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Thermal isomerization studies of the two lowest molecular weight components of a nadimide end-capped thermoset

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SUMMARY

The mechanism of endo-exo isomerization of nadimide groups was investigated on 4,4'-methylene dianiline bis-5-norbornene-2, 3-dicarboximide (named PDO) which involves three configuration isomers and on a nadimide end-capped oligomer (PD1) both corresponding to the lowest molecular weight species of an oligobenzhydrol-imide nadimide end-capped thermoset (IP960). Isomerization kinetic versus temperature and pressure was studied by ^{1}H nuclear magnetic resonance. The results indicate that isomerization leads to a thermodynamic mixture composed of almost equal amounts of endo and exo configurations. It was also observed that thermal isomerization of PDO was possible below its melting point and that thermal isomerization under reduced pressure produced maleimide derivatives.

INTRODUCTION

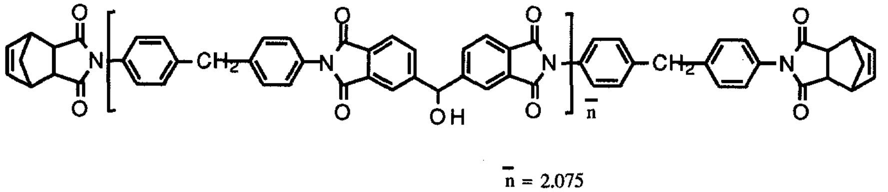
Recent years have shown an always increasing demand for polymer composite matrixes usable in high temperature applications. Nadimide end-capped polyimides such as NASA developed PMR15 and CEMOTA manufactured IP960 (a benzhydrol unit instead of a benzophenone one, shown on Scheme 1) are among the most valuable resins used in this field. Considering their synthesis, processability and bulk properties, the advantages and disadvantages of each one were previously investigated (1-3).

In other respects, a study emphasized the importance of the starting molecular distribution on the mechanical properties of the polynadimide network (4) and particularly the influence of the low molecular weight components. This paper deals with the thermal behavior of the two smallest bisnadimide species which belong to the nadimide end-capped oligomers distribution. The synthesis and the ^{1}H NMR characterization of these components (Scheme 2) are described.

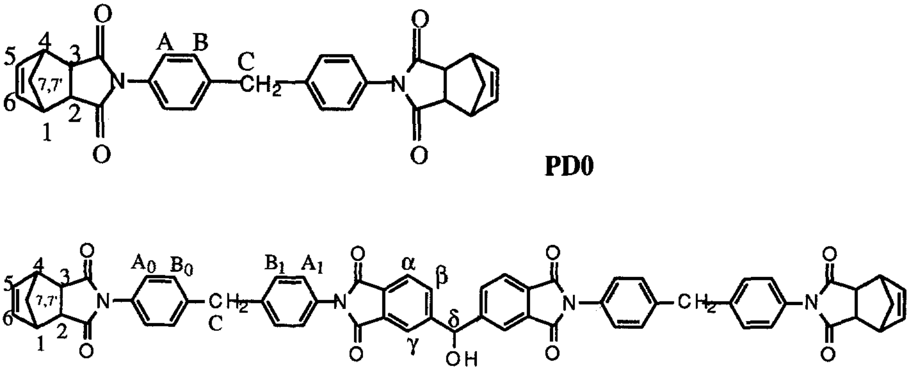
Due to the high reactivity of "nadic acid-ester" towards 4,4'-methylene dianiline (MDA), PDO is the major component of both IP960 and PMR15 resins. Its concentration can reach 50 molar% in pre-imidized PMR15 (3) and 35 molar% in IP960 oligomer mixture (4). PD1 is a model compound corresponding to an oligomer with a polymerization degree equal to 1 in the basic IP960 resin .

Several works (3,5) were devoted to the study of PDO. It was noticed that the endo-exo isomerization occurs at 260-285°C (slightly above its melting point:

244°C). It was also pointed out that polymerization occurred in the same temperature range. Later it was shown that the isomerization process could be observable as soon as 220°C (6). Moreover, drying the amorphous IP960 resin we also noticed that isomerization took place under reduced pressure at 160°C far below the glass transition temperature of the resin (Tg=180°C) (7). So a fundamental question arises: is the thermal isomerization really possible in the solid state? We investigate in details the thermal behavior of PD0 and PD1 to state precisely the pressure and temperature effects and to determine the composition and the final physical state of the isomer mixture.



Scheme 1: IP960



PD0

PD1

Scheme 2: PD0 and PD1 structures and protons labeling

EXPERIMENTAL

Synthesis of PD0: A solution 4,4'-diamino diphenylmethane (MDA, 99.13g (0.5mol) in NMP (180ml) at room temperature) is dropwise added to a stirred solution of nadic anhydride (NA, 164.16g (1.0mol) in NMP (300ml) at 50°C). The reaction mixture is maintained at 50°C for three additional hours and heated at 150°C for three hours. The final cooled solution is poured into methanol (300ml) to precipitate the PD0. The white precipitate is filtered, washed with methanol and dried under reduced pressure at 120°C for twenty hours.

Prior to use, NMP is dried over molecular sieves (0.4nm). PD0 ^1H NMR chemical shifts are given in Table 1.

Synthesis of PD1: PD1 was prepared by reacting at 130°C (7hours) in diglyme (450ml) a mixture of dimethylester of benzhydrol tetracarboxylique acid (31.90g; 0.082mol) with an excess of MDA (163.0g; 0.823mol). The resulting purified product (20.0g; 0.029mol) is then treated with two molar equivalents endo nadic anhydride (9.84g; 0.060mol) in diglyme (90ml) at 160°C for 3 hours under stirring. After work up and purification by column chromatography, PD1 was obtained with 28% yield in good purity. ^1H NMR chemical shifts are given in Table 7 (left column).

PD0 and PD1 isomerizations were conducted separately into glass tubes sealed under inert atmosphere which were put in a regulated oven for required time and temperature.

PD0 isomers separation was achieved by column chromatography on silica gel 60 (Fluka). Using a product/silica gel ratio of 1/100 and using dichloromethane followed by a mixture of 2 volume% of acetone in dichloromethane as eluents. The first eluted product was the XX isomer, followed by the NX and then the NN isomers.

The ^1H NMR spectra were run at 50°C in solution of DMSO-d_6 (2.502ppm) on a-Varian Unity Plus spectrometer operating at 500MHz.

RESULTS AND DISCUSSION

PD0 STUDY

It is now well established that upon heating endo mononadimide (8) or endo-endo bisnadimide model compounds (5) are converted into exo isomers. The synthetic PD0 which is in endo-endo (NN) configuration, heated at 210°C during 24 hours into a sealed tube led to a mixture of 3 isomers with endo-endo (NN), endo-exo (NX) and exo-exo (XX) configurations. In order to fully identify these isomers, they were separated by column chromatography on silica gel and ^1H NMR analyzed.

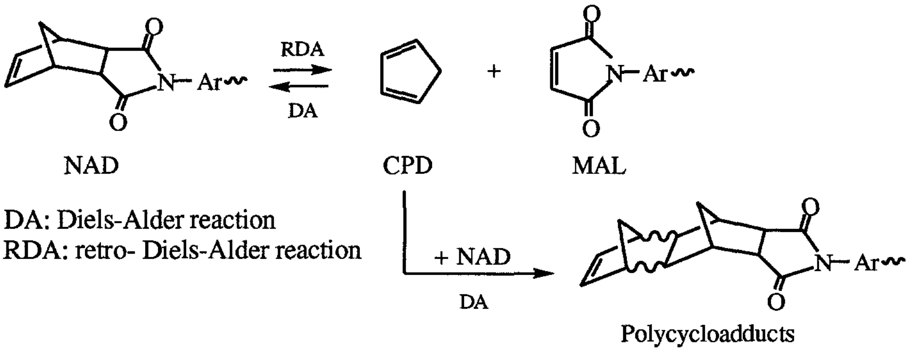
The results are given in Table 1. Chemical shifts were assigned with respect to mononadimides ones (9) and are in agreement with literature data (3,6).

Table 1 - Chemical shifts (in δ scale (ppm)) of PD0 isomers (DMSO-d_6 solution) after heating at 210°C for 24 hours.

^1H type	NN	NX		XX	Signal multiplicity
		N	X		
1,4	3.33	3.33	3.20	3.21	bs
2,3	3.46	3.47	2.84	2.84	bs
5,6	6.18^{1}	6.20^{2}	6.36^{3}	6.36^{3}	t
7,7'	1.60^{3}	1.60^{3}	1.40^{4} 1.47^{4}	1.41^{4} 1.47^{4}	2d
A	7.03^{5}	7.03^{5}	7.18^{6}	7.19^{6}	d
B	7.29^{5}	7.30^{5}	7.34^{6}	7.35^{6}	d
C	3.99	4.02		4.05	s

1) ^3J=1.8Hz 2) ^3J=1.5Hz 3) bs 4) ^2J=10.0Hz 5) ^3J=8.0Hz 6) ^3J=8.5Hz

The three isomers are mainly differentiated by the chemical shift of the CH_2 group (C) belonging to MDA unit. The other proton signals are not identical depending on endo or exo configuration, but both types of signals are present in the NX isomer, so they do not allow to determine the isomer ratio. It is worth to note that few percents of polycycloadducts (Scheme 3) are yet formed (δCH_2 at 4.00 and 4.26ppm; $\delta CH=$ at 6.02ppm) which are often interfering with the determination of the relative isomer concentration of PD0.



Scheme 3: Mechanism of polycycloadduct formation

Based on the CH2 integrations, the PDO isomerization at 210°C was determined as a function of reaction time and pressure.

a) Isomerization versus reaction time.
The results are summarized in Table 2.

Table 2 - PDO (NN) isomerization at 210°C : isomer ratio versus reaction time

Reaction time	Relative isomer percentages NN	NX	XX	7,7'/C signal ratio
0	100	0	0	2.03
2H30	73	24	3	2.00
5H	52	38	10	2.00
18H^{1}	44	44	12	2.03
20H^{1}	37	48	15	2.00
24H^{1}	32	50	18	1.93^{3}
43H^{1,2}	28	51	21	1.83^{3}
73H^{1,2}	28	49	23	1.83^{3}

1) polycycloadducts resulting from CPD reaction on nadimides are formed
2) polycycloadducts can be estimated to 4-5 molar%
3) small discrepancies to the theoretical value of 2 are due to the formation of polycycloadducts.

The proportions of NX and XX isomers are increasing with reaction time to reach the thermodynamically controlled mixture after 24 hours. The isomer ratio is approximately 30/50/20 (NN/NN/XX). If we consider that potential energy for the endo and exo configurations are very close as it was shown for mononadimide models (8), this result is very close to the expected statistical ratio (25/50/25),

Moreover we wanted to check if starting from NX and XX isomers, the same final isomer ratios were obtained (Table 3). This is roughly the case for the NX isomer but not for the XX isomer. This result can be explained on the basis of two facts:
1) the isomerization is slower for the XX isomer (as it can be anticipated from the literature (9) in the field of Diels-Alder reactions) than for the NX and NN isomers;
2) due to the possible formation of polycycloadducts, the DA/RDA equilibria are disturbed relatively to statistic. It was shown (6,10) that polycycloadducts are

mainly derived from nadimide with exo configuration. Therefore the formation of polycycloadducts is kinetically favored for NX and XX and statistically for the latter (compared to the former).

Table 3 - PD0 isomerization (210°C/24H) : isomer ratio versus the starting reactant configuration

starting material configuration	Relative isomer percentages[1] NN	NX	XX
NN	32	50	18
NX	30	51	19
XX	23	43	34

1) polycycloadducts molar concentration : <4% form NN, 5% from NX and 7% from XX (percentages are relative to the overall PD0).

b) Isomerization versus reduced pressure.

PMR type resin processing's are often including steps which are conducted under reduced pressure to remove solvents or condensation by-products (1). In other respects, the final step for the preparation of neat IP960 powder (used to produce bulk crosslinked samples consists in drying the precipitated resin under rough conditions: high temperature (160°C) and under reduced pressure (10mbar). As mentioned before isomerization takes place so we decided to study the PD0 thermal behavior under reduced pressure (Table 4).

Table 4 - PD0(NN) isomerization at 210°C under reduced pressure (10mbar) versus reaction time.

Reaction time	Relative isomer percentages NN	NX	XX	7,7'/C signal ratio
0	100	0	0	2.03
5H	63	33	4	1.78
10H	43	53	4	1.25
16H	10	66	24	0.74
22H	8	71	21	0.72
29H	7.5	69	22.5	0.67

1) C is the overall signal of central methylene group of all present species

In the last column we notice a progressive decrease in the ratio 7,7'/C proton. This indicates a cyclopentadiene loss.

Moreover, the ^1H NMR spectrum of reaction mixtures showed new signals at 7.15ppm and at 4.05ppm. The 7.15ppm resonance is characteristic of the two ethylenic protons of a maleimide function and the 4.05ppm one is attributed to the protons belonging to the corresponding MDA methylene (11).

Comparison of the loss of cyclopentadiene (estimated from the ratio 7,7'/C) correlates well with the appearance of the maleimide groups (evaluated from integration of the CH_2 signals of this structure) (Table 5).

Table 5 - Loss of cyclopentadiene versus appearance of maleimide species at 210°C under reduced pressure (10mbar) as a function of time.

Reaction time (hours)	0	5	10	16	22	29
loss of CPD(molar%)[1]	0	12	38	63	64	67
Appearance of maleimide(molar%)[2]	0	16	34	58	62	61

1)from relative integration of 7,7' protons of nadimide versus overall CH_2 signal.

2)from relative integration of CH_2 maleimide signal versus CH_2 nadimide isomers.

Under reduced pressure DA/RDA equilibria are shifted toward the RDA due to the release of gaseous cyclopentadiene (Scheme 4).

$$\text{Nadimide Endo} \rightleftarrows \text{Maleimide} + \text{CPD}\uparrow \leftrightarrows \text{Nadimide Exo}$$

Scheme 4: Displacement of equilibria toward the formation of CPD and maleimides under reduced pressure.

Therefore it appears that any drying step under reduced pressure may bring about drastic effects on the chemical structure and so on the mechanical properties of the crosslinked product.

c) Isomerization versus temperature.

The melting points of NN, NX and XX PDO isomers are respectively 244, 234 and 241°C (from DSC analysis at 10°C / minute).

The lowest melting point is 234°C for the PDO NX isomer. This temperature is higher than the previous isothermal treatment (210°C). It demonstrate that isomerization can take place even though the compound is in a solid state (12). This observation led us to study the isomerization process at temperatures below the different PDO melting points (Table 6). We determined reaction times to reach 30 molar% of exo configuration for different temperatures starting from the N-N derivative.

Table 6 - Reaction time necessary to reach 30 molar% of exo configuration[1] as a function of temperature from PDO(NN).

Temperature	190°C	200°C	210°C
Time	89H	24H	8H30

1) Relative integration of NMR signals of 7,7' protons (exo vs endo)

An increase of 10°C in temperature reduces the reaction time in the solid state of about 65%. The isomerization occurs as early as 190°C; this is a very important result because published works consider that isomerization starts from 220°C (6) and for other (5) 250°C, which is above the melting point of PDO isomers (or glass transition temperature of the bisnadimide oligomers).

PD1 STUDY

As expected, synthetic PD1 exhibits an endo-endo configuration: the ^{1}H NMR chemical shifts of the norbornene unit are very similar to the NN PD0 ones (Tables 7 and 1 left columns). For MDA moieties we observed two kinds of aromatic protons:

- the ones on the nadimide side (labeled A_0, B_0),
- the ones on the benzhydrol side (labeled A_1, B_1).

The chemical shift of the MDA methylenes is slightly displaced downfield (4.03ppm) if compared to the value of NN PD0 (3.99ppm, see Table 1).

The signals of the protons of benzhydrol unit exhibited two doublets (with a typical ortho coupling (α,β)) and a singlet (γ). These signals are enlarged due to small long range couplings (meta, para).

PD1 was isomerized at 210°C for 24 hours into a sealed tube and the crude product was ^{1}H NMR analyzed (Table 7). All the signals of the NN isomer are still present but signals of X configuration are also observed. As noticed for PD0, it is not possible to differentiate the three expected isomers (NN,NX and XX) from the chemical shifts of the norbornene units as well as from aromatic proton signals of MDA units. The MDA methylenes protons of isomerized PD1 gave only two signals: 4.03 (as observed for NN isomer) and 4.06ppm. They could be attributed to "overall" endo and exo configuration respectively, like the other signals (norbornene and MDA aromatic protons). The protons of benzhydrol unit give the same spectra for N and X forms.

Table 7 - Chemical shifts (in δ scale (ppm)) of PD1 isomers (DMSO-d_6 solution)

^{1}H type	N	X
1,4	3.33^1	3.21^1
2,3	3.48^1	2.84^1
5,6	6.21^1	6.36^1
7,7'	1.60^1	1.41^7 and 1.47^7
A_0	7.04^2	7.20^8
B_0	7.33^2	7.40^8
C	4.03^3	4.06^3
A_1	(*)7.34^4	(+)7.35^9
B_1	(*)7.36^4	(+)7.38^9
α	7.99^5	7.99^5
β	7.92^5	7.92^5
γ	8.02^1	8.02^1
δ	6.21^6	6.21^6
OH	6.60^6	6.60^6

1) broad singlet 2) d ^3J=8.0Hz3)s 4) d ^3J=8.5Hz 5)bd ^3J=7.5Hz
6) d ^3J=4.0Hz 7) d ^2J=10.5Hz 8) d ^3J=8.0Hz 9) d ^3J=8.5Hz
(*,+) assignments can be reversed; at lower field (250MHz) these signals appear as a broad singlet.

The product after thermal treatment is a mixture of endo and exo configurations in a 1/1 molar ratio.

It should be noticed that the ^{1}H NMR spectrum of PD1 isomerized for 24H at 210°C exhibits the presence of a small amount (5 molar%) of polycycloadducts. This may be attributed to the lower softening point (160°C) of amorphous PD1 compared to PD0, inducing a faster isomerization kinetics.

CONCLUSION

Thermal isomerization studies of PD0 and PD1 showed that the thermodynamically controlled product is close to a 1/1 mixture of endo and exo configurations of nadimide groups. As it could not be anticipated, the endo-exo transformation is effective far below the melting point of PD0, demonstrating the solid state activity of the isomerization process.

Under reduced pressure isothermal treatment produced maleimide end-capped molecules. This is due to retro Diels-Alder reactions which correspond to the basic mechanism of the nadimide endo/exo isomerization. Considering the composite processing, the formation of maleimide species has to be carefully considered because it may alter the thermomechanical properties of the crosslinked material (due to the relatively lower thermal stability of the polymaleimide structure) (13).

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