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Fluorine-19 NMR monitored thermal imidization of bicyclo[2.2.2]oct-7-ene systems

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Abstract

Fluorine-19 NMR analyses allowed to obtain kinetic data about bicyclo[2.2.2]oct-7-ene dianhydrides thermal imidization. It was evidenced that the high reactivity of such a substrate is owing to the combined effects of bifunctionality and ethenylene bridge. This latter effect is inhibited by the presence of an electron-withdrawing group on the double bond. A basic solvent (NMP) does favor the amic acid intermediate formation; an acidic solvent (*m*-cresol) does accelerate the amic acid cyclization to imide. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Imidization reaction; Bicyclo[2.2.2]octene bisanhydride; Reactivity parameters

1. Introduction

The color of aromatic polyimides owing to electronic conjugation or to charge complex transfer [1] is a drawback for some electronic and optoelectronic applications.

In order to reduce chain conjugation, different approaches were checked, by either using aliphatic diamines [2] or alicyclic dianhydrides [3]. Gel formations were observed when aliphatic diamines were used and in this case specific methods were required to obtain polyimide solution. Whereas alicyclic anhydrides allow the same synthetic procedures to be currently adopted with aromatic dianhydrides.

Matsumoto et al. [4,5] and Chun [6,7] described the synthesis and properties of some polyimides derived from: bicyclo[2.2.2]octene-2,3,5,6-tetracarboxylic dianhydride (BCODA), bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride (BCODA-sat) and bicyclo[2.2.2]heptane-2,3,5,6-tetracarboxylic dianhydride (BCHDA). The authors observed the highest reactivity for BCHDA and explained it by the highest energy strain of the bicycloheptane system.

In a previous work [8] we obtained some BCODA derived polyimides through a Diels–Alder reaction between bismaleimide and bisdihydrophtalimide and very interesting optical properties were observed for the materials (UV cut-off at 350 nm). But as polycondensation using BCODA is the easiest method to obtain the same polymers, we tried to understand the different factors governing this dianhydride reactivity towards aromatic amines (Fig. 1).

This work was conducted using different anhydrides (Table 1) allowing to take the cyclic system nature, the simple or double anhydride structure and the olefinic or saturated nature of the bridge into account. Kinetic comparison was performed with 4-fluoroaniline (4-FA) through ^{19}F NMR analysis [9] in usual polycondensation solvents (NMP, *m*-cresol).

2. Experimental

2.1. Materials

Prior to use 4-Fluoroaniline (Fluka) was distilled under reduced pressure. Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (Aldrich) was recrystallized from acetonitrile. *Cis*-cyclohexane-1,2-dicarboxylic anhydride (Acros) was recrystallized into acetic anhydride. *Cis*-1,2,3,6-tetrahydrophthalic anhydride (Acros) and bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (Acros) were only dried under vacuum (80°C, 5 h). Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride was

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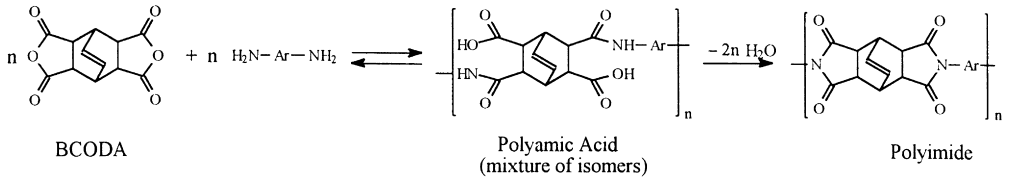


Fig. 1. Polycondensation: polyimide formation via polyamic acid intermediate.

obtained from Prof. Matsumoto [3]; it was a 70/30 mixture of *exo–exo* and *exo–endo* isomers and was dried under vacuum (80°C, 5 h). Bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic 2,3:5,6-dianhydride-7-acid (BCODA-Ac), 7-methylester of bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic 2,3:5,6-dianhydride (BCODA-Es) and 7-(4′-methoxyphenylene)ester of bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic 2,3:5,6-dianhydride (BCODA-HEs) were synthesized by Diels–Alder reactions at 170°C–200°C for 3 h between maleic anhydride in excess and corresponding coumalic acid derivatives. Anhydrides were stored under anhydrous atmosphere (dessicator). High quality *N*-methyl pyrrolidone (NMP) and *m*-cresol were stored over molecular sieves (0.3 nm).

2.2. Instrumentation

Proton and carbon-13 nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC 250 instrument operating at 250 and 62.9 MHz respectively using dimethylsulfoxide (DMSO-d_6) as solvent. Reported chemical shifts are given in δ scale and in ppm relative to tetramethylsilane (TMS) used as an internal standard. Fluorine-19 NMR spectra were recorded on a Bruker DR 400 instrument operating at 376.4 MHz and using NMP as the sample solvent, unless otherwise noted. All reported chemical shifts are given in δ scale and in ppm relative to fluoroform; they were determined using 4-fluoroaniline as internal standard, whose chemical shift is $-$ 129.48 ppm relative to fluoroform. Such an internal standard allowed to explore a small spectral width ($-$ 98 to $-$ 148 ppm) in order to obtain a good spectrum resolution. An 80° pulse was applied every 4.5 s. An internal lock was used by inserting a capillary tube containing a lock solvent (DMSO-d_6) into the 5 mm NMR tube containing the dissolved sample. The use of an internal lock solvent and an internal standard allows the analyses to be carried out in uncontaminated NMP mixtures. Unless otherwise noted, 7% (weight/weight) solutions were used and all spectra were proton decoupled. All coupling constants are given in Hz.

2.3. Kinetic monitoring

2.3.1. Anhydride reactivities

The anhydride (0.5 mmol for monoanhydride and 0.25 mmol for dianhydride) is dissolved in NMP (1.5 ml) upon heating. After cooling to room temperature, 4-FA (0.6 mmol) is added (the excess is used to calibrate the chemical shift scale all along the kinetic study). The reaction mixture is then poured into the NMR tube which is immediately introduced into the spectrometer probe. The spectrometer was programmed to run periodically a spectrum at predetermined temperatures in order to follow in situ, first the addition of 4-FA to anhydride and then the amic acid cyclization step.

2.3.2. Solvent effects

BCODA (0.25 mmol) is dissolved either into *m*-cresol or NMP (9 ml).

2.4. Imide preparation

Imides were prepared by stirring the appropriate amine and anhydride mixtures in NMP (92 wt%) at 150°C under nitrogen atmosphere. Reaction time is indicated for each compound. After cooling at room temperature, the black homogeneous reaction mixtures were poured into ice-cold water. The precipitates were filtered, washed with water and vacuum dried at 85°C. Yields were almost quantitative.

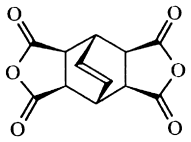
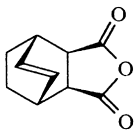
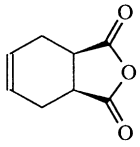
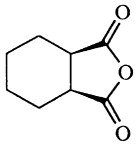
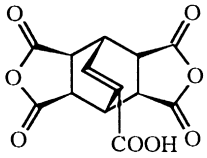
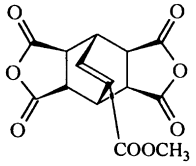
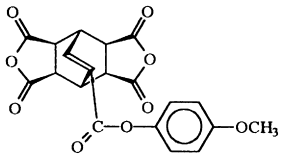
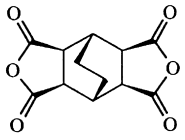
2.4.1. Exo-N-(4′-fluoro)phenyl-bicyclo[2.2.2]oct-5-ene-2,3-dicarboximide (Fig. 2)

Reaction time: 19 h (m.p.: 193°C–195°C). NMR ^{1}H(250 MHz) (DMSO-d_6): 1.26 and 1.64 (2*dl*, ^2J = 7, 2 × 2H, $H_{a,a'}$); 3.03(*bs*, 2H, H_b); 3.05(*bs*, 2H, H_d); 6.19(*bs*, 2H, H_c); 7.0 – 7.3 (*m*, 4H, $H_{g,h}$). NMR ^{13}C (62.9 MHz) (DMSO-d_6): 23.3(2C, C_a); 31.7 (2C, C_b); 43.9 (2C, C_d); 116.0 ($^2J_{CF}$ = 23, 2C, C_h); 128.6 ($^4J_{CF}$ = 3, 1C, C_f); 129.1 ($^3J_{CF}$ = 9, 2C, C_g); 132.5 (2C, C_c); 161.5($^1J_{CF}$ = 245, 1C, C_i); 178.1 (2C, C_e). NMR ^{19}F (376 MHz): $-$ 112.1. Elemental analysis $C_{16}H_{14}FNO_2$: calculated C: 70.84%; H: 5.20%; N: 5.16%; F: 7.00%; O: 11.80%. Found C: 69.62%; H: 5.25%; N: 5.65%; F: 6.97%.

2.4.2. Exo–exo-bis[N-(4′-fluoro)phenyl]-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxydiimide (Fig. 3)

Reaction time: 7 h (m.p.: 313°C–315°C). NMR ^{1}H (250 MHz) (DMSO-d_6): 3.33 (*bs*, 4H, H_c); 3.51 (*bs*, 2H, H_a); 6.30 (*bs*, 2H, H_b); 7.1–7.4 (*m*, 8H, $H_{f,g}$). NMR ^{13}C (62.9 MHz) (DMSO-d_6): 34.1 (2C, C_a); 42.6 (4C, C_c); 116.1 ($^2J_{CF}$ = 22, 4C, C_g); 128.4 ($^4J_{CF}$ = 3, 2C, C_e); 129.2($^3J_{CF}$ = 9, 4C, C_f); 131.2(2C, C_b); 161.6 ($^1J_{CF}$ = 246,

Table 1
Structures of studied anhydrides

Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCODA) (*exo–exo*)	
Bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (BOA) (*exo* towards the double bond bridge)	
Cis-1,2,3,6-tetrahydrophtalic anhydride (THPA)	
Cis-cyclohexane-1,2-dicarboxylic anhydride (CDA)	
Bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic-2,3:5,6-dianhydride-7-acid (BCODA-Ac) (*exo–exo*)	
7-Methylester of bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic-2,3:5,6-dianhydride (BCODA-Es) (*exo–exo*)	
7-(4′-Methoxyphenylene)ester of bicyclo[2.2.2]oct-7-ene-2,3,5,6,7-pentacarboxylic-2,3:5,6-dianhydride (BCODA-HEs) (*exo–exo*)	
Bicyclo[2.2.2]octane-2,3,5,6-tetracarboxylic dianhydride (BCODA-Sat) (*exo–exo*)	

2C, C_h); 176.9 (4C, C_d). NMR ^{19}F (376 MHz): − 112.7. Elemental analysis $C_{24}H_{16}F_2N_2O_4$: calculated C: 66.36%; H: 3.71%; N: 6.45%; F: 8.74%; O: 14.73%. Found C: 65.78%; H: 3.63%; N: 6.68%; F: 8.53%.

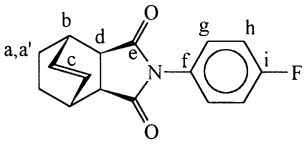


Fig. 2. *Exo-N*-(4′-fluoro)phenyl-bicyclo[2.2.2]oct-5-ene-2,3-dicarboximide structure.

2.4.3. Cis-N-(4′-fluoro)phenyl-1,2-cyclohexanedicarboximide (Fig. 4)

Reaction time: 45 h (m.p.: 150°–152°C). NMR ^1H (250 MHz) (DMSO-d_6): 1.3–1.5 and 1.7–1.8 (2*m*, 2 × 2H, $H_{a,a',b,b'}$); 3.1–3.2 (*m*, 2H, H_c); 7.3–7.4 (*m*, 4H, $H_{f,g}$). NMR ^{13}C (62.9 MHz) (DMSO-d_6): 21.6 (2C, C_a*); 23.5 (2C, C_b*); 39.4 (2C, C_c); 115.9 ($^2J_{CF}$ = 23, 2C, C_g); 128.9 (1C, C_e); 129.4 ($^3J_{CF}$ = 8, 2C, C_f); 161.5 ($^1J_{CF}$ = 245, 1C, C_h); 178.7 (2C, C_d). * assignments can be reversed. NMR ^{19}F (376 MHz): − 112.3. Elemental analysis $C_{14}H_{14}FNO_2$: calculated C: 68.00%; H: 5.71%; N: 5.66%; F: 7.68%; O: 12.94%. Found C: 68.02%; H: 5.81%; N: 5.87%; F: 7.64%.

2.4.4. Cis-N-(4′-fluoro)phenyl-1,2,3,6-tetrahydrophtalimide (Fig. 5)

Reaction time: 64 h (m.p.: 131°C–132°C). NMR ^1H (250 MHz) (DMSO-d_6): 2.27 and 2.43 (2*bd*, ^2J = 15, 2 × 2H, $H_{b,b'}$); 3.2–3.3 (*m*, 2H, H_c); 5.9–6.0 (*m*, 2H, H_a); 7.2–7.3 (*m*, 4H, $H_{f,g}$). NMR ^{13}C (62.9 MHz) (DMSO-d_6): 23.4 (2C, C_b); 38.9 (2C, C_c); 116.0 ($^2J_{CF}$ = 22, 2C, C_g); 127.9 (2C, C_a); 128.8 (1C, C_e); 129.2 ($^3J_{CF}$ = 9, 2C, C_f); 161.5 ($^1J_{CF}$ = 245, 1C, C_h); 179.4 (2C, C_d). NMR ^{19}F (376 MHz): − 112.8. Elemental analysis $C_{14}H_{12}FNO_2$: calculated C: 68.56%; H: 4.93%; N: 5.71%; F: 7.75%; O: 13.05%. Found C: 68.34%; H: 4.99%; N: 6.06%; F: 7.79%.

3. Results

3.1. Kinetical data achieving

The analytical data are based on relative integrations of ^{19}F NMR resonances measured as a function of the 4-fluoroaniline conversion to amic acid and then to imide (Table 2).

4-FA was selected for this study to follow the kinetic controlled product formation through ^{19}F NMR analyses. If ^1H decoupled, the ^{19}F resonance of any kind of formed product from 4-FA will be a single line signal (singlet). The ^{19}F NMR is a good tool allowing straight reaction solution

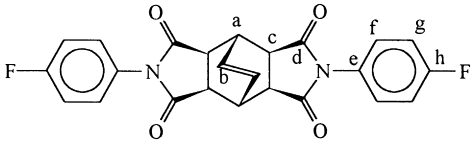


Fig. 3. *Exo–exo*-bis[*N*-(4′-fluoro)phenyl]bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxydiimide structure.

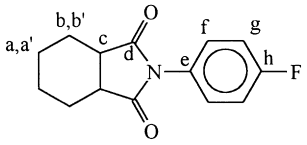


Fig. 4. *Cis-N*-(4′-fluoro)phenyl-1,2-cyclohexanedicarboximide structure.

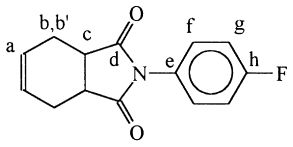


Fig. 5. *Cis-N*-(4′-fluoro)phenyl-1,2,3,6-tetrahydrophtalimide structure.

analyses without interference with the solvent NMR resonances (if not fluorinated). Thus kinetic studies were conducted in usual polycondensation solvents (NMP, *m*-cresol) directly in the NMR spectrometer.

4-FA was used in excess so it can act as an internal standard for NMR analyses.

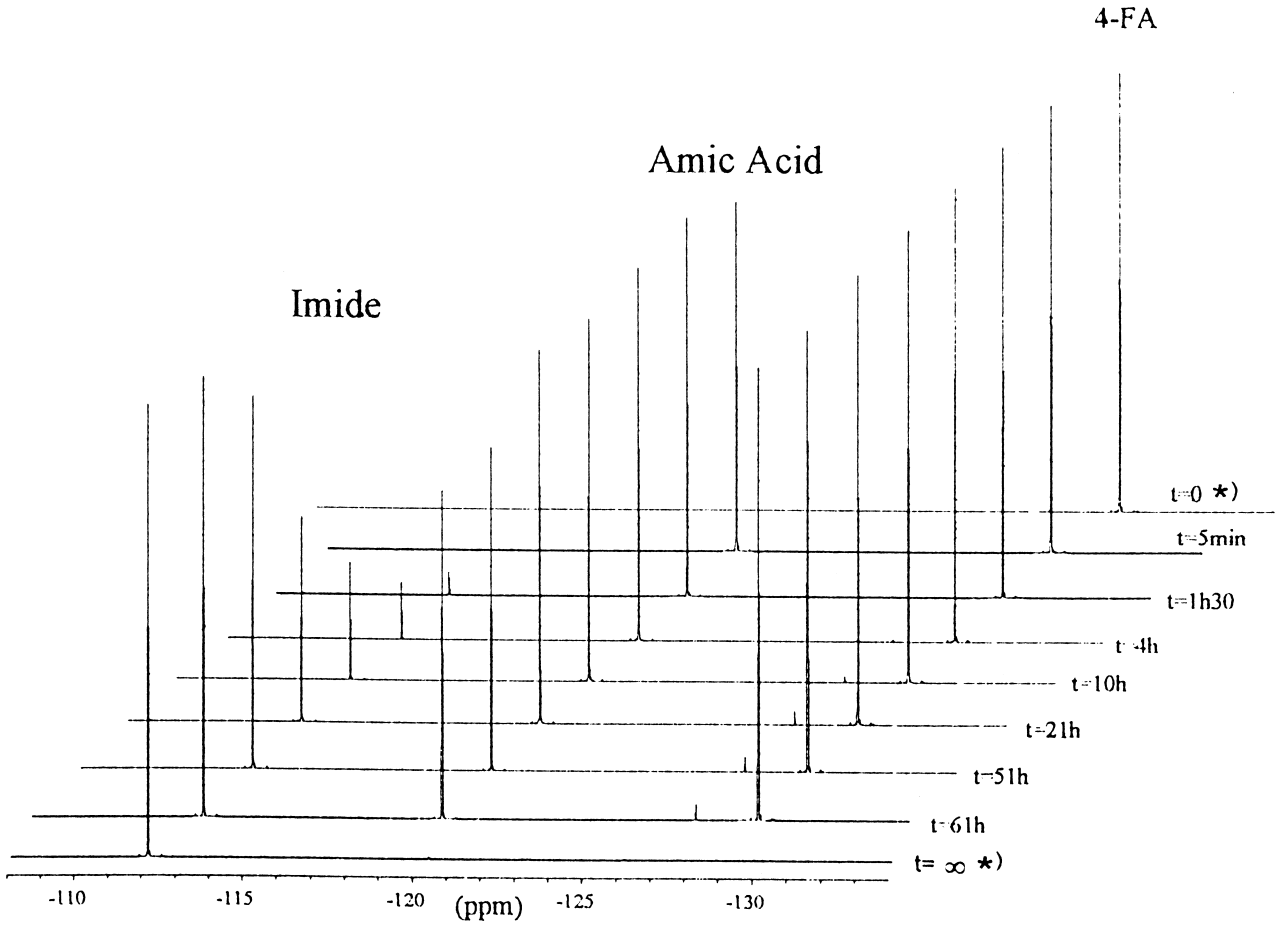
Table 2
^{19}F chemical shifts of species implied in the imidization of 4-FA

	^{19}F chemical shifts (ppm)
4-Fluoroaniline	− 129
4-Fluoroanilinamic acids	− 120[a], − 121/ − 119[b]
4-Fluoroaniline imides	− 112[a], − 113.5/ − 111.5[c]

[a] Only one resonance signal with monoanhydrides.
[b] Many resonance signals with *exo–exo* dianhydrides owing to the formation of intermediates.
[c] Only one resonance signal for the *exo–exo* bisimide.

^{19}F NMR analyses as a function of the time of BOA reaction with 4-FA at 66°C in NMP are shown in Fig. 6 and as it can be seen the reaction goes slowly enough to allow the observation that the amic acid intermediate and its disappearance leading to the final imide.

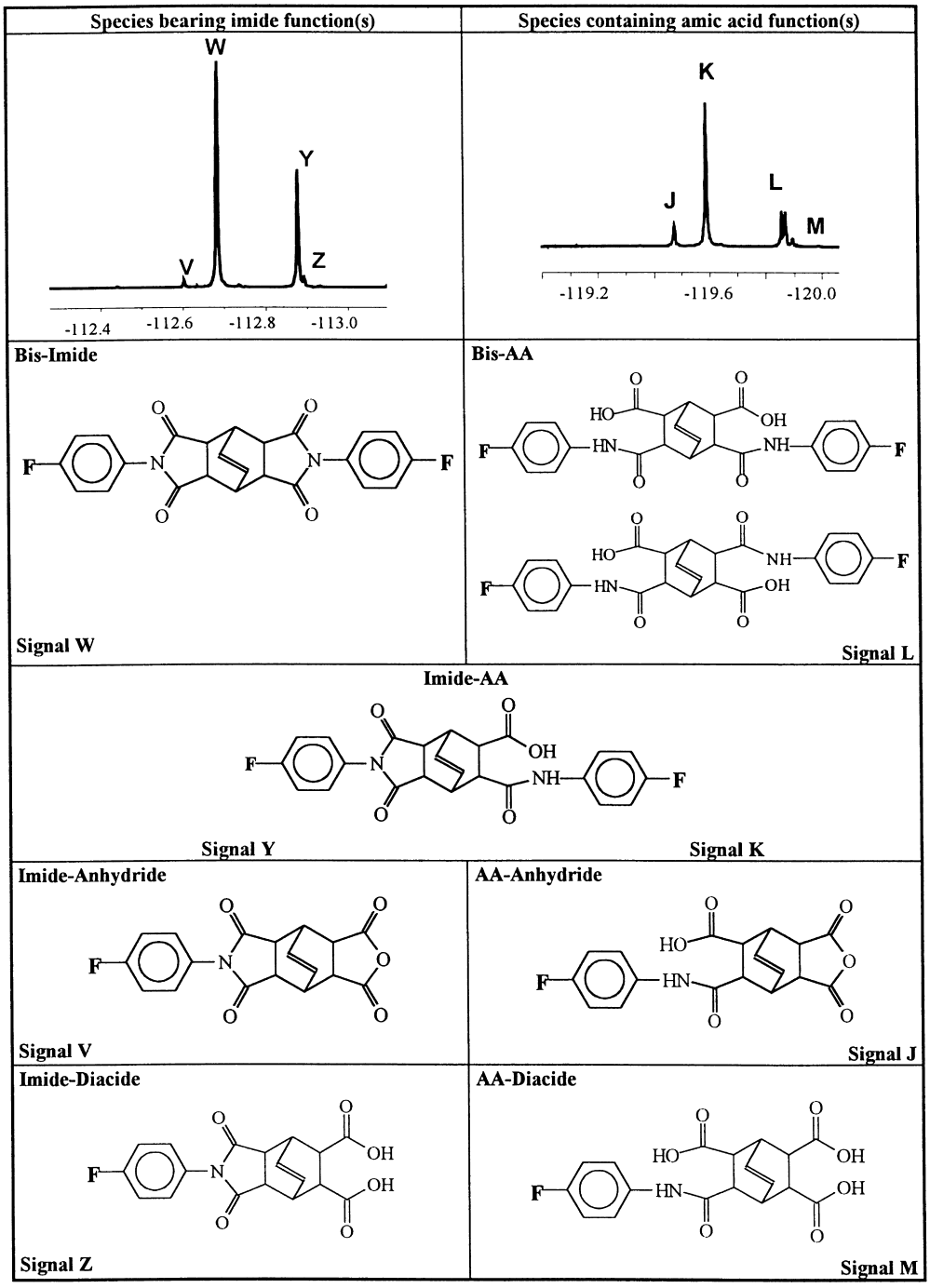
The reaction of a bisanhydride such as BCODA or BCODA-Sat gives a most complex spectrum owing to the formation of different kinds of intermediates as shown in Table 3 for the BCODA reaction.



*) spectrum for t=0 and t=∞ are issued of analyses independently of the kinetic measurements

Fig. 6. ^{19}F chemical shift changes as a function of time during the reaction of BOA with 4-FA at 66°C in NMP.

Table 3
^{19}F chemical shifts assignments of fluorinated species formed during the reaction of BCODA with 4-FA



The two-line signal L is one of the first appearing; it is assigned to two isomeric forms of the bis-amic acid (Bis-AA). After 2 h at 66°C, this signal intensity decreases in favor of two other signals of equal intensity K and Y; they were assigned to an entity bearing an amic acid function on one side of the molecule (K) and an imide one on the other side (Y). By the end of the reaction the only remaining signal is W which is owing to bis-imide. Four small resonances J, M, V and Z were also observed; they were assigned as indicated in Table 3.

For any kind of substrate it was possible to quantify the imide functionality relative amounts (^{19}F resonance located between −111.5 and −113.5 ppm) and the amic acid one (^{19}F resonance located between −119 and −121 ppm) as well as the unreacted 4-FA (containing introduced excess).

Table 4
Calculated strain energy release for amic acid formation obtained from the Chem D Pro (4.0) software (Cambridge Soft)

Anhydrides	Potential strain energy[a]			ΔE[b]
	Anhydride	Monoamic acid	Diamic acid	
CDA	28.7	− 2.8	—	− 31.5
BOA	34.6	12.0	—	− 22.6
BCODA	53.2	37.6	20,0	− 33.2
BCODA-sat NN	61.2	*	*	*
NX	56.3	*	*	*
XX	55.9	31.4	14.4	− 41.5

[a] Arbitrary relative units.
[b] ΔE = amic acid energy − anhydride energy.

According to Matsumoto et al. (for NMR characterization [2] of bis anhydrides BCODA-sat), experimental data show that XX and NX isomers react at about the same rate for both amic acid formation and imide cyclization.

The quantitative estimate of the first reaction step advancement was done from the relative integrations of ^{19}F NMR signals by using Eq. (1) corresponding to the consumed 4-FA or otherwise the percentage of reacted anhydride.

$$\frac{\sum \text{Imide} + \sum \text{AA}}{\sum \text{All fluorinated species}} \times (100 + \%4 - \text{FA excess}). \quad (1)$$

For the second reaction step advancement estimation we used Eq. (2) which allows to quantify the imide formed from amic acids.

$$\frac{\sum \text{Imide}}{\sum \text{Imide} + \sum \text{AA}} \times 100. \quad (2)$$

Table 5
Calculated strain energy for imide formation obtained from the Chem 3D Pro (4.0) software (Cambridge Soft)

Anhydrides	Potential strain energy[a]		ΔE[b]
	Amic acids	Imides	
BOA	12.0	19.5	7.5
BCODA	20.0	20.9	0.9
BCODA-sat XX	14.4	23.3	8.9

[a] Arbitary relative units.
[b] ΔE = imide strain energy − amic acid strain energy.

4. Discussion

4.1. Reaction at room temperature: amic acid formation

The conversion levels at room temperature of 4-FA reacting with BCODA, BCODA-Sat, CDA and BOA as a function of time are shown in Fig. 7.

These behaviors can be explained considering the strain energy liberated by opening the anhydride ring of the different products. The Chem D Pro software (Cambridge Soft) allows to calculate the most stable conformation of an organic system and Table 4 shows the calculated minimal potential energy for each anhydride and for the corresponding amic acid after reaction with aniline. The energy difference ΔE between the potential energy of the amic acid and the one of the anhydride is the liberated strain energy in an arbitrary unit. So to the highest negative ΔE value corresponds the highest anhydride reactivity. These results are in agreement with the experimental curves.

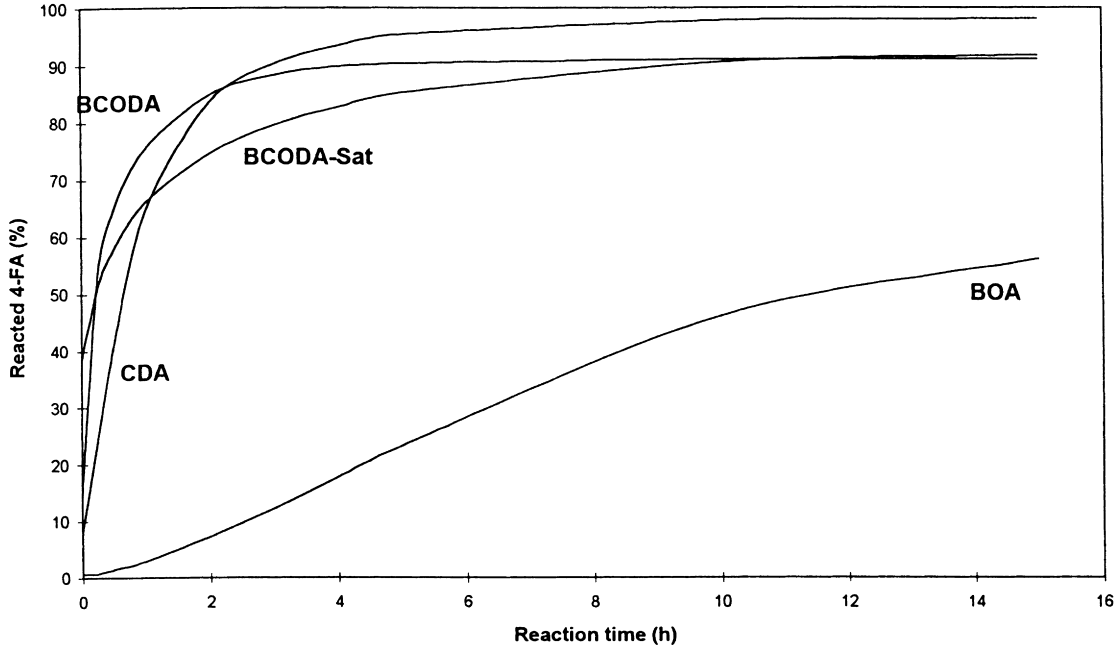


Fig. 7. Reacted 4-FA versus reaction time with some anhydrides (in NMP, at room temperature).

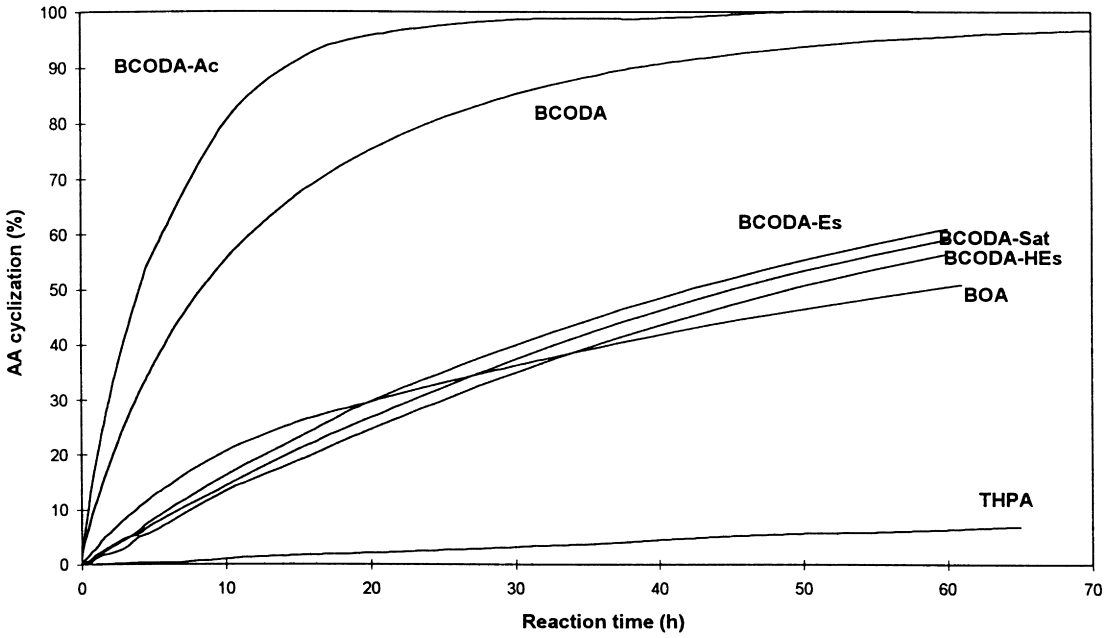


Fig. 8. Cyclization of amic acids to imides versus reaction time (in NMP, at 66°C).

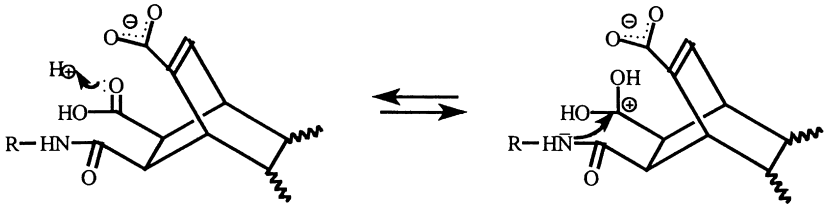


Fig. 9. Possible prototropy for BCODA-Ac amic acid.

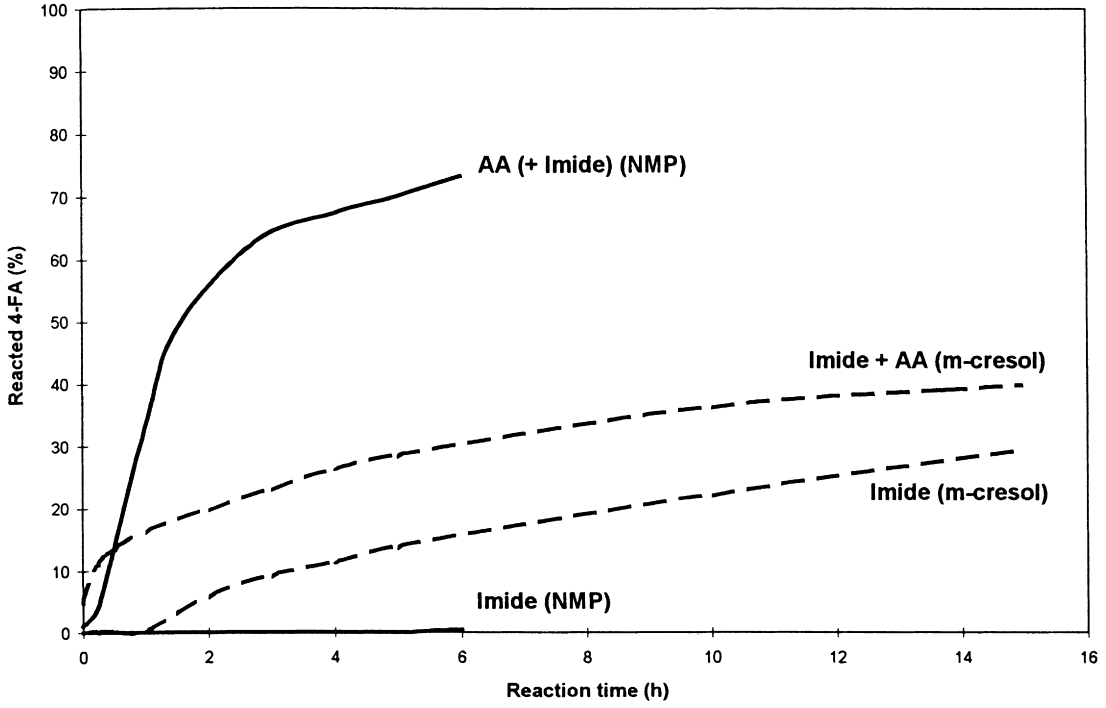


Fig. 10. Relative formation of amic acids and imides from BCODA and 4-FA as a function of reaction time at room temperature in NMP and *m*-cresol.

4.2. Reaction at 66°C: imide formation

At 66°C we took the formation of the imide ring from amic acids into account, according to the Eq. (2).

The comparison after 10 h reaction shows the highest conversion for BCODA-Ac (80%) followed by BCODA (50%); BCODA-Es, BCODA-HEs, BCODA-Sat and BOA react very slowly (Fig. 8).

First, it is interesting to compare BCODA, BCODA-Sat and BOA. By using the same Chem D software, we calculated the energy differences between the amide acids and the corresponding imides (Table 5). In that case, the energy difference ΔE is positive, which means that the imides are more strained than the amic acids. It can be seen in Table 5 that the lowest ΔE is observed for the BCODA diimide, in agreement with the experimental results. In contrast the presence of a carboxylic group (BCODA-Ac) enhances reactivity. A possible explanation could be a prototropy between the two carboxylic groups of the amic acid intermediate (Fig. 9). Thus the electrophilicity increase of the carbon atom undergoing the nucleophilic attack facilitates the imide ring formation.

4.3. Solvent effect

Various solvent effects have already been observed. The imidization reaction rates seem correlated with the reaction solvent acidity or basicity [10–13]. The model reaction of BCODA and 4-FA was studied in NMP and *m*-cresol. Owing to the lower solubility of amic acids and imides in *m*-cresol, reactions were conducted at room temperature with the same low concentration (0.25 mmol/9 ml) for both solvents and monitored by ^{19}F NMR measurements. Eqs. (1) and (2) were used to determine the two reaction steps. The results of this solvent study are shown in Fig. 10. From this diagram, it is seen that amic acid formation is facilitated by using a NMP medium but imide formation does not occur. The use of *m*-cresol as a solvent induces an almost equal rate for both reaction steps.

The amic acid formation is therefore favored by an aprotic solvent and the imide formation by an acidic solvent.

5. Conclusion

The high reactivity of BCODA toward imidization reaction is mainly owing to the combined effect of its bisanhydride functionality and to the presence of a double bond in the bicyclo[2.2.2] substrate. This activation is particularly effective in the reaction cyclization step which is rate determining for the overall reaction. Calculations of strain energy modifications during the processes are in agreement with the observed reactivities.

Electron withdrawing substituent, such as ester group, positioned on the double bond decreases the cyclization reaction rate. Conversely, a carboxylic acid substituent accelerates the cyclization step. Monoanhydrides are less reactive than bisanhydride whatever the substrate structure is.

The reaction rate is solvent dependent:

- the amic acid formation is favored by NMP, and
- the cyclization of amic acid to imide is faster in *m*-cresol.

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