WAXD Evidence for a Thermally Induced Isomerization in the Crystalline State of a Nadimide End-Capped Thermoset Model Compound

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ABSTRACT: The kinetically controlled thermal isomerization of the nadimide endo to exo configuration was investigated in the solid state. Experiments were conducted on 4,4′-methylene dianiline bis-5-norbornene-2,3-dicarboximide, which is the lowest molar mass compound common to two nadimide end-capped thermosets (the well-known commercially available PMR-15 and a soluble oligobenzhydrolimide). WAXS diffractograms of isomerized moieties, recorded at increasing temperatures, lead to the conclusion that the isomerization can occur in the crystalline state, through retro-Diels−Alder and Diels−Alder reactions.

Introduction

Nadimide end groups are used in the formulation of high-temperature performance matrixes. Perhaps the most famous is the well-known NASA developed PMR-15 thermoset oligoimide leading to a heat resistant network. These polymers are already in use in the aerospace industry for application at 300 °C.[1]

Using a similar strategy, an other oligoimide containing a benzhydrol unit instead of the benzophenone one, which leads to an enhanced solubility, was synthesized a few years ago[2] (Figure 1). The thermal reaction steps of the nadimide end groups during cross-linking have already been widely investigated but still appeared to be of recent interest.[3] It has been shown that, before cross-linking, an endo−exo isomerization takes place (Figure 2) and the authors discussed the mechanism and the type of control (kinetic vs thermodynamic) occurring in this type of reaction.[4,5] Most of the experimental observations dealing with the reactivity of nadimide moieties come from studies on model compounds with or without solvent, but no definite conclusion has been reached concerning the factors controlling the reaction.[4−9]

Different teams have already investigated the thermal behavior of bis nadimides, either model or oligomers,[6,10−13] and shown that endo−exo isomerization was associated with the polymerization process. The 4,4′-methylene dianiline bis-5-norbornene-2,3-dicarboximide (abbreviated PD0, see Figure 3) was studied by our group,[14,15] and it was shown that the isomerization process is kinetically controlled. It should be noted that this model compound, which presents two nadimide groups, is the lowest molecular weight common component of PMR-15 and benzhydrolbisnadimide (BBN) imide telechelic oligoimides.

This conclusion arises from the fact that isomerization takes place, either from the endo configuration or from the exo one, at a temperature lower than the melting temperature of the molecule. The main arguments of this demonstration are summarized in the following statements:

(1) The same thermodynamical product (i.e. a mixture of endo−endo (or NN), endo−exo (or NX) and exo−exo (or XX) isomers in the approximate proportion 1/2/1) was obtained after thermal treatment at 210 °C (i.e. 20 to 34 °C away from the melting points), whether the starting molecule was the synthesized endo−endo compound (T_m = 244 °C) or the endo−exo and exo−exo isomers (T_m = 231 and 241 °C, respectively). The latter were obtained through separation by column chromatography of the isomerized endo−endo molecule.

(2) It was shown that, for the endo−endo double configuration molecules, the same reaction product was obtained when the reaction temperature ranged from 210 to 180 °C (as measured at 10 °C steps), although, as could be expected, longer reaction times were necessary at lower temperatures.

These results clearly showed the occurrence of an isomerization process in the solid state. The purpose of this work is to establish the nature of the solid state which is the host of the thermal reaction. X-ray diffraction was selected to follow the reaction in terms of changes in the solid state, as it can yield information on the crystal forms present and on the changes in amorphous vs crystalline content.

Experimental Section

Synthesis of PD0. A solution of 4,4′-diamino diphenylmethane (MDA, 99.13 g (0.5 mol) in NMP (180 mL) at room temperature) is added dropwise to a stirred solution of nadic anhydride (NA, 164.16 g (1.0 mol) in NMP (300 mL) at 50 °C). The reaction mixture is maintained at 50 °C for 3 h and heated at 150 °C for an additional 3 h. The final cooled solution is poured into methanol (300 mL) to precipitate the PD0. The white precipitate is filtered, washed with methanol, and dried under reduced pressure at 120 °C for 20 h. Prior to use, NMP is dried over molecular sieves (0.4 nm).

Isomerization of PD0. PD0 isomerizations were achieved in glass tubes sealed under inert atmosphere.

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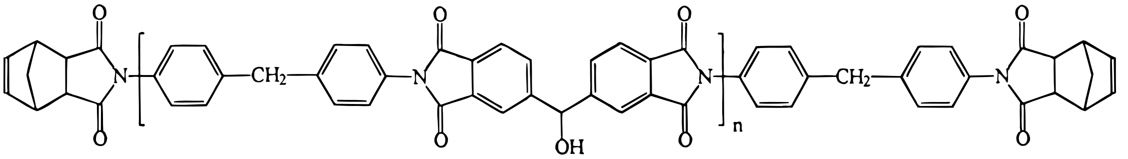

Figure 1. Soluble nadimide end-capped oligobenzhydrolimide.

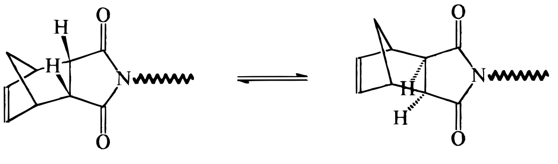

Figure 2. Endo to exo izomerization mechanism.

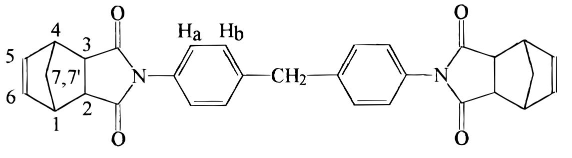

Figure 3. 4,4′-Methylene dianiline bis-5-norbornene-2,3-dicarboximide (abbreviated PD0) and ^{1}H NMR labeling.

These were placed in a regulated oven for the required time at different temperatures. All measurements were made on independent tubes and after cooling of the powders.

Obtention of pure forms. Samples of pure endo−endo and exo−exo forms have been obtained by separation on a chromatography column of the synthesized compound.

^{1}H NMR spectra were run at 50 °C in a solution of DMSO-d_6 (2.502 ppm) on a Varian Unity Plus spectrometer operating at 500 MHz. Chemical shifts are given in δ scale (ppm), Protons are labeled in Figure 3.

NN isomer: 1.60 (bs, 4H, H-7,7′); 3.33 (bs, 4H, H-5,6); 3.47 (bs, 4H, H-2,3); 3.99 (s, 2H, CH_2); 6.20 (bs, 4H, H-5,6); 7.03 (d, J = 8 Hz, 4H, Ha); 7.29 (d, J = 8 Hz, 4H, Hb).

XX isomer: 1.41−1.47 (2d, 4H, J = 10 Hz, H-7,7′); 2.84 (bs, 4H, H-2,3); 3.21 (bs, 4H, H-1,4); 4.05 (s, 2H, CH_2); 6.36 (bs, 4H, H-5,6); 7.19 (d, J = 8.5 Hz, 4H, Ha); 7.35 (d, J=8.5 Hz, 4H, Hb).

NX isomer: 1.41−1.47 (2d, 2H, J = 10 Hz, H-7,7′(X)); 1.60 (bs, 2H, H-7,7′(N)); 2.84 (bs, 2H, H-2,3(X)); 3.20 (bs, 2H, H-1,4(X)); 3.33 (bs, 2H, H-1,4(N)); 3.47 (bs, 2H, H-2,3(N)); 4.02 (s, 2H, CH_2); 6.20 (bs, 2H, H-5,6(N)); 6.36 (bs, 2H, H-5,6(X)); 7.04 (d, J = 8.5 Hz, 2H, Ha(N)); 7.18 (d, J = 8.5 Hz, 2H, Ha(X)); 7.30 (d, J = 8.5 Hz, 2H, Hb-(N)); 7.33 (d, j=8.5 Hz, 2H, Hb(N)). For this isomer, protons are labeled (N) or (X) depending on the configuration of the closest nadimide moiety.

Differential scanning calorimetry (V40B du Pont 2000) was used at 10 °C/min to determine the melting point of each pure isomer. It leads to the following values: T_m values of NN, NX, XX are respectively 244, 231, and 241 °C.

X-ray Characterization. Wide-angle X-ray diffraction (WAXD) experiments were conducted using a Rigaku RU200BH rotating anode generator at 55 kV and 190 mA. The monochromatized X-ray beam consisting of Cu Kα, Ni-filtered radiation, with a wavelength of 1.54 Å, was used for the measurements. The WAXD experiments were performed in the $\theta-2\theta$ geometry. Isomerized powders were inserted in 2 mm diameter glass capillaries for measurements.

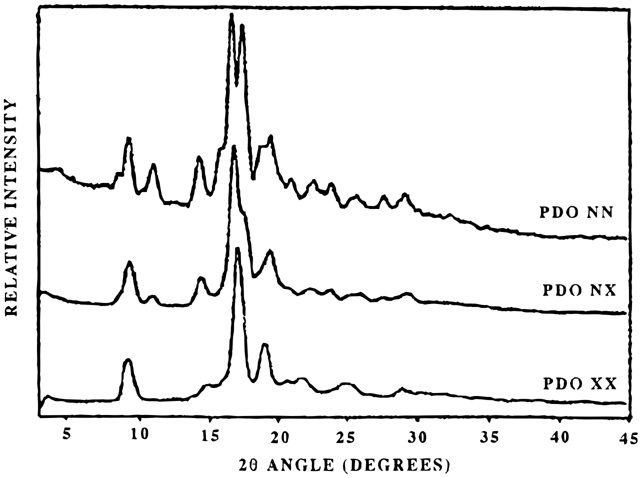

Figure 4. WAXS diffractogram of synthesized PD0 and of pure isomers.

Table 1. Thermal Isomerization of Endo−Endo PD0 (NN) at 210 °C as a Function of Reaction Time: Relative Percentages of Isomers (^{1}H NMR Analysis)

time	0	3 h	5 h	7 h	10 h 30 min	12 h 30 min	14 h 30 min	20 h	24 h
NN (%mol)	100	73	68	59	55	50	45	37	32
NX (%mol)	0	24	27	34	37	39	41	48	50
XX (%mol)	0	3	4	7	9	11	14	15	18
tot. N (%mol)	100	85	81.5	76	73.5	68.5	65.5	61	57
tot. X (%mol)	0	15	18.5	24	26.5	31.5	34.5	39	43

Results and Discussion

In Table 1 are summarized the results of PD0 isomerization at 210 °C vs time. The composition of the isomerized powders was followed using ^{1}H NMR; the proportion of the relative isomers being determined using a method was given in a previous article.[14] Percentages of NN, NX, and XX, as well as the total percentage of endo and exo, are indicated. The molar percent of NN gradually decreases, and after 24 h only 32 mol % NN remains. At the same time, the percentage of NX and, to a lesser extent, of XX slowly increases. After 24 h, half of the powder is composed of the NX molecules, whereas 18 mol % of XX is obtained. Since the melting point of the starting component, NN, is well over that of the temperature at which the reaction is performed (244 vs 210 °C), it can clearly be concluded that such an isomerization takes place below the melting point.

X-ray measurements were performed on the same batches of compounds as those for which NMR spectra had been measured. Figure 4 shows the X-ray diffractogram for the synthesized PD0 endo−endo moiety. Several well-defined diffraction peaks are observed, indicative of the crystallinity of the compound. The

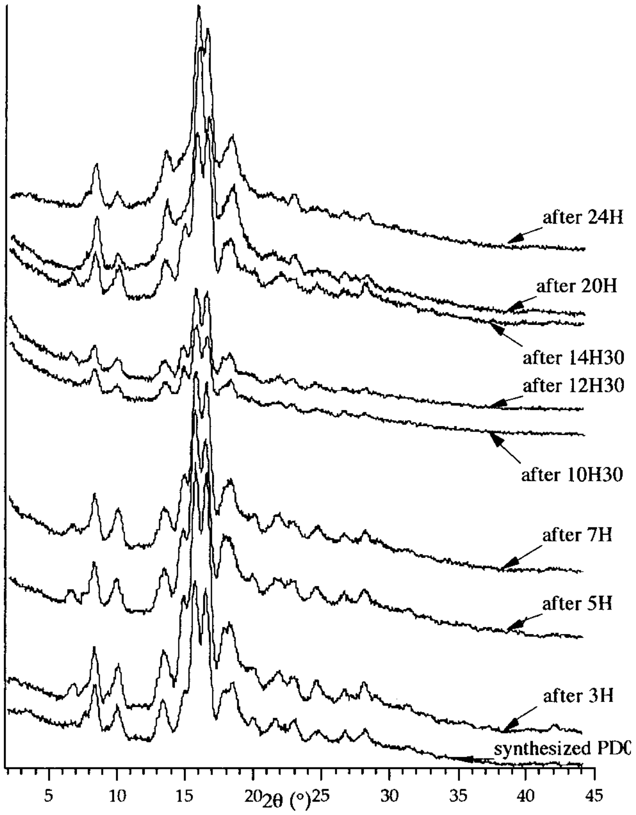

Figure 5. WAXS diffractograms of isomerized PD0 at 210 °C with aging time.

occurrence of a broad, weak scattering profile beneath the finer diffraction peaks, centered between 13 and 30°, can be associated with the presence of a small fraction of amorphous phase. Changes in the crystalline structure can be followed by X-ray diffraction.

In Figure 4 are appended the diffraction peaks of pure endo–exo and exo–exo PD0. As it can be seen, except for the disappearance of the peak located at 10.99, the peak positions are for the most part the same, the main differences being related to relative intensities of the different peaks for the three compounds. This indicates that the unit cells are very similar. In the diffraction diagram of the exo–exo compound, less peaks are observed, indicative of a higher symmetry. The major difference between this spectrum and that of the two other isomers is the occurrence of the most intense diffraction peak of this compound exactly at the midpoint of those of endo–endo and endo–exo compounds (17.11 vs 16.82 and 17.57° for endo–exo and 16.58 and 17.45° for endo–endo). Small differences in relative intensities of the peaks denote changes in the spatial distribution of the electron density, which is assigned to the change in configuration. These differences may however be difficult to detect in mixtures of endo and exo configurations. Fluctuations in intensities related to changes from one main form to the other should however clearly be observable. On the other hand, the amorphous phases connected to scattering profile decrease from NN to XX isomers.

Diffractograms of the isomerized mixture are presented in Figure 5. These are reported in increasing heating time order from bottom to top, the uppermost spectrum corresponding to 24 h heating at 210 °C. These can be separated in three main groups: from 0 to 7 h, from 10 h 30 min to 12 h 30 min and from 14 h 30 min to 24 h. Table 2 summarizes the position and the relative intensity of diffraction peaks for the three pure crystal forms.

In the first group, from 0 to 7 h, the diffractograms are relatively unchanged. The relative peak intensities remain approximately constant, indicating that the crystal structure is not modified appreciably in this time range. Within experimental error, the scattering profile between 13 and 24°, which pertains to the amorphous phase, also remains constant, indicating that no significant change in the crystallinity is occurring. However, it must be recalled that, for these samples, the isomerization after 7 h of reaction has already proceeded, and 24 mol % of exo configuration (mainly on the NX isomer) is present, as determined from ^{1}H NMR. These two observations can be conciliated if the diffractogram of the endo–exo molecules is considered. This compound is the one which will bring the major contribution to the total exo configuration (34 mol % for NX isomer vs 7 mol % for XX isomer).

The second group is composed of spectra taken at 10 h 30 min and 12 h 30 min. These differ from the previous ones mostly by a marked enhancement in the scattering profile at low diffraction angles ($2\theta < 5°$) and by a weaker intensity of the diffraction peaks. As the changes are systematic with reaction time, they cannot be due to an experimental artifact, such as those sometimes observed following an improper placement of capillary in the beam. Scattering profiles of this sort are associated with the presence of noncorrelated domains of different densities in the powder.[16] The presence of holes in the structure constitutes the most probable source of density fluctuations. The resulting lower density of the powder would also mean a lower overall intensity of the diffraction peaks, since the powders were always deposited in a similar way in 2 mm glass capillaries. Therefore, the decrease in diffraction peak intensities is not believed to be related in a decrease in crystallinity, but simply to the method of preparation of the samples.

The most probable cause of holes trapped in the powder is related to the reaction itself, due to the fact that small amounts of cyclopentadiene.[14] Diffusion of cyclopentadiene in the crystals toward defect zones or toward the amorphous phase could explain the formation of holes. Crystal breakage could also be associated with changes in local density upon cyclopentadiene diffusion. As the reaction proceeds, endo–endo unit cells, now forming smaller and smaller monocrystalline entities, could lead to defects inside bigger crystals of the major form, in which they would be embodied.

Optical microscopy was used to verify this possibility. A thin monocrystalline lamella was isomerized directly on a glass lamella at 210 °C. As expected, since the temperature remained under the melt point, the shape of the crystal was maintained. Under cross-polarized light, before reaction, the monocrystal was characterized by a complete light extinction upon rotation. After reaction, however, a mosaic of small birefringent domains of homogeneous sizes could be observed. This clearly proves that isomerization induces lamella breakage. It must be noted that the crystalline phase is favored under the experimental conditions used to isomerize, since powders were always heated under their melting point. Under these conditions, the mol-

Table 2. Position (in Two Diffraction Angles and in *d*-Spacing) and Relative Intensity of Diffraction Peaks for the Three Pure Crystal Forms

PD0 NN			PD0 NX			PD0 XX		
2θ (deg)	*d* spacing	*I*	2θ (deg)	*d* spacing	*I*	2θ (deg)	*d* spacing	*I*
8.62	10.3	5						
9.34	9.47	30	9.29	9.51	30	9.25	5.56	30
10.99	8.05	25	10.87	8.14	5			
14.23	6.22	30	14.40	6.15	20			
						14.76	6.00	10
15.85	5.60	10						
16.58	5.35	100	16.82	5.27	100			
						17.11	5.18	100
17.45	5.08	90	17.57	5.05	50			
18.78	4.72	10						
19.42	4.57	25	19.32	4.59	20	19.03	4.66	25
20.96	4.24	5	20.83	4.26	3	20.50	4.33	5
						21.67	4.10	10
22.46	3.96	5	22.13	4.02	3			
23.86	3.73	5	23.69	3.76	3			
			24.93	3.56	3	24.84	3.58	15
25.51	3.49	5						
			25.945	3.43	3			
27.55	3.24	5	27.50	3.24	3			
29.11	3.07	5	29.28	3.05	5	28.87	3.09	5

ecules should arrange themselves mostly in a stable structure i.e., the crystalline state.

In the third and last group of spectra (from 14 h 30 min to 24 h), the evolution is reversed: The intensity of the low-angle scattering profile progressively decreases, whereas the crystalline peak intensities progressively increase and tend toward a maximum. This clearly indicates that the maximum cyclopentadiene production stage is over and that the samples are now close to equilibrium.

Changes in relative intensities of the crystalline peaks are also evident. Peaks at 10.99, 14.23, and 16.58° have decreased significantly in intensity. When comparing the diffraction profiles of the spectra to those of the pure compounds, it is clear that the exo-endo structure has become the major crystalline phase. A small amount of the more symmetrical exo–exo form may also be present, but this is much more difficult to verify, especially since at the end of the reaction only 18 mol % exo–exo is present.

This new crystalline phase is forming compact entities in the polycrystalline powder. The scattering profile recovers its initial aspect since holes in the structure, initiated by reorganization of endo–endo crystals, have collapsed. It was verified that this phenomenon could not be associated with melting followed by crystallization during isomerization: samples were taken from the reaction and immediately dipped into liquid nitrogen to freeze in the structures. The resulting diffractograms presented the same features as the ones recorded after a slow cooling. Therefore, isomerization in the crystal phase must occur.

X-ray diffraction data on single crystals would be necessary to determine the exact packing adopted by the molecules in these three cases, but unfortunately no crystal suitable for X-ray structure determination were obtained. Nevertheless, the fact that the unit cell dimensions and structures appear, from the comparison of the diffraction diagrams of the stereoisomers, to be very similar, so it can be proposed that thermal transformation from the endo–endo form to the endo–exo or exo–exo forms does not encompass an energetical barrier related to a change in crystalline form and that passing by an intermediate amorphous phase is not essential.

The thermal isomerization process of nadimide groups in the solid state can therefore be described using three main steps:

During the first step, between 0 and 7 h at 210 °C, the diffractograms are not significantly changed, the major crystalline phase present is that of the endo–endo compound, and reaction occurs in a homogeneous crystalline state,

During the second step, perturbations in the diffractogram at 10 h 30 min at 210 °C indicate the appearance intensity fluctuations, which are associated with defects and holes in the crystals, are related to limited cyclopentadiene production and molecular rearrangements.

During the third step, the major crystalline phase clearly evolved to endo–exo, and defects are eliminated from the structures as witnessed by the reversible evolution of the low-angle scattering profile.

Conclusion

From the evolution of the X-ray diffractograms recorded during an endo to exo thermal isomerization performed at a temperature below the melting point, it can be concluded that the reaction occurs in the crystalline phase. Three distinct steps have been identified. The first proceeds without disruption of the crystalline phases. In the second, crystalline defects such as holes become important, although the overall crystallinity is maintained. In the final stage, the crystal form of the major structure slightly changes, and holes disappear from the structures.

Numerous examples of $[2 + 2]\pi$ photochemical reactions have been reported in the crystalline phase.[17] However, the present study is, to the best of our knowledge, the first to report a thermally induced $[4 + 2]\pi$ Diels–Alder reaction in the crystalline phase as well as for the reverse Diels–Alder reaction. Orbital control during these two solid-state reactions is probably their only common factor, since it is well-known that photochemical reactions in the crystalline state are fast and present well defined transition states and intermediates. The present thermal reaction, on the other hand, takes a longer time to reach equilibrium, and no intermediate was yet formally identified. A point that remains to be clarified is the influence of crystal defects on the reaction. For this, a single-crystal structure of the endo–endo molecule determination is essential. A possible solid-state reaction mechanism could then be proposed via modeling, and the possibility that cyclopentadiene fragments diffuse in the crystalline lattice could be evaluated. Unfortunately, as mentioned earlier, no crystals suitable for X-ray structure determination have been obtained.

The present model compounds investigation is also interesting in terms of oligomer reactivity. It has been noticed that isomerization of 100 mol % endo-synthesized oligobenzhydrolimide could be obtained during the drying period at 160 °C (20 deg lower than the T_g of the oligomer), to yield a 1:1 configuration ratio. This clearly indicates that the oligomer can react in the solid state. Consequences of this observation with be discussed in a forthcoming paper.[18]

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