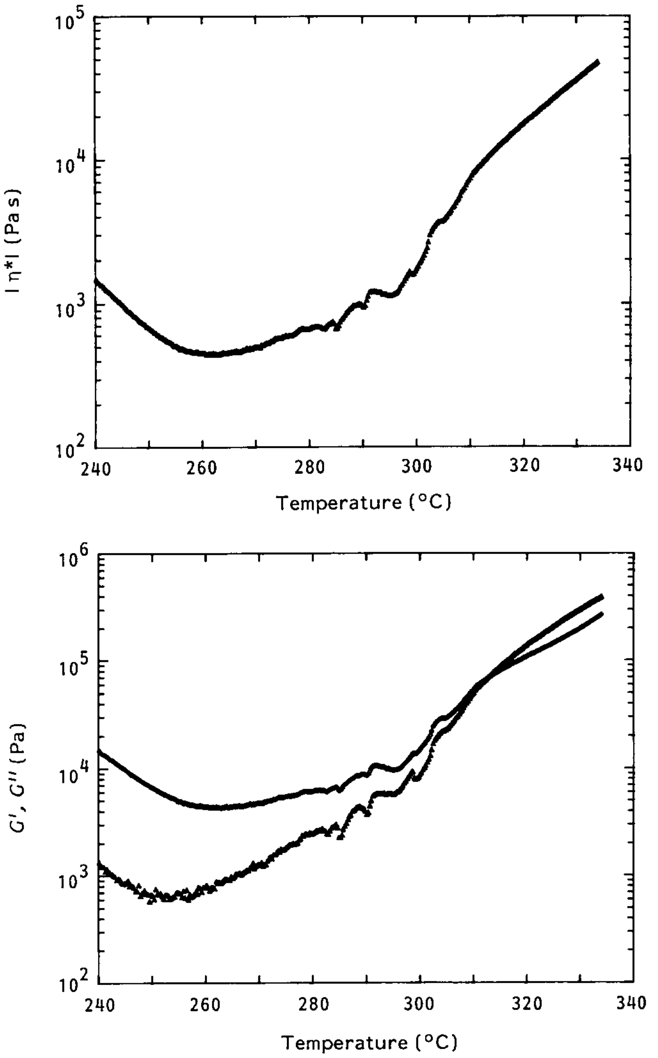

Figure 4 Rheological behaviour of the precipitated resin II-17: (a) *G'*, *G''* and $|\eta^*|$ *versus* temperature

Rheological and thermomechanical characterization

The II-17 resin from the two-step process was selected owing to its long shelf life (>120 days) and its dynamic viscosity ($\eta_d = 18\,000$ cP) suitable for processing conditions.

Rheological analysis. The rheological behaviour of the precipitated II-17 resin was studied with a Rheometrics RMS 800 viscoelasticimeter. The evolutions of G', G'' and $|\eta^*|$ *versus* temperature are presented in *Figure 4*. The resulting rheological characteristics are: $|\eta^*|$ minimum = 450 Pa s at $T = 260$°C; gel point ($G' = G''$) = 315°C with a 2°C min^{-1} heating rate.

The irregularities observed in the variations of G', G'' and $|\eta^*|$ are due to the formation of cyclopentadiene blisters in the melting product by thermal retro-Diels–Alder reaction of nadimide groups.

Film study. Films of polymerized II-17 resin were obtained following two different cure schedules: cycle 1—3 h at 100°C, 2 h at 300°C; cycle 2—3 h at 100°C, 1 h at 300°C, 1 h at 340°C. The results from the thermomechanical analysis (penetrating mode), thermogravimetric analysis and mechanical dynamic tests on the Rheovibron apparatus are listed in *Table 4*. Cure cycle 2, requiring a final step at 340°C, leads to films with a higher glass transition temperature ($T_g = 314$°C), higher thermostability and lower tan δ maximum. This behaviour could be attributed to a higher crosslinking density of the polynadimide network cured up to 340°C.

Laminate evaluation. Four-ply laminates were prepared from graphite-fibre-reinforced prepreg tape. Laminates were cured according to the following schedule: 16 h at 100°C, 1 h at 300°C, 1 h at 340°C; heating rate 1°C min^{-1}; pressure 0.5 MPa at $T = 260$°C; cooling rate 2°C min^{-1} to 150°C and natural cooling to room temperature. The final resin content of the laminate was about 35 wt%.

The dynamic mechanical behaviour was investigated on a Rheometrics RMS 800 viscoelasticimeter. *Figure 5* shows the evolutions of G', G'' and tan δ with temperature. The elastic modulus G' of four-ply laminate is 5.2 GPa at room temperature and 78% of this starting value is maintained at 300°C. No optimization of the cure schedule involving a postcure step was made. So, higher thermomechanical properties can be expected from further matrix evaluation.

CONCLUSIONS

This study concerning a thermosetting resin based on nadimide end-capped fluorinated oligomers highly

Table 4 Thermomechanical properties of films of polymerized II-17 resin

	T_g[a] (°C)	ΔP[b] at 400°C (wt%)	ΔP at 500°C (wt%)	Tan δ[c] Maximum	T_{max} (°C)
Cycle 1	306	5	22	0.10	350
Cycle 2	314	3 0[d]	17 6[d]	0.06	358

[a] T_g: glass transition temperature from t.m.a. with a 5°C min^{-1} heating rate

[b] ΔP: weight loss from t.g.a. with a 5°C min^{-1} heating rate under air atmosphere

[c] Tan δ: mechanical loss factor from Rheovibron spectrometer with a 2°C min^{-1} heating rate and 11 Hz oscillating frequency

[d] T.g.a. under argon

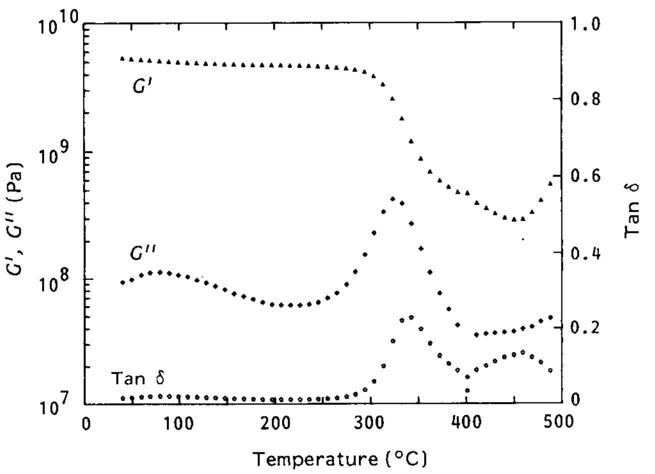

Figure 5 Viscoelastic behaviour of four-ply laminate from resin II-17: *G'* and *G''* *versus* temperature

soluble in diglyme (60 wt%) pointed out the following features:

The influence of the synthetic process—one step or two steps—on the molecular distribution of the final product and thus on the shelf life of the resin in diglyme solution.

The efficiency of the molecular-weight calculation from ^{1}H n.m.r. data in the case of nadimide end-capped oligomers containing MDA methylene groups.

The interesting potential properties of this fully imidized resin as a matrix for high-performance composites with service temperatures near to 300°C.

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