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Application of ^{19}F -NMR Toward Chemistry of Imide Materials in Solution

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17.1. INTRODUCTION

Polyimides have become attractive materials for many applications demanding high-performance qualities of thermal, oxidative, and chemical resistance.¹⁻⁶ Since the discovery of a facile two-step synthetic method for the preparation of aromatic polyimides (PI) almost 30 years ago, concern has persisted regarding several unquantified variables associated with the chemistry of these polymers. The main reason for this concern has been the inability to distinguish among all of the possible species present in the reaction system (see Figure 17.1). Thermal or chemical conversion of the amic acid precursor results in a complex mixture of many different chemical species. Anhydride and amine starting materials may reappear owing to amic acid equilibration and/or hydrolysis. Imide and isoimide groups may begin forming with the liberation of water. Additionally, the anhydride formed can hydrolyze to the acid compound in the presence of liberated water, which can eventually recyclize at sufficiently high temperatures and again react with the free amine groups present. Figure 17.1 is in fact oversimplified in that all of the pathways illustrated are actually occurring on two sides of the macro-molecular species, resulting in, e.g., half-imides/half-amic-acids. Moreover,

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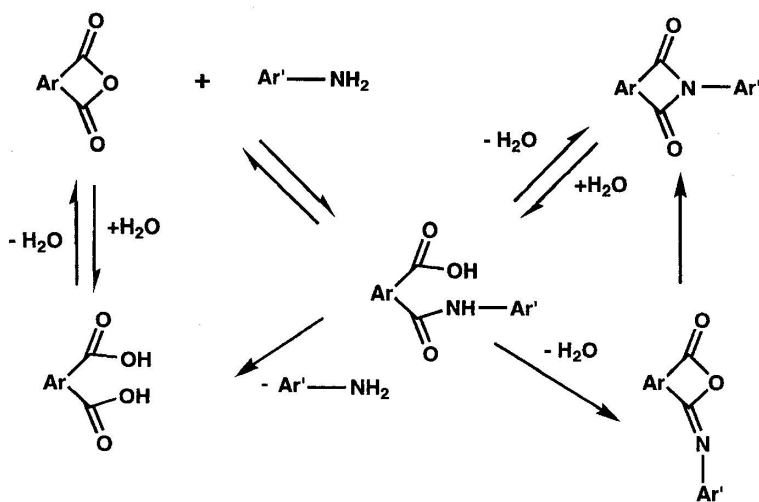


Figure 17.1. Possible reactions and equilibria for imide formation and/or degradation.

isomeric species with the linked dianhydrides can display different reactivities in any of the reactions shown in Figure 17.1.

Several techniques have proved valuable in providing a better understanding of the chemical transformations taking place during imidization. The main tool available presently utilized for spectroscopically determining chemical species present in a poly(amic acid) (PAA) or PI reaction system is FTIR.⁷⁻⁹ By the careful use of FTIR, one can analyze the formation of anhydride or imide groups and follow the imidization process; however, much discrepancy has centered on the choice of observed FTIR bands and the effects of side reactions, solvent, and other variables. Another tool available for imide and amic acid studies is UV spectroscopy.¹⁰ Recently, employment of UV-vis absorption and fluorescence spectroscopy has shown the advantageous ability to follow several types of intermediates in the imidization process.¹¹⁻¹⁵ Other promising analytical tools include potentiometric titration for calculating imidization conversion¹⁶ and HPLC.¹⁷ Perhaps the most promising technique, which has yet to find routine applications in the study of amic acid and imide chemistry, has been nuclear magnetic resonance (NMR) techniques.¹⁸⁻²⁵ Reasons for its limited usage include complex spectra for amic acids, spectral interference owing to presence of solvents, uncertainties of peak identification, and limited solubility of polyimides; however, the amic acid redistribution or equilibrium reactions have been studied using this technique.²⁶ A novel ¹⁵N-NMR solid state technique for the study of amic acid curing in the solid state, as well as its application to imide hydrolysis, has recently been described.²⁷

The goal of this research was to shed further light on the solution chemistry of amic acid and imide materials using ^{19}F -NMR. Several immediate advantages of this technique were obvious in advance. Studies could be performed in any solvent desired, with no spectral interference from the solvents. Industry has demonstrated a preference for *N*-methylpyrrolidinone (NMP) as a solvent for PAA and, in the case of soluble PIs, for the final polymer. Utilization of an external lock solvent and fluorinated standards would allow the investigations to be carried out in an “uncontaminated” NMP setting.

^{19}F -NMR is a high sensitivity technique (80–90% sensitivity of ^1H -NMR), where chemical shifts depend, at least to a large degree, on the chemical environment of the fluorine atoms.²⁸ Although utilized in numerous studies, perhaps most notably in Taft’s well-known work relating resonance and inductive effects in *p*- and *m*-substituted fluorobenzenes, respectively,^{29,30} surprisingly little has been published regarding the use of this technique for the study of reaction mechanisms or pathways. Other studies have confirmed that ^{19}F -NMR is uniquely suited for the study of isomer formation and other structural information for nitrogen substituted fluorobenzenes.^{31–33} Using it as a tool for structure confirmation, some workers have reported ^{19}F -NMR spectra of perfluorinated polyimides.³⁴ Thus the fluorine atom can be viewed as “a distant but sensitive observer removed from the confusion of the chemical battlefield by the rigid benzene ring.”²⁹ We felt that by the careful selection of fluorinated aromatic model compounds and reaction conditions, amic acid equilibration and/or hydrolysis, imide hydrolysis, and other possible side reactions could be identified. This chapter summarizes model compound behavior and applications of this technique, such as amic acid isomer distributions and imide solution hydrolysis.

17.2. EXPERIMENTAL SECTION

17.2.1. Instrumentation

^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC 250MHz instrument utilizing DMSO-d_6 as solvent. Reported chemical shifts were referenced to TMS. Calculated ^{13}C -NMR chemical shifts were obtained by applying standard shift additivity rules and other data from simple models and from the literature.^{35–41} ^{19}F -NMR spectra were recorded on a Bruker AC 200 MHz instrument operating at 188 MHz using NMP as a sample solvent. All chemical shifts were referenced to CFCI_3 . An external lock solvent (C_6D_6) was utilized by inserting a 4-mm NMR tube containing the sample dissolved in NMP into a 5-mm NMR tube containing a few drops of lock solvent. In all cases, a 90° (3.0- μs) pulse was applied 32 times with a delay of 2 s. Unless

otherwise noted, 2% (wt/wt) solutions were utilized for study. Spin-spin coupling constants are given in Hz; $^1J(\text{C}, \text{F})$ is normally taken to be a negative value.⁴²

17.2.2. Materials

All anhydride and amine compounds were of the highest quality commercially available. Aniline (AN) was distilled under reduced pressure; phthalic anhydride (PA) was sublimed and stored under anhydrous conditions. High-quality NMP (BASF) was stored over molecular sieves. All other reagents were used as received from commercial sources as follows: 4-fluoroaniline (4-FA) (99%, Aldrich Chemical Co.), 3-fluorophthalic anhydride (3-FPA) (Fluorochem Ltd.), 2,2-bis(3,4-carboxyphenyl)hexafluoropropane dianhydride (6FDA) (monomer grade, Hoechst), 2,2-bis(4-aminophenyl)hexafluoropropane (6FDM) (99%, Chriskev Co., Inc.), 1,1'-bis(3,4-carboxyphenyl) sulfone dianhydride (SDA) (99%, Chriskev Co., Inc.), 1,1'-oxydiphthalic anhydride (ODPA) (Occidental Chemical Co.), (4-aminophenyl)phenyl ether and 4-aminophenylbenzophenone (Aldrich Chemical Co.).

Amic acids (AA) were prepared by two different methods. Stirring appropriate mixtures of amine and anhydride overnight in NMP yielded solutions of the desired amic acid suitable for ^{19}F -NMR studies. In order to discern a crude isomer composition, ^{13}C -NMR was performed on compounds prepared by a literature procedure utilizing chloroform as a solvent.⁴³ This technique gave very high yields of very high-purity monoamic acid as the materials precipitated from the reaction mixture.

Synthesis of many of the imide model compounds has been described previously.⁴⁴⁻⁴⁶ ^{13}C -NMR data for compounds described here for the first time are summarized in Table 17.1. Those carbon atoms not numbered on the 4-FA part of the amic acid model compounds occurred at approximately the same chemical shifts regardless of the nature of the anhydride residue.

17.3. RESULTS AND DISCUSSION

17.3.1. Model Compound Studies

We have previously discussed many types of fluorinated imide model compounds.⁴⁴⁻⁴⁶ Figures 17.2 and 17.3 illustrate the ^{19}F -NMR of two pertinent series of materials based on 6FDA and 4-fluoroaniline, respectively. These spectra will be referenced throughout this chapter and will thus be discussed briefly below.

Table 17.1. ^{13}C -NMR Chemical Shifts for a Series of 4-Fluoroaniline-Based Model Amino Acids Prepared and Isolated from Chloroform (Isomer Formed in Excess Denoted by *)

Carbon No.	I		II				
	Chemical shift found (calculated)		Chemical shift found (calculated)				
	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{H}^a$	$\text{R}_1 = \text{NO}_2;$ $\text{R}_2 = \text{H}^b$	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{H}^*$	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{NO}_2$	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{Br}^*$	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{CH}_3^*$	$\text{R}_1 = \text{H};$ $\text{R}_2 = \text{C}(\text{CH}_3)_3^*$
1	138.9 (139.8)	116.8 (117.1)	n/o (125.3)	131.5 (131.0)	132.4 (131.7)	130.5 (130.0)	130.0 (129.7)
2	128.0 (128.0)	159.6 (164.5)	n/o (149.7)	124.7 (124.9)	132.1 (132.9)	130.1 (130.4)	126.4 (126.3)
3	131.9 (131.9)	118.3 (116.5)	n/o (124.7)	147.8 (149.5)	122.6 (123.7)	139.3 (138.7)	152.3 (151.6)
4	129.6 (129.5)	131.8 (133.5)	n/o (132.8)	126.8 (127.1)	134.6 (135.1)	132.2 (132.6)	128.8 (128.5)
5	129.7 (129.7)	123.8 (123.6)	n/o (133.8)	129.9 (128.9)	130.2 (129.6)	128.0 (127.9)	127.9 (127.6)
6	130.1 (130.1)	137.6 (141.4)	n/o (140.7)	144.0 (145.6)	137.7 (138.2)	136.2 (136.7)	136.4 (136.7)
	138.9 (139.8)	127.3 (126.8)	135.0 (132.9)	139.3 (140.7)	140.7 (141.4)	139.5 (139.7)	139.1 (139.4)
	128.0 (128.0)	158.8 (162.8)	148.0 (147.3)	122.9 (123.2)	130.7 (131.2)	128.5 (128.7)	124.7 (124.6)
	131.9 (131.9)	119.9 (118.9)	127.1 (127.8)	148.8 (151.9)	125.5 (126.2)	142.4 (141.1)	155.0 (154.0)
	129.6 (129.5)	131.0 (131.1)	130.4 (130.6)	124.6 (124.7)	132.6 (132.7)	130.0 ^c (130.2)	126.2 (126.1)
	129.7 (129.7)	126.1 (125.3)	135.5 (135.5)	131.2 (130.6)	131.9 (131.3)	130.0 ^c (129.6)	129.9 (129.3)
	130.1 (130.1)	131.2 (131.7)	131.0 (132.0)	136.6 (135.9)	129.3 (128.5)	127.0 (127.0)	127.1 (127.0)

^a For phthalic anhydride based compound, no isomeric forms possible.

^b For 3-nitrophthalic anhydride, only isomer II formed.

^c Assignments possibly reversed.

17.3.1.1. Models Based on 2,2-Bis(3,4-Carboxyphenyl)Hexafluoropropane Dianhydride (6FDA)

Four 6FDA related compounds were studied. The dianhydride (6FDA), tetracarboxylic acid (6FDA TA) and aniline-based diamic acid (6FDA/AN DAA), and diimide (6FDA/AN) were prepared and their respective ^{19}F -NMR spectra measured (Figure 17.2). Each model, with the exception of diamic acid, displayed one signal, with the chemical shift moving upfield as those groups on the aryl rings became more polar in nature. One benefit of this technique is the ability to quantify the amounts of the three possible isomeric amic acid structures. Data from our ^{13}C -NMR measurements and from current literature²⁵ suggest formation of the *p*-isomer in excess of the *m*-isomer, presumably owing to the higher electrophilicity of the carbonyl group para to the 6F group. For the diamic acid model prepared in NMP at 2 wt% solids, the percentage of the three isomers from downfield to upfield was 14 (*m,m*): 39(*m,p*): 47(*p,p*), corresponding to 33% meta and 67% para isomeric proportions.

17.3.1.2. Models Based on 4-Fluoroaniline (4-FA)

A series of four models related to 4-fluoroaniline was studied. The amine (4-FA) and the phthalic anhydride-based amic acid (4-FA/PA AA), imide (4-FA/PA), and isoimide (4-FA/PA II) were prepared and studied by ^{19}F -NMR as illustrated in Figure 17.3. Well-separated chemical shifts were observed for this set of model compounds; a range of about 16 ppm between the amine and the imide was found. The chemical shift for each compound moved upfield as the group para to it became more electron-releasing in character. Decoupling of the fluorine signal from the aryl protons simplified each spectrum from a nonet (triplet of triplets, see Figure 17.3b and c) to a singlet (Figure 17.3a and d). The transmission of polar changes through bonds capable of transferring electron density (e.g., ether or in this case amide) resulting in large ^{19}F -NMR shifts for aryl fluoride compounds has been noted before.^{32,33}

Such a large chemical shift range for these models compared to the 6F model compounds was expected based on the electronic nature of the bonds through which electron density (as measured by ^{19}F -NMR chemical shift changes) was being measured. For the 6F compounds, electron density is changing on the aryl carbon atom attached to the hexafluoroisopropyl group; however no mechanism for the transfer of π -electron density (the major contributor to ^{19}F -NMR chemical shift changes) to the fluorine atoms is available. Thus only polar or inductive changes can be observed for the 6FDA system. On the other hand, for the 4-FA compounds, it is well known that ^{19}F -NMR is a very sensitive tool for directly measuring electronic density changes brought about primarily by resonance

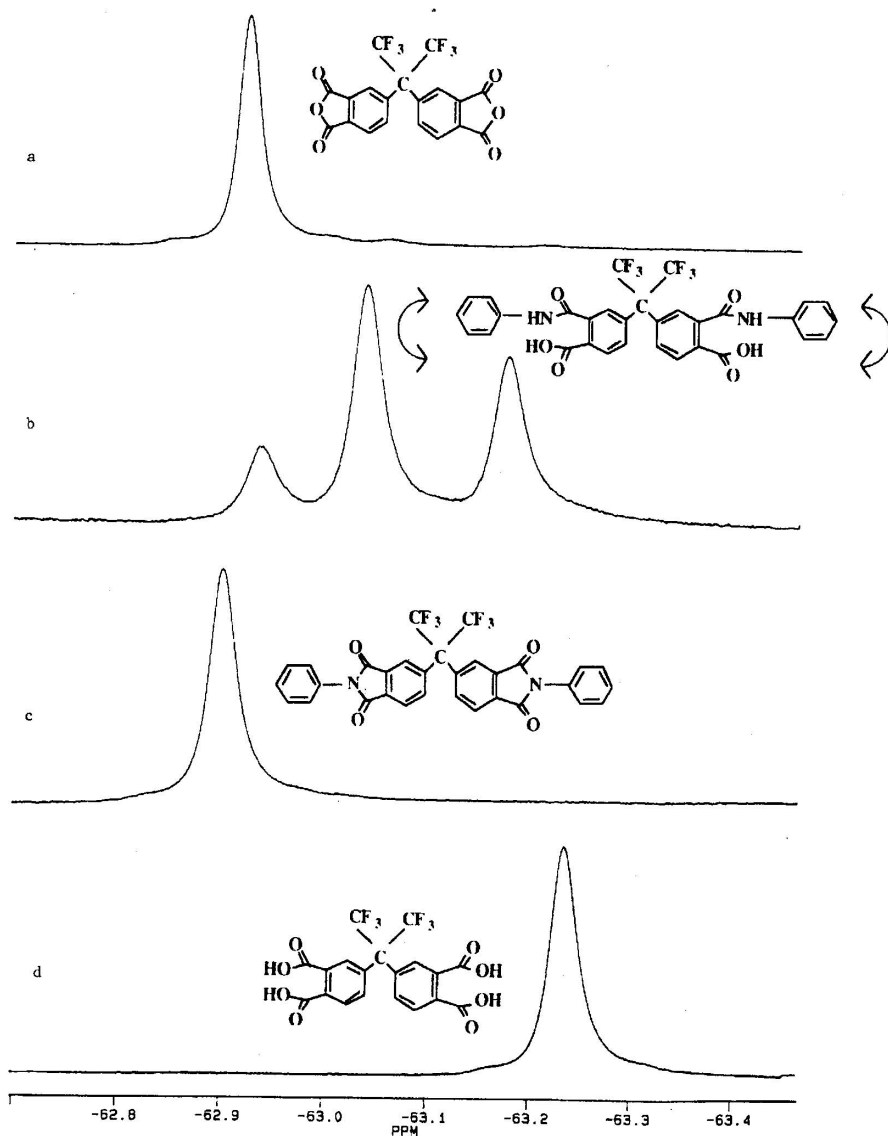


Figure 17.2. ^{19}F -NMR spectra of 6FDA based model compounds: (a) 6FDA; (b) 6FDA/AN DAA; (c) 6FDA/AN, and (d) 6FDA TA (Reprinted from C. D. Smith *et al.*, *Polymer* 34, 4852–4862. Copyright (1993), with kind permission from Elsevier Science, Ltd., The Boulevard, Langford Lane, Killington OX5 1GB, UK).

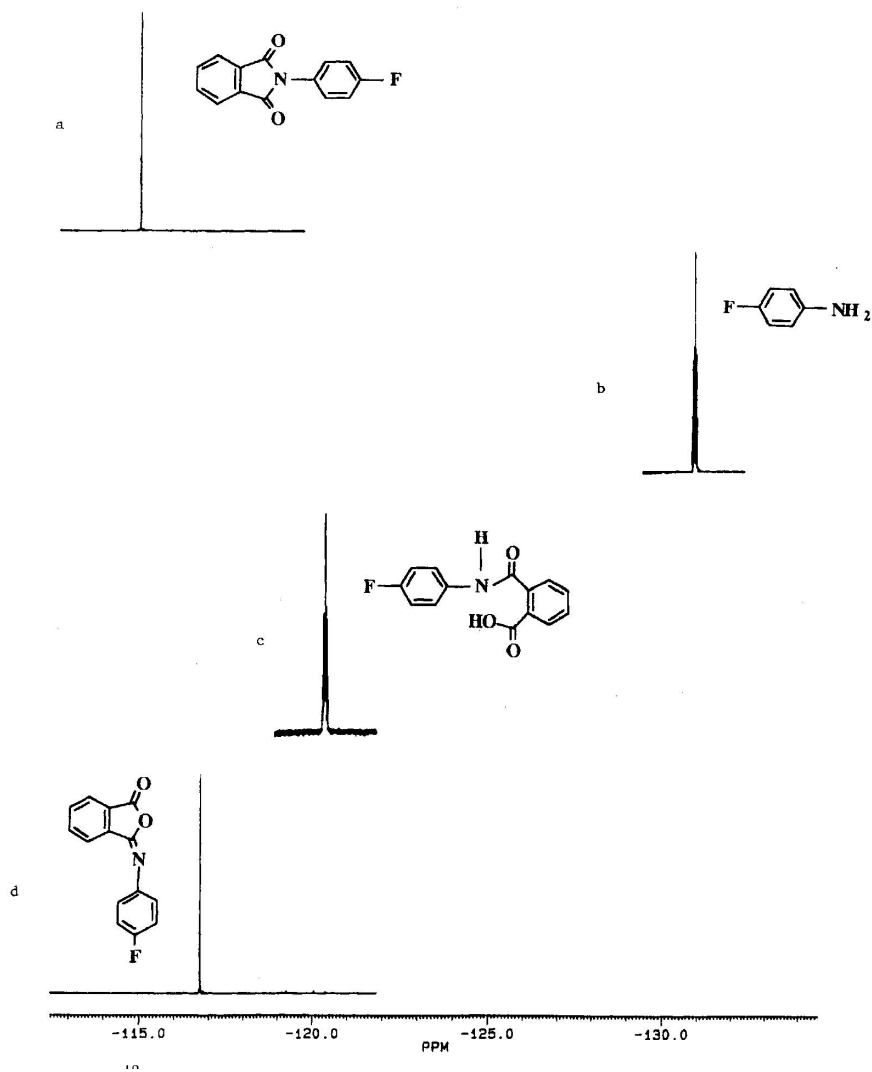


Figure 17.3. ^{19}F -NMR spectra of 4-FA based model compounds: (a) 4-FA/PA; (b) 4-FA; (c) 4-FA/PA AA and (d) 4-FA/PA II (Reprinted from C. D. Smith *et al.*, *Polymer* 34, 4852–4862. Copyright (1993), with kind permission from Elsevier Science, Ltd., The Boulevard, Langford Lane, Killington OX5 1GB, UK).

effects for para-substituted fluorobenzenes, resulting in a broad array of ^{19}F -NMR chemical shift values.²⁹

17.3.2. Applications of ^{19}F -NMR to Imide and Amic Acid Technology

Several phenomena unique to imide and amic acid chemistry are well suited for study by ^{19}F -NMR. Several representative applications are described below.

17.3.2.1. Amic Acid Isomer Formation

When a substituted anhydride or dianhydride is reacted with an amine (or diamine in the case of polyimides), two or three isomeric species can be formed, respectively. In order to study the formation of different isomers and the factors that affect isomer distribution, several researchers have studied amic acid formation by both NMR techniques^{17–23,25} and chromatography.¹⁷ Quantitative analysis of such compositions is difficult by conventional ^{13}C -NMR alone because of the complexity of the spectra. Thus, isomer analysis is typically measured by ^{13}C -NMR peak height measurements, not a particularly satisfying technique. While it has proven valuable for identifying the major isomer present in two isomer mixtures, only in certain cases has ^{13}C -NMR proved suitable for quantifying three isomer compositions, owing to the extreme complexity of the spectra.²⁶

(a) *Model Monoamic Acids.* In order to obtain a basic level of understanding regarding the formation of amic acid isomers, a series of 4-fluoroaniline-based model compounds was prepared and analyzed by both ^{13}C -NMR and ^{19}F -NMR. The use of ^{13}C -NMR concurrently with ^{19}F -NMR can yield much information regarding amic acid chemistry, while neither technique alone can quantify and identify each isomeric product in this case. Though ^{19}F -NMR can normally quantify the species formed, it cannot identify the chemical structure of each isomer. An additional advantage of using these two NMR techniques together was the value of investigating solvent effects on isomer formation.

Initially, a series of monoamic acids was prepared in chloroform from substituted phthalic anhydrides and 4-fluoroaniline (Figure 17.4). These syntheses resulted in nearly quantitative yields of crystalline amic acids, which precipitated from the chloroform solvent when cooled. The ^{13}C -spectra were measured on these compounds; Table 17.1 summarizes the data and indicates in each case which isomer was preferentially formed in chloroform from similar carbon peak heights. Most of the results followed the expected trend; as the electron-withdrawing capability of any substituent increased, the carbon with which that substituent could interact by resonance became more electrophilic and was subsequently attacked preferentially by 4-FA. For example, in 4-nitrophthalic

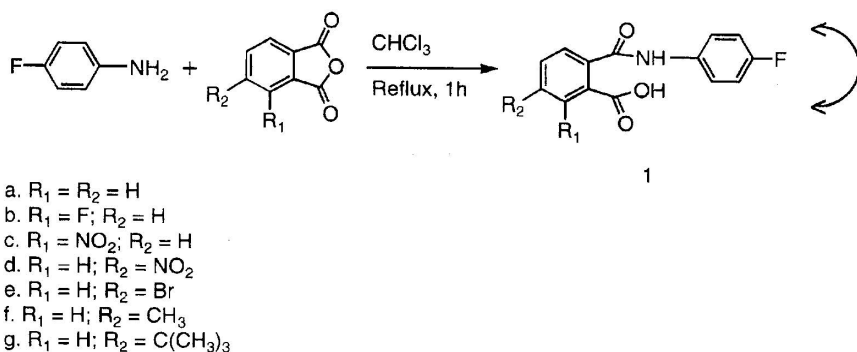


Figure 17.4. Syntheses of monoamic acid model compounds. The double arrow represents the two possible isomers.

anhydride, the carbonyl group para to the strongly electron-withdrawing nitro group is more electrophilic than the carbonyl group meta to the nitro group. Thus, the para isomer of **1d** is more likely to be formed, and indeed this was observed. For inductively electron-donating groups (i.e., methyl **1f**, *t*-butyl **1g**), the meta isomer was slightly favored. Surprisingly, for the 3-nitrophthalic anhydride (**1c**), only ortho attack was observed owing to the very strong directing power of the ortho-substituted nitro group.

For nonquantitative ^{13}C -NMR techniques, this could be the extent of the analysis possible. However, the combination of ^{19}F -NMR with ^{13}C -NMR allowed us to quantitatively calculate the isomer composition and to investigate solvent effects on isomer formation. Figure 17.5 illustrates these concepts. Two possible isomers (structures in Figure 17.5) can be formed from the reaction of 3-fluorophthalic anhydride with 4-fluoroaniline. Upon formation of the amic acid based on 3-fluorophthalic anhydride with 4-fluoroaniline, two isomers were found in both NMP and chloroform reactions as shown by the ^{19}F -NMR spectra in Figure 17.5a and b, respectively. Two signals were observed for each type of fluorine atom, labeled as F_1 and F_2 for the anhydride and amine fluorine atoms respectively. Ortho and meta isomers were formed in a ratio of 4.75 : 1 in solution in NMP, while the same ratio was 1.04 : 1 in chloroform, where the product precipitated. The major isomer was the ortho in each case as determined by ^{13}C -NMR of the chloroform prepared amic acid (Table 17.1).

Other monoamic acids were investigated by ^{19}F -NMR and the data are summarized in Table 17.2. A variety of complex phenomena was observed. For some cases, similar isomer compositions were seen in both NMP- and in $CHCl_3$ -prepared monoamic acids (compounds **1c** and **1g**), and in other syntheses, a reversal of the favored isomer was observed (compounds **1d** and **1e**). Amounts of one isomer increased when NMP was used (compound **1b**). Finally, the 4-methylphthalic anhydride amic acid (**1f**) displayed a single signal in the ^{19}F -

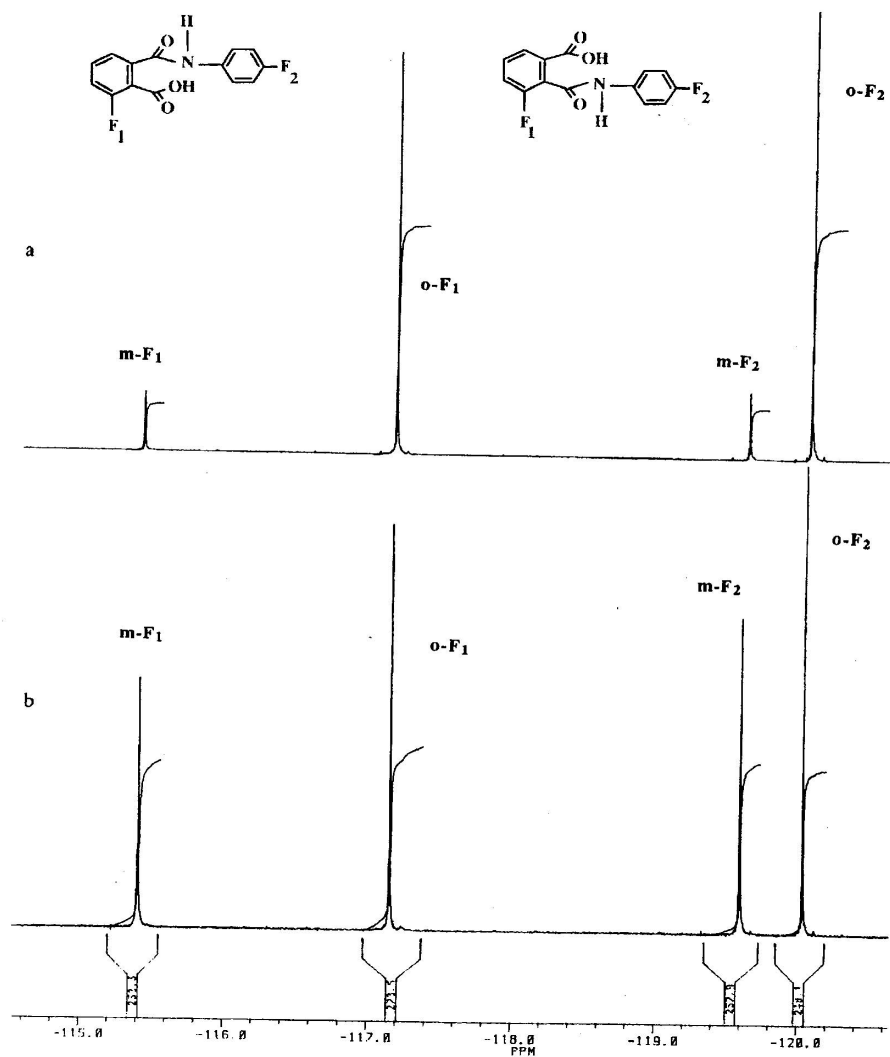
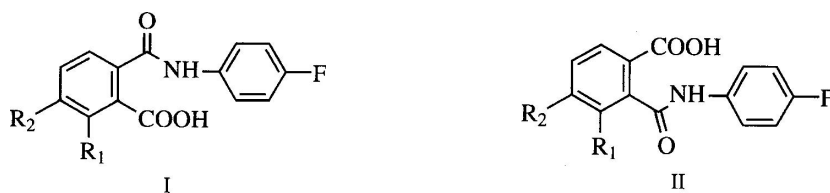


Figure 17.5. ^{19}F -NMR spectra of 3-FPA/4-FA AA: (a) prepared in NMP in homogeneous solution, and (b) prepared from precipitative reaction in chloroform (Reprinted from C. D. Smith *et al.*, *Polymer* 34, 4852–4862. Copyright (1993), with kind permission from Elsevier Science, Ltd., The Boulevard, Langford Lane, Killington OX5 1GB, UK).

Table 17.2. ^{19}F -NMR Isomer Compositions for Various Monoamic Acids

R ₁	R ₂	CHCl ₃ preparation		NMP preparation	
		% I	% II	% I	% II
F	H	49	51	17	83
NO ₂	H	0	100	0	100
H	NO ₂	55	45	32	68
H	Br	62	38	37	63
H	CH ₃	no difference observed		no difference observed	
H	<i>t</i> -Butyl	48	52	45	55

NMR spectra when made. from chloroform or NMP, although ^{13}C -NMR indicated that both isomers were present. Evidently, the methyl group is not significantly different electronically from a hydrogen atom for the sensitivity of the distant fluorine atom. The isomer composition of the chloroform prepared amic acids do not change over time when it is stored in NMP, so amic acid equilibria phenomena were not behind these observations. Therefore, although the technique for observing the isomer distributions offers quite detailed results, for some systems the amic acid isomer distribution that was formed still cannot be described in a straightforward way.

(b) *Model Diamic Acids.* Use of 6FDA model compounds allowed us to measure directly the composition of the three possible isomers in a dianhydride system, as discussed previously. Although this is a valuable model study, quantitative analysis is somewhat difficult because of the lack of a suitable baseline between the signals in Figure 17.2b. A series of amic acid model compounds based on 6FDA and 4-FA as prepared in different solvents at 2% concentration and their ^{19}F -NMR spectra were compared (Figures 17.6 and 17.7). These spectra were measured in the same solvent in which they were synthesized. Each spectrum consisted of two parts, one corresponding to the hexafluoroisopropyl (6F) group around -63 ppm (Figure 17.6) and the other to the aromatic fluorine part of the molecule around -120 ppm (Figure 17.7). Analysis of these spectra revealed quite complex behavior for the different solvents, as summarized in Table 17.3. The sample prepared in NMP gave almost an identical spectrum as

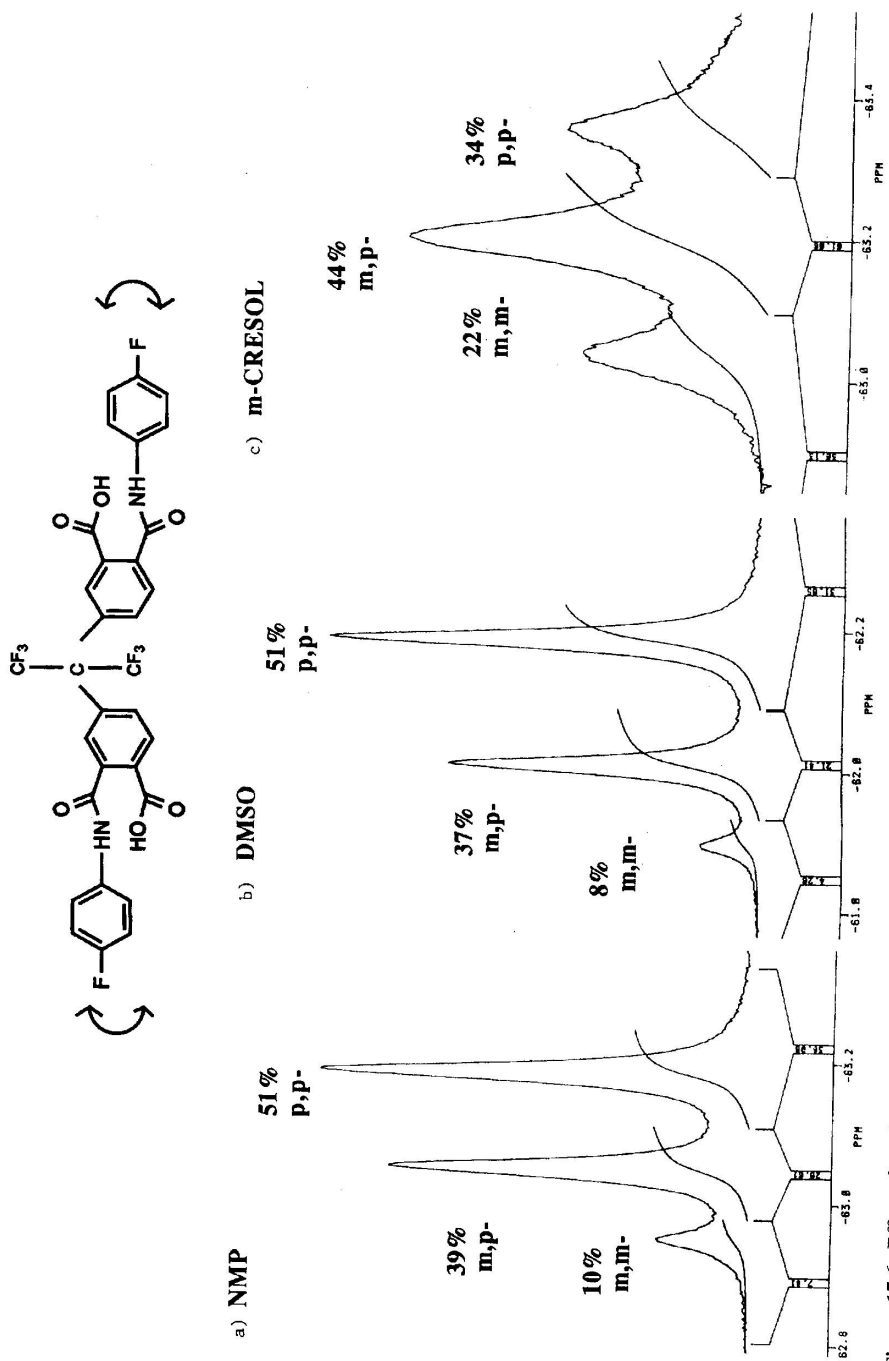


Figure 17.6. Effect of synthetic solvent on the hexafluoroisopropyl region of the ^{19}F -NMR spectra for 6FDA/4-FA prepared in: (a) NMP; (b) DMSO, and (c) *m*-cresol.

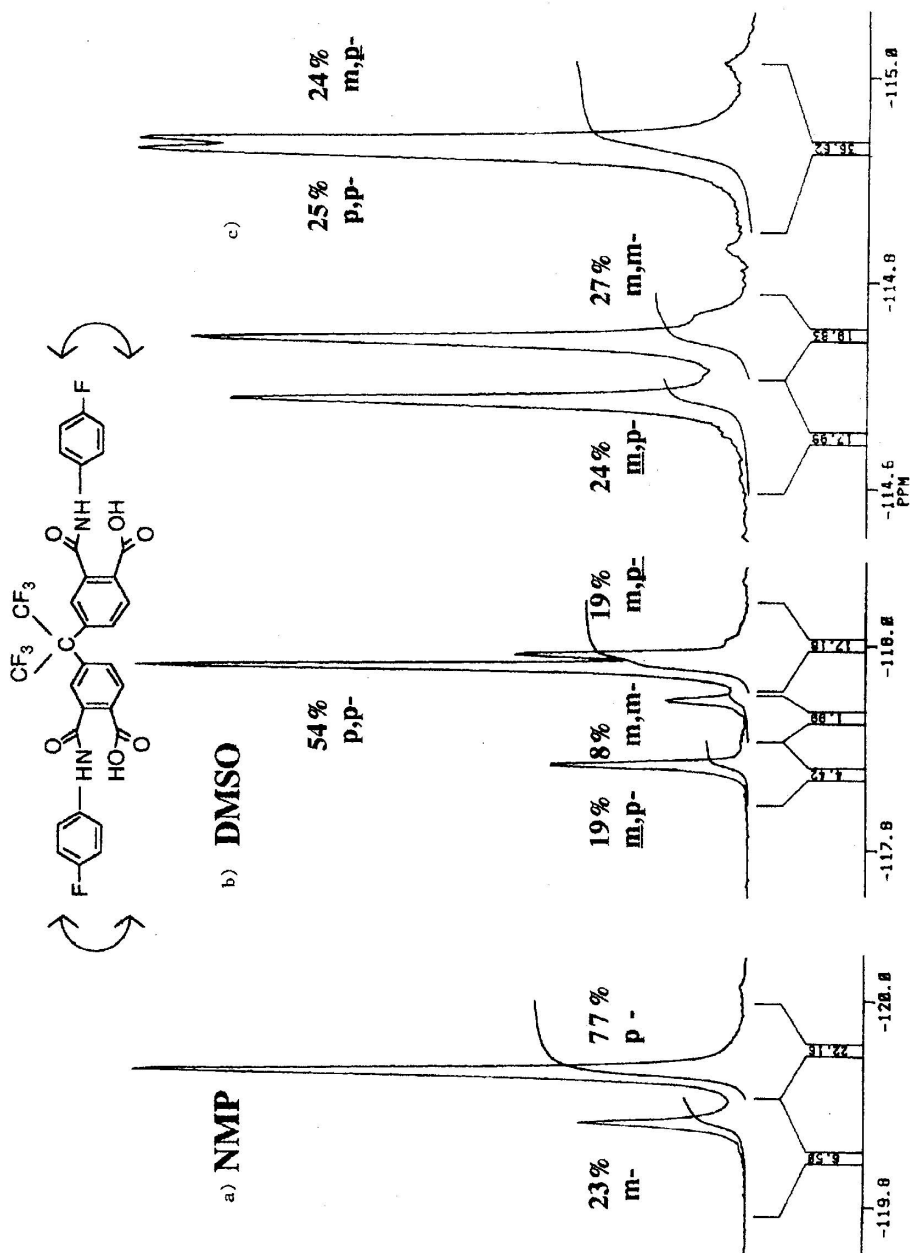
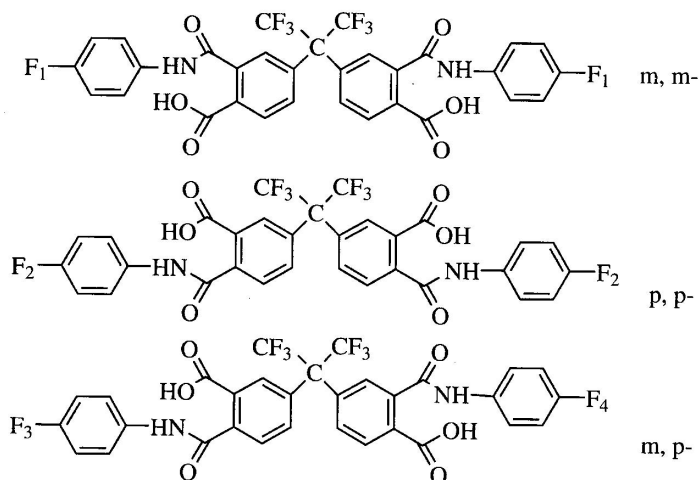


Figure 17.7. Effect of synthetic solvent on the aryl fluoride region of the ^{19}F -NMR spectra for 6FDA/4-FA prepared in: (a) NMP; (b) DMSO, and (c) *m*-cresol.

Table 17.3. Solvent Effects on Isomer Distribution of 6FDA/4-FA DAA



Solvent	6F region			Aryl fluoride region		Calculated ^a	
	<i>m,m</i> -	<i>m,p</i> -	<i>p,p</i> -	<i>m</i> -	<i>p</i> -	<i>m</i> -	<i>p</i> -
NMP	10	39	51	23	77	30	70
DMSO	8	37	55	27	73	27	73
<i>m</i> -Cresol	22	44	34	51	49	44	56

^a Calculated by $m- = m,p- / 2 + m, m-$; $p- = m,p- / 2 + p,p-$

the aniline-based amic acid in the aliphatic fluoride region, which was expected since amine basicity has been reported not to affect isomer composition.

The aryl fluoride part of the spectrum provided further insight into the isomeric composition. This region consisted of two peaks in NMP, which gave a ratio of 23 : 77. Considering the nature of the 6F connecting group, which cannot transfer electron density by resonance mechanisms, only two signals were expected, as only two types of aryl fluorides were possible. Thus, the two signals were assigned as the meta isomers at -119.88ppm and the para isomers at -119.93ppm . If one calculates the total amount of meta and para isomers from the aliphatic region integration by dividing the *m,p*-isomer content by two and adding this number to both the *m, m*- and *p,p*-isomer contents, the result in this case was 29.5:70.5. These amounts correspond well to the integration of the aryl fluoride part of the spectrum, considering the proximity of the three peaks in the aliphatic fluoride region.

As shown in Table 17.3 and Figures 17.6 and 17.7, the other polar solvents yielded significantly different spectra. For the amic acids prepared in DMSO and *m*-cresol, the 6F region was essentially identical to the NMP-prepared sample; however, for the aromatic regions, four peaks were observed instead of two. The structures in Table 17.3 can aid in this discussion. Each of the *p,p*- and *m, m*-isomers should yield one signal in the ^{19}F -NMR spectra since the aryl fluorine atoms on all of these molecules are equivalent. For the *m,p*-isomer, the two fluorines are not chemically equivalent to each other and should thus yield two peaks.

The important issue is whether *all* fluorine atoms para (or meta) to the connecting group are equivalent. In other words, in the structures shown in Table 17.3, both $F_1 = F_1$ and $F_2 = F_2$ are true (=signifies chemical equivalence); however, does $F_2 = F_3$ or $F_1 = F_4$? Obviously, this depends on the nature of the connecting group. A connecting group that is only capable of polar or inductive effects, such as methylene or the 6F, should yield spectra of only two peaks for amic acid isomer mixtures since each aryl fluoride is basically isolated from the other aromatic ring. The chemical shift of F_3 would be the same as F_2 , since it is not affected by the position of the other amide bond. Therefore all fluorine atoms para to the connecting group should yield one signal while all fluorine atoms meta to the connecting group should yield a different signal. While this was the case for the 6FDA/4-FA DAA prepared in NMP, four peaks were observed in DMSO and *m*-cresol in the aromatic fluoride region as shown in Figure 17.7. A possible cause for this phenomenon is the difference in solvent complexation ability with the amic acids. Amide solvents such as NMP are known to complex with amic acids, while less is known about DMSO or phenolic solvent complexing ability.⁴⁷⁻⁵¹

Similar to the monoamic acids, amic acid model compounds of other dianhydrides with 4-fluoroaniline gave varied results, as shown in Figures 17.8 and 17.9. The diamic acid isomeric mixture of PMDA (Figure 17.8) showed two signals for the two possible isomers, while that of amic acid based on a bridged dianhydride (Figure 17.9) displayed four peaks. Assignments of the signals in the spectra were based on literature and simple resonance arguments. For the PMDA amic acid, the diamic acid based on two meta amide groups is the major isomer formed. The first nucleophilic attack is a random process, while the second attack is at the remaining most electrophilic carbonyl group. As acid groups are stronger electron-withdrawing groups than amides, the second attack favors the carbonyl para to the acid formed from the first addition. The ratio of *m*- to *p*- isomers was 3:2.

In some cases where bridged dianhydrides were used, four signals were observed in NMP, evidently because of the ability to transfer π -electron density through such bonds as ether, sulfone, or ketone as discussed above. As an example of such behavior, the diamic acid isomeric solution based on 1,1'-bis(3,4-carboxyphenyl)sulfone dianhydride (SDA) displayed the spectrum illustrated in

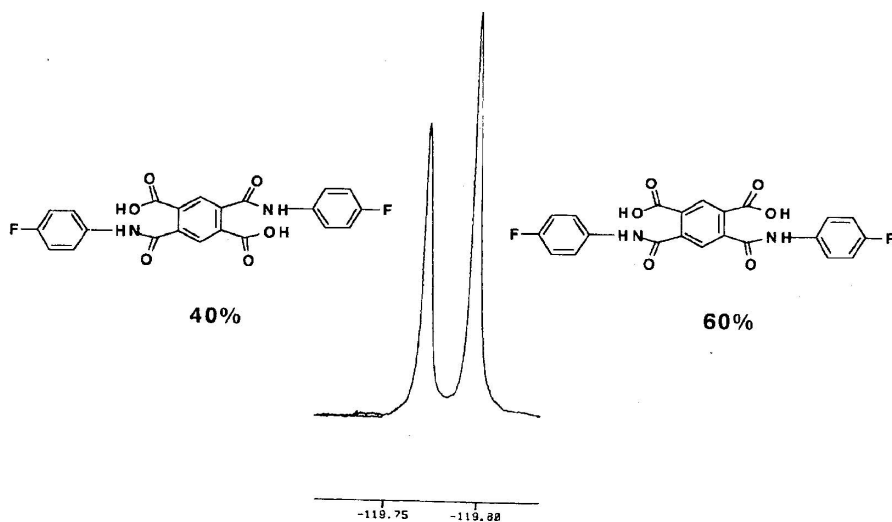


Figure 17.8. ^{19}F -NMR spectra PMDA based 4-FA model compound prepared in NMP

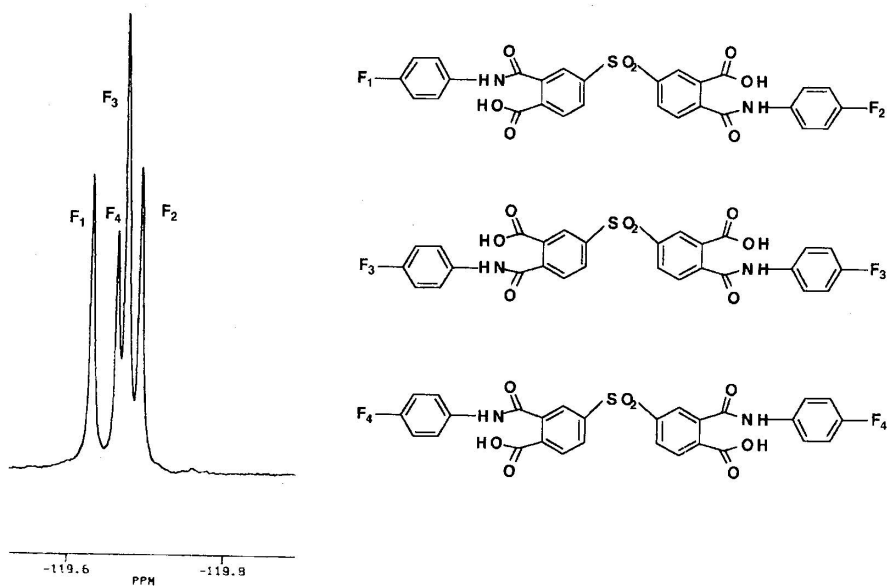


Figure 17.9. ^{19}F -NMR spectra SDA based 4-FA model compound prepared in NMP.

Figure 17.9. The structures of this isomeric mixture are identical to those in Table 17.3 when substituting the 6F group with SO₂. Within a range of 0.2 ppm, four signals were clearly discernible, with the two outer peaks giving nearly the same value for integration (25 and 23%). These signals were assigned to the two fluorine atoms (F₄ downfield and F₃ upfield) on the *m,p*-isomer, for a total of about 48% of that isomer. The largest peak in the spectrum, corresponding to 34% of the total signal, was assigned to the *p,p*-isomer (F₂ above). Since the electron-withdrawing character of the sulfone group is quite strong, the amine should attack preferentially at the most electrophilic site para to the sulfone. Finally, the *m,m*-isomer, corresponding to the smallest signal and F₁ above, made up the remaining 18% of the mixture.

17.3.2.2. Amic Acid Equilibria

Several studies have recently confirmed the reversibility of the amic acid formation reaction^{14,17,52–59}; it has been known for some time that this reaction becomes quite important as the temperature of the system is raised.^{60,61} Thus upon heating a poly(amic acid) solution, the side reactions that were shown in Figure 17.1 become increasingly significant. One important requirement for any technique used for studying these numerous reactions is the capacity to quantify all of the species present simultaneously. Heating a 2% NMP solution of the 4-FA/PA AA model at 90°C overnight in air resulted in the ¹⁹F-NMR spectrum shown in Figure 17.10a. Under these experimental conditions, a distribution of 83% amic acid, 2% free amine (4-FA), and 6% imide resulted. The fourth peak in the spectrum at –128.9 ppm (9% of total signal) was due to a side reaction of the amine, which was not eliminated by performing the reactions under nitrogen, suggesting that it is not a partially oxidized form of 4-FA. We have observed this same peak when solutions of amic acid based on 4-fluoroaniline were reinvestigated after storage at room temperature in air for over 2 weeks. Since much less equilibration of amic acids occurs at room temperature, longer times were required for the observation of this peak at ambient conditions. This finding has implications for long-term storage of poly(amic acid) materials, which we are currently investigating. Although it is known that equilibrated anhydride can hydrolyze to its acid form, thus shifting the equilibrium shown in Figure 17.1 toward starting materials, side reactions of the liberated amine starting material can be another potentially limiting reaction. The side reaction is possibly one with the solvent or an impurity in NMP, as we have observed this unknown compound in mixtures of NMP and 4-FA alone heated to 90°C for extended times.

An identical experiment to the one above in the presence of water (2 wt %, corresponds to 13.4 mol water per amic acid group) gave significantly different results (Figure 17.10b). Both more imide (10%) and more free 4-fluoroaniline (16%) were formed, with the remaining composition 71% amic acid and 4% the

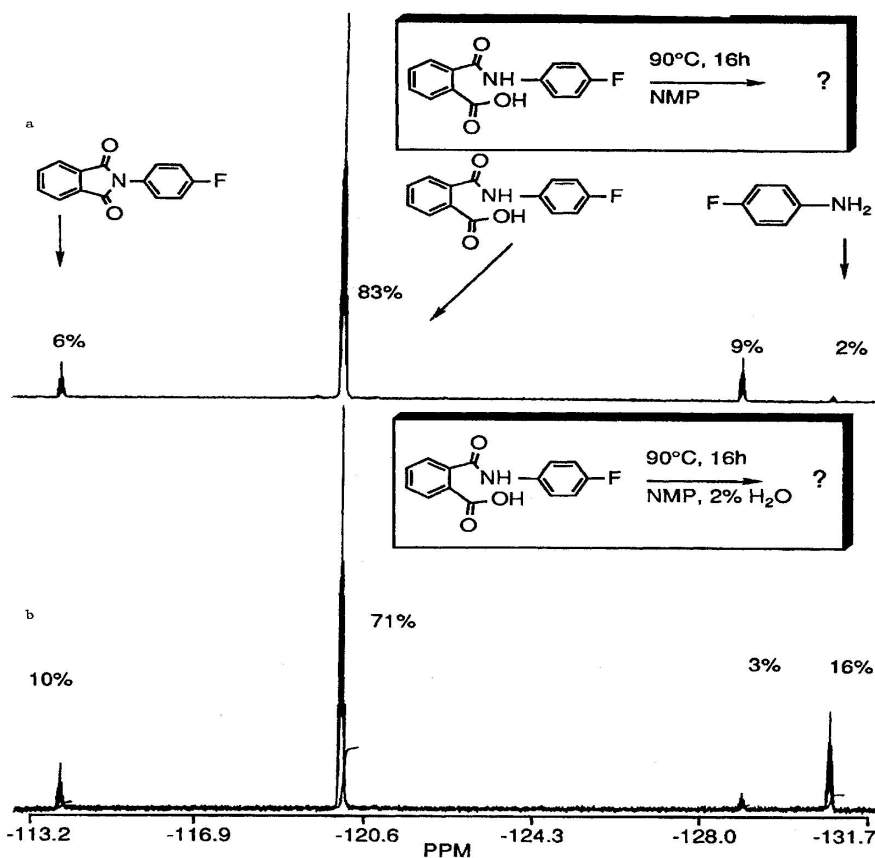


Figure 17.10. ^{19}F -NMR spectra of: (a) 4-FA/PA AA heated in NMP at 90°C for 16 h, and (b) 4-FA/PA AA heated in NMP at 90°C for 16 h, in the presence of 2% water.

unknown. The presence of much more amine in wet NMP when compared to the equilibrium reaction under anhydrous conditions can be explained by the rapid hydrolysis of any equilibrated anhydride. Formation of more imide than the anhydrous sample was probably due to catalysis of amic acid to imide transformation by the water present or by the hydrolyzed product, phthalic acid. Organic aromatic and general acid catalyzed imide formation is a known process.⁶²

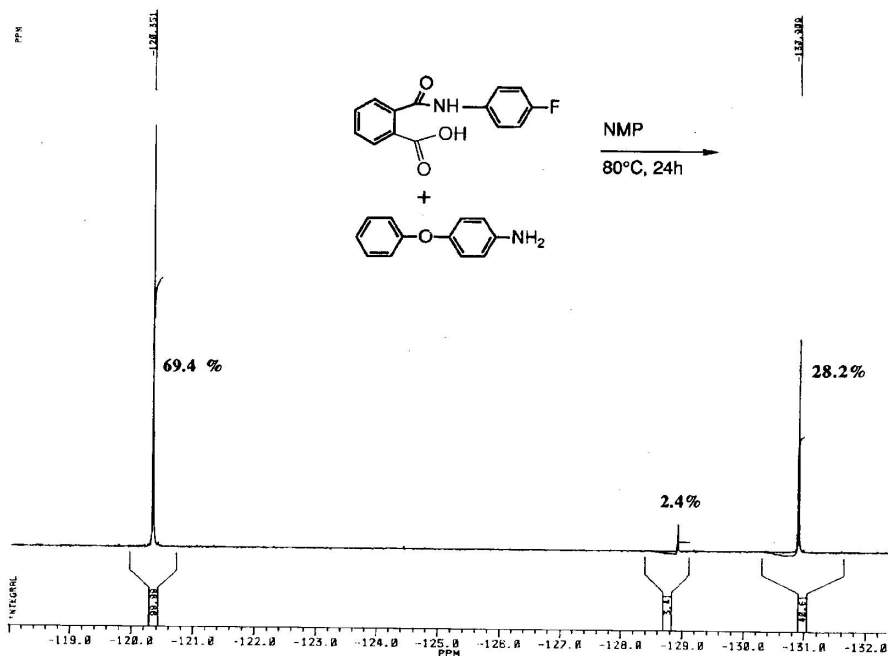
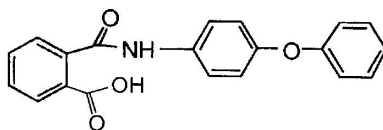


Figure 17.11. ^{19}F -NMR spectrum of 4-FA/PA AA heated in NMP at 80°C for 24 h with a stoichiometric amount of (4-aminophenyl)phenyl ether.

Therefore, when thermal imidization is chosen as the procedure for ring closure, many of the reactions that were illustrated in Figure 17.1 can occur. Amine and anhydride end groups form from the initially high-molecular-weight poly(amic acid) and any anhydride groups formed are likely to hydrolyze to the acid form from any water liberated by imidization, unless the water is quickly removed from the system. Ultimately, at sufficiently high temperatures and long enough times, the imide chains will “heal” to give high-molecular-weight polyimides.⁶³ Any copoly(amic acids) are likely to scramble to a more random copoly(amic acid) when heated in solution, depending on the nucleophilicity of the liberated amine groups.²⁶ An example of this behavior is shown in Figure 17.11, in which the experiments described in Figure 17.10 were repeated in the presence of equimolar amounts of (4-aminophenyl)phenyl ether (ADPE). Now nearly 30% free 4-FA was observed as opposed to 2% free 4-fluoroaniline (Figure 17.10a) in the absence of the more nucleophilic amine ADPE. Upon equilibration of 4FA/PA AA and liberation of free phthalic anhydride, the more nucleophilic ADPE preferentially reacts with the free anhydride. In essence, the ADPE molecule “traps” any free phthalic anhydride, forming the nonfluorinated structure shown in Scheme 1 and liberating free 4-FA.



Scheme 1

Thermal imidization presents an interactive array of desired and undesired reactions, which may lead to complete imidization under driving conditions. On the other hand, chemical imidization presents a different set of synthetic challenges on which we will soon publish.

17.3.2.3. Imide Solution Hydrolysis

Relative to what is known regarding many physical characteristics of this family of polymers, hydrolytic stability remains comparatively unexplored. Among the reasons for this low level of research activity is the difficulty of accurately determining the chemistry occurring in these traditionally insoluble compounds. Hydrolytic stability of polyimides in the solid state has been investigated in terms of its effects on mechanical properties^{64–66} or viscosity changes.⁶⁷ Additionally, chemical changes have been investigated by FTIR⁶⁸ and model-compound studies.⁶⁹ Some instances of polyimide failure during use in high-water-content environments have also been published.^{70,71} Alkaline hydrolysis of imides (Gabriel-type synthesis) is well known, but neutral solution hydrolytic stability of aryl imides has not been studied in chemical detail. Our interest for this part of the project was the behavior of a series of imide compounds toward water in polar aprotic solvents at high temperatures, which should also be a measure of solid state hydrolytic stability under extreme conditions. Additionally, insight could be gained regarding the merit of water removal from polyamic acid solutions during imidization.

The poly(amic acid) and the fully imidized polymer based on 6FDA and *m*-phenylene diamine were prepared and their ^{19}F -NMR spectra measured, as shown in Figure 17.12a and b, respectively. Whereas only a single peak at -62.87 ppm was observed for the polyimide, indicating complete imidization, three peaks were seen (-62.92 , -63.03 , and -63.18 ppm) for the poly(amic acid) mixture. These peaks are known to correspond to the isomeric amic acid composition,⁴⁴ with the para-linked isomers predominant in the 6F case. This polyimide was dissolved at 2 wt % solids in NMP, and 20% (v/v) water was added to the solution. This homogeneous mixture was refluxed over a period of time and samples were taken for analysis by ^{19}F -NMR. Figure 17.12c and d illustrates these spectra. The polyimide had obviously undergone serious degradation, probably forming a blend of many chemically different species. In an effort to detail the changes taking place upon hydrolysis, model compounds were studied.

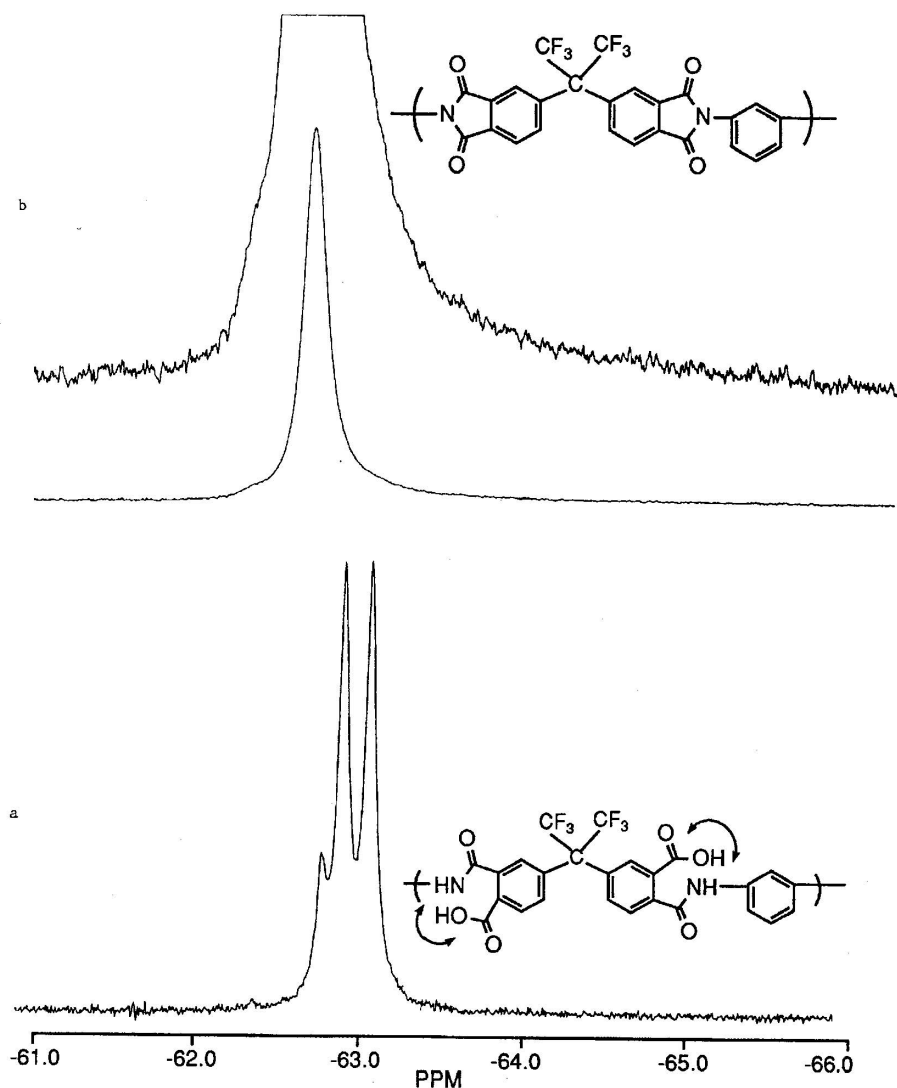


Figure 17.12. ^{19}F -NMR spectra of 6FDA/*m*-PD in various stages of hydrolysis: (a) poly(amic acid) solution in NMP prior to water addition, (b) polyimide solution in NMP prior to water addition.

The 6FDA/4-FA material was the first model compound studied because it had two types of fluorine atoms. Figure 17.13 illustrates the changes in the ^{19}F -NMR spectra upon solution hydrolysis. Before exposure, the completely imidized compound displayed two sharp singlets at -62.90 ppm and -113.8 ppm; however, after exposure to hydrolysis conditions, significant degradation occurred, resulting in the formation of many chemical species. The identity of the species in

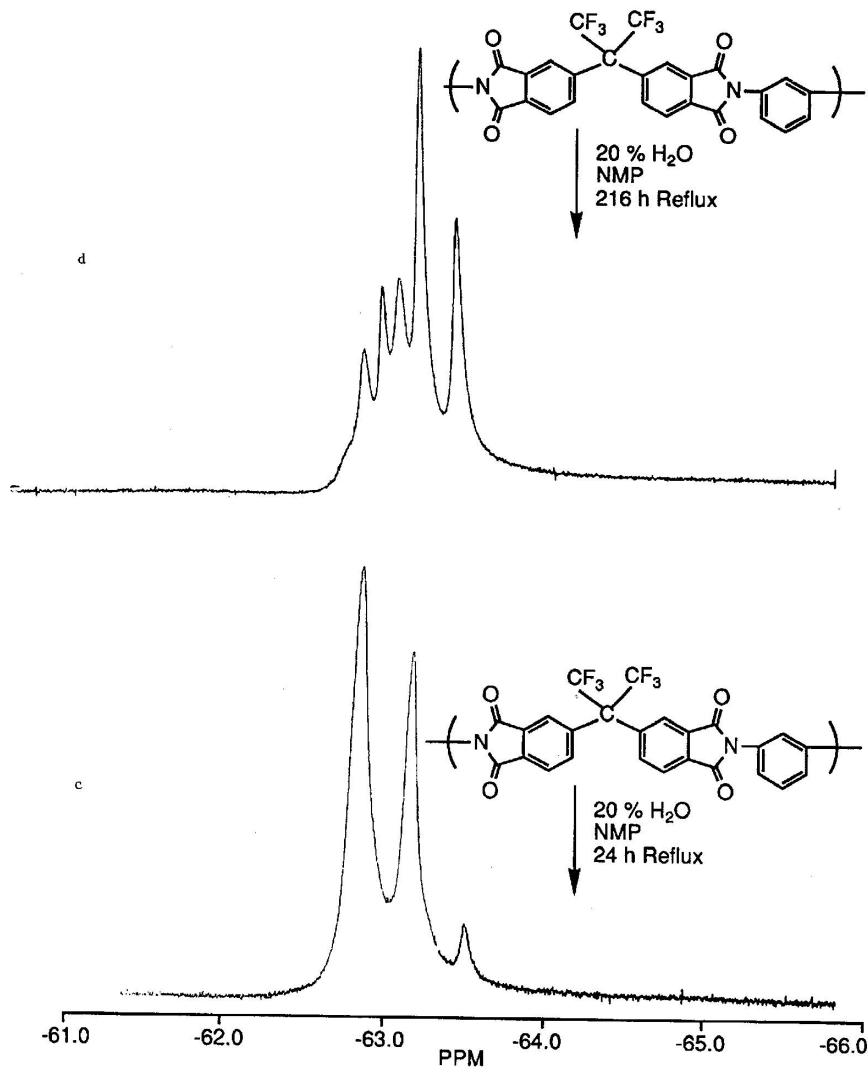


Figure 17.12. ^{19}F -NMR spectra of 6FDA/*m*-PD in various stages of hydrolysis: (c) polyimide after 24 h at reflux in the presence of 20% water in NMP, (d) polyimide after 216 h at reflux in the presence of 20% water in NMP.

Figure 17.13a were confirmed from previous model experiments.⁴⁴ Owing to the isomeric content of the model compound amic acids, multiple peaks for these species in the amic acid region of the spectra are usually observed.^{44,45} Although the 6F part of the spectrum is difficult to analyze, one can easily identify amic acid and amine materials present in the mixture from the peaks near -120 and -129

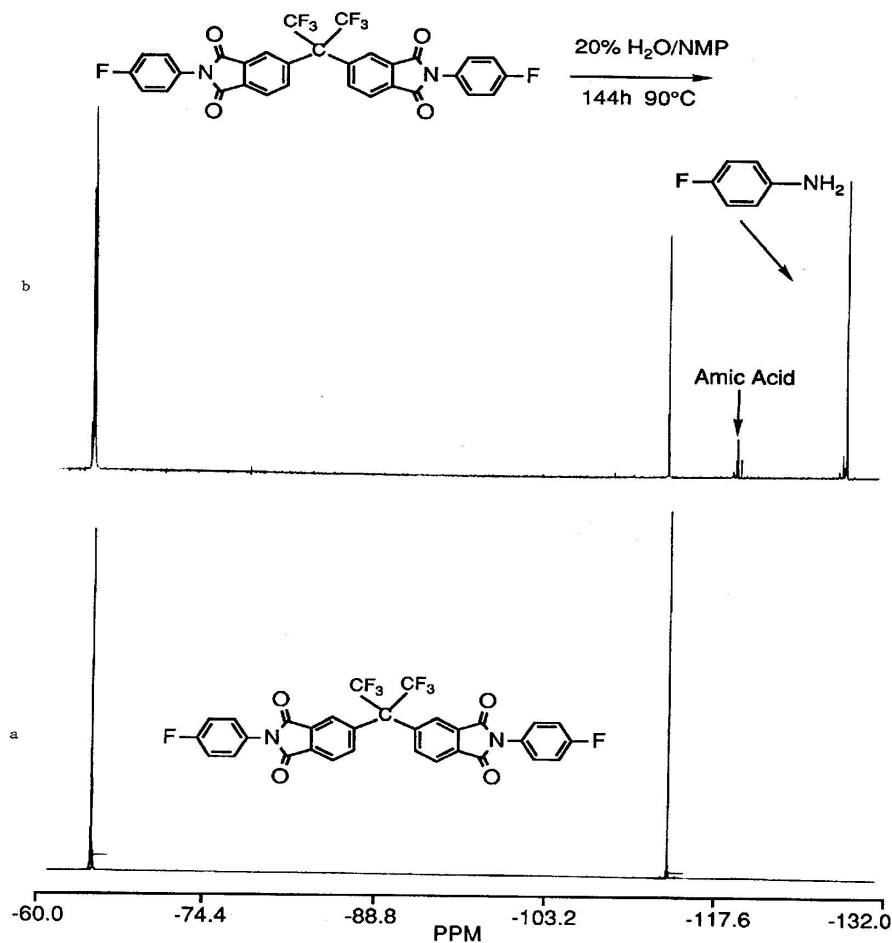


Figure 17.13. ^{19}F -NMR spectra in NMP of: (a) 6FDA/4-FA and (b) 6FDA/4-FA after 144 h at 90°C in the presence of 20% water in NMP.

ppm in the aryl fluoride part of the spectrum. The reaction yielding the amine 4-FA could result from one of two pathways: (1) hydrolysis of the amic acid or (2) equilibration of the amic acid at the elevated temperature to the corresponding amine and anhydride. Amic acids are well known to equilibrate at elevated temperatures in aprotic dipolar solvents^{26,56,63}; also, others have reported on the hydrolytic stability of amic acids.⁵⁵ Separation of these two phenomena cannot

be carried out under these conditions, but we have observed this equilibration of amic acids at elevated temperatures in anhydrous NMP by ^{19}F -NMR.⁴⁴

Other model compound hydrolysis experiments confirmed this generic behavior. The dependence of hydrolysis on chemical structure of the model compounds was observed between the 4-FA imide compounds of SDA and ODPA. Under the same hydrolysis conditions, the highly electron-withdrawing sulfone group induced much more reaction of both the imide and the amic acid species than the ODPA analogue, as shown in Figure 17.14. Also, amines that

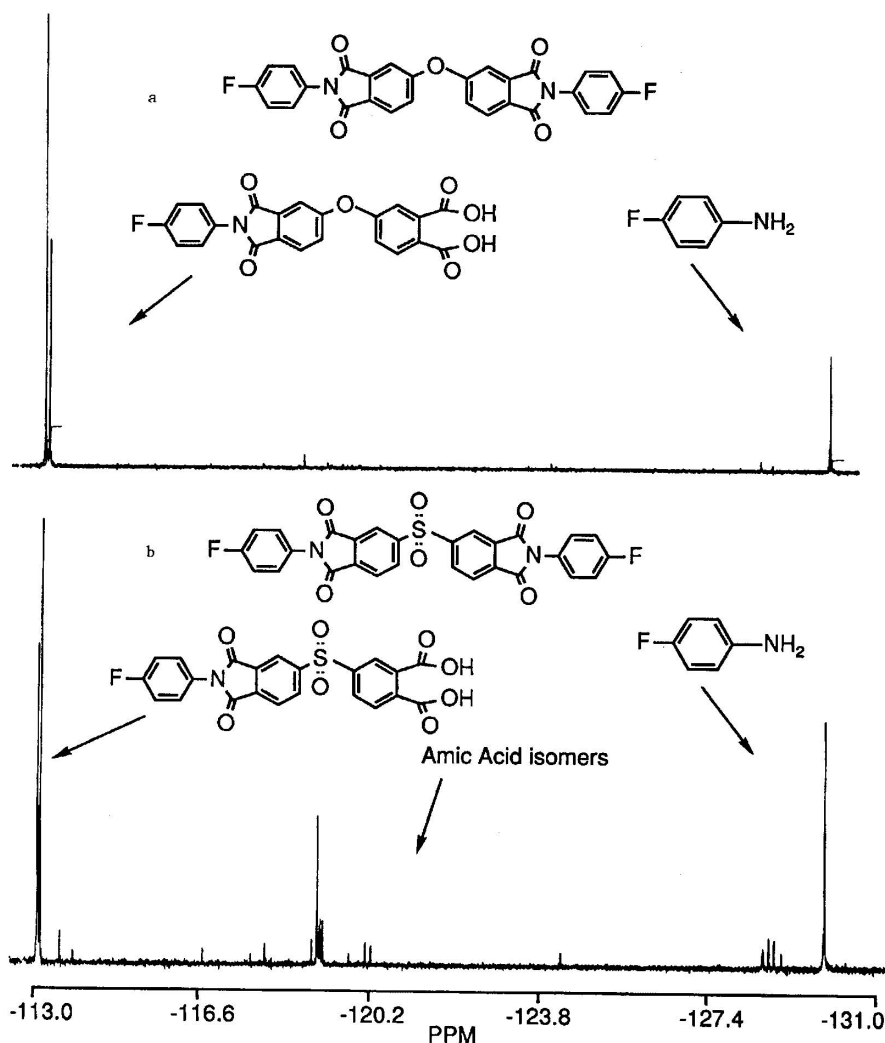


Figure 17.14. ^{19}F -NMR spectra in NMP of hydrolysis reactions with 20% water at 90°C for 24 h of: (a) ODPA/4-FA and (b) SDA/4-FA.

donated electron density to the imide ring, such as ADPE, were hydrolyzed less than those in which electron density was pulled from the imide link. This is clearly illustrated in Figure 17.15, in which the 6FDA model compounds with aniline, 4-aminobenzophenone (ABP), and ADPE were hydrolyzed under the same conditions. Before hydrolysis, all of these materials displayed a single peak. It should be noted that the electron-poor imide ring on the ABP/6FDA model compound was degraded twice as much as the aniline-based model and nearly fivefold more than the protected imide link in 6FDA/ADPE.

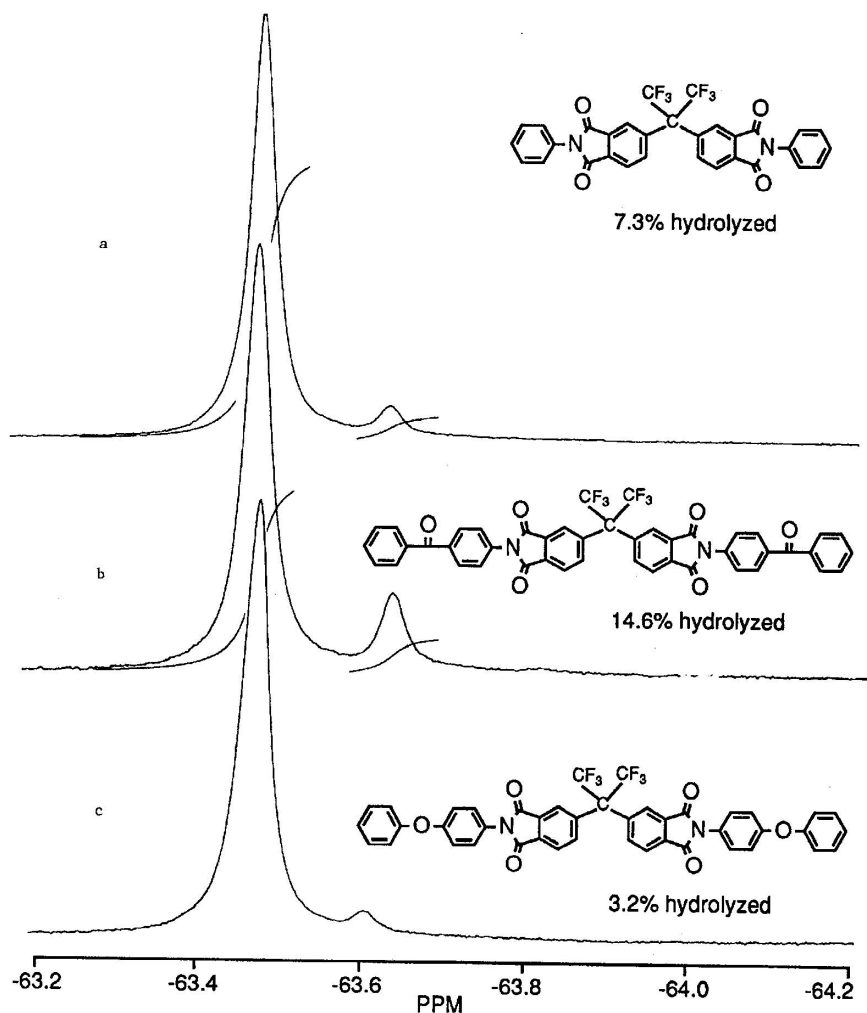


Figure 17.15. ^{19}F -NMR spectra in NMP of hydrolysis reactions with 2% water at 80°C for 24 h of: (a) 6FDA/AN, (b) 6FDA/ABP, and (c) 6FDA/ADPE.

17.4. CONCLUSIONS

^{19}F -NMR has been shown to offer a number of advantageous qualities for the study of imide chemistry in solution under various conditions. Included among these benefits is the ability to measure many of the separate chemical species present in solution without isolation of products. This ^{19}F -NMR tool was useful for the investigation of various aspects of solution imide chemistry, such as amic acid isomer formation, amic acid equilibria, and imide hydrolysis. Surprising results were observed for amic acid isomer formation in model compounds, in which for the first time amine basicity was seen to affect isomer formation in solution. Electronic or inductive effects of substituents on anhydrides affected the isomer distribution formed in the expected ways. Regarding hydrolysis, anhydrides containing electron-withdrawing groups hydrolyzed much more readily than their electron-donating counterparts. Thus, the imides containing sulfone- and hexafluoroisopropyl-linking groups were more susceptible to this hydrolysis than the ether-linked imides. Similarly, compounds based on amines containing electron-withdrawing groups suffered more degradation than the electron-releasing linked amines. Fluorinated polyimides showed similar behavior in solution when compared to model compounds.

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