

**^{15}N NMR Spectroscopy as a method for comparing the rates of imidization of
several diamines**

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Abstract

The relative rates of the conversion of amide-acid to imide was measured for a series of aromatic diamines that have been identified as potential replacements for 4,4'-methylene dianiline (MDA) in high-temperature polyimides and polymer composites. These rates were compared with the ^{15}N NMR resonances of the unreacted amines. The initial rates of imidization track with the difference in chemical shift between the amine nitrogens in MDA and those in the subject diamines. This comparison demonstrated that ^{15}N NMR spectroscopy is appropriate for the rapid screening of candidate diamines to determine their reactivity relative to MDA, and can serve to provide guidance to the process of creating the time-temperature profiles used in processing these materials into polymer matrix composites.

Introduction

High-temperature polyimides have found widespread use in aerospace applications because of their high use temperatures (approaching 350 °C) and high specific strength. The initial approach to create such materials was to react an aromatic diamine with an aromatic dianhydride to form a poly(amic acid). This reaction happens almost immediately. Upon heating the poly(amic acid) closes to form the imide.

This approach suffers from several significant difficulties. Since the reaction to form the poly(amic acid) is immediate, an aggressive solvent such as N-methylpyrrolidone (NMP) must be used to keep the growing polymer in solution. A buildup in viscosity as the imidization reaction progresses traps both the water produced as a by-product and any residual solvent. Composite parts made from these materials typically suffer from voids due to these trapped volatiles.

A substantial improvement in polyimide synthesis and processing was made by the development of the Polymerization of Monomer Reactant (PMR) process at the NASA Lewis Research Center. (now the John. H. Glenn Research center at Lewis Field)[1] The PMR process adds an initial step to convert the anhydrides to acid-esters (typically, but not exclusively, methyl esters) and adds a similarly modified mono-anhydride as an end-cap. The resulting solution is comprised of the ester-acid of the anhydride monomer, the ester-acid of the anhydride end cap, and the diamine, typically at high concentrations (>50 wt% solids) in methanol. These modifications allow for the extended stability of the reactants in solutions of low-boiling solvents. Conversion of the anhydride functionalities to acid-esters prevents the immediate reaction with the amine,

instead requiring conversion of the acid-esters to anhydride, which then react with amines to form amic acids. [2]

The end cap monomer typically serves two functions. First, it prevents the polymer chain length from building continuously. Instead, oligomers are formed whose melt viscosities are low enough to allow water and methanol to escape during the cross-linking step. Second, the end caps allow cross-linking between oligomer chains at elevated temperature, providing a means to produce the extensive 3-dimensional structure that gives these polymers their typical temperature resistance.

The most commercially successful material in the PMR family of polymers is PMR-15, a high-temperature polyimide produced from the reaction of 4,4'-methylene dianiline (MDA) (**1**), the dialkyl ester of 3,3',4,4'-benzophenone tetracarboxylic acid (BTDE) (**2**), and the monoalkyl ester of 5-norbornene-2,3-dicarboxylic acid (NE) (**3**). The PMR-15 monomers are typically dissolved in methanol, with the ratios of monomers calculated to produce an oligomer with a molecular weight of 1500 g/mole. Molecular weight control in these systems is statistical, so a range of repeat unit values arises in the polymer primarily which runs from 0 (two NEs reacted with an MDA) up to 3 or 4, with the bulk of the chains having 2 repeat units.

While the temperature, mechanical, and thermo-oxidative performance of PMR-15 is quite good, it is not sufficient for a number of applications where higher use temperatures or longer service lifetimes are desirable. In addition, although the material itself is inexpensive, elevated manufacturing costs arise due to health and safety issues since MDA is a mutagen and suspect carcinogen [3]. Because of the use of discrete monomers in solution, the PMR process is ideal for tailoring polymer performance through the use of alternate monomers.

Substitution of monomers, particularly diamines, may require changes to the processing cycles used to cure the resin. Curing of PMR-15 and related polymers is done in an autoclave or hot press following a time-temperature-pressure-vacuum profile intended to complete the imidization reaction, drive off remaining volatiles, consolidate the composite, and form the crosslinked structure. The choice of times and temperatures is driven by the imidization and crosslinking reactions, which can vary with the selection of monomers. Development of an effective cure cycle is critical to the successful development of a new resin formulation. Much of the development of new cure cycles is done by trial and error, starting from a cycle that is known to work for a similar material. This can be both time-consuming and wasteful, particularly for a formulation that contains components whose reactivity differs considerably from more commonly used monomers.

Development of a technique to predict the relative reactivity of a new diamine in comparison with, for instance, MDA would allow new cure cycles to be created with some advanced knowledge, and should shorten the development time. An obvious solution to this problem would be to determine the rate of the imidization reaction with a new diamine through a series of kinetics experiments. While this would undoubtedly provide the desired information, this is a substantial project in its own right. A simpler and more straightforward technique is desirable.

It was reasoned that, since the position of a Nuclear Magnetic Resonance line is dependant not just on the nucleus and the magnetic field, but also on the electronic environment that the nucleus finds itself in that variations in reactivity should be reflected in variations in the position of the NMR resonance.

A series of diamines were examined as alternates to MDA, with the goal of finding a non-toxic substitute that has the same or better processing parameters and end-use characteristics. Examining their ^{13}C NMR spectra did show differences in the spectra between the various candidates, but the spectra were complex enough to make an unambiguous judgment difficult.

It was then theorized that the ^{15}N spectra of these same diamines could simplify the picture dramatically. Any symmetrical diamine would be expected to show a single ^{15}N resonance, as the two amine nitrogens would be equivalent. Unsymmetrical diamines would be expected to show two nitrogen resonances. A diamine with an amine ^{15}N peak significantly shifted away from the amine in MDA would be expected to differ in reactivity from MDA. Since the acquisition of a ^{15}N NMR spectrum is relatively straightforward, requiring only an overnight acquisition in moderately concentrated samples, ^{15}N NMR spectroscopy could serve as an effective screening technique for newly developed diamines.

In order to test this hypothesis the ^{15}N NMR spectra of several candidate diamines was obtained, as well as kinetics data on their reactivity with NA to form an imide.

Experimental

Solution NMR spectra were obtained on a Varian Unity Inova 400 MHz NMR spectrometer using a 10mm broadband probe.

^{15}N NMR spectroscopy

All ^{15}N NMR spectra were obtained at 40.5 MHz using a gated decoupling sequence for Nuclear Overhauser Effect suppression. The probe and sample temperature

was regulated at 30 °C. Samples were run in 10mm O.D. Wilmad 516-CC-10 external reference tubes, referenced to neat CH₃NO₂ at 0.0 ppm. The delay between the excitation pulse and the beginning of data acquisition was extended to 585.6 μsec to allow for the decay of the transmitter pulse. Typical acquisitions used a 27.7° acquisition pulse to allow the relaxation delay to be shortened to 5 sec, yielding a 15.7 hr experiment.

¹⁵N NMR spectroscopy of amines

Samples were prepared in d₆-DMSO to be ca. 0.1 M in diamine and run without further handling

¹⁵N NMR spectroscopy of amides

Samples prepared in d₆-DMSO to ca. 0.1 M in diamine had an equimolar amount of NA added to them before transfer the sample tubes and spectroscopy was undertaken

¹⁵N NMR spectroscopy of imides

Samples prepared in d₆-DMSO to c.a. 0.1 M in diamine had an equimolar amount of NA added, followed by heating to 150 °C for several hours to effect conversion from amide to imide. These samples were then cooled to room temperature and transferred to sample tubes before spectroscopy was initiated.

Kinetics experiments

For each of the subject compounds, a sufficient amount of diamine to make a 0.1 M solution in 30 ml total volume was placed in a 50 ml round-bottom flask with septum port, followed by ca. 0.4925 g of bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride (Nadic Anhydride). Approximately 8 g of 4 Å molecular sieves were added and the flask fitted with a drying tube. The entire apparatus was weighed and ca. 30 ml of anhydrous 1-methyl-2-pyrrolidone added by syringe. The apparatus was then weighed and the volume of solvent calculated using its published density. (1.03 g/ml)

Once the diamine and anhydride had dissolved, an approximately 3 ml initial ($t=0$ sec) sample was withdrawn and the flask suspended in a silicone oil filled temperature bath equilibrated at 150 °C. Samples of approximately 3 ml were withdrawn at intervals.

¹³C Spectroscopy for kinetics samples

All ¹³C NMR spectra were obtained at 100.5 MHz using a gated decoupling sequence for Nuclear Overhauser Effect suppression. Each sample was run in a 7" long 10 mm NMR sample tube with a Wilmad WGS-10BL stem coaxial insert filled with *d*₆-DMSO. Each tube was then placed in standard 10 mm turbine and loaded into the carousel of the autosampler installed on the NMR instrument. The probe and sample temperature was regulated at 30 °C. Completed spectra were phased, referenced to *d*₆-DMSO at 39.5 ppm, baseline corrected, and integrated using typical procedures.

Discussion

MDA is a mutagen and suspect carcinogen. Because of the substantial amount of free MDA present in the traditional hand-layup of high performance composites substituting a non-toxic diamine for MDA could greatly reduce the need for personnel protection. It has been suggested that MDA's physical size and relative planarity allows it to intercalate into the DNA molecule, interfering with transcription and thereby causing mutations [4-6]. The diamines chosen for this study represent different ideas about how to modify the structure to prevent the mutagenic effects of MDA. In the case of BIS-M, BIS-P, BAX and CO-BAX, the backbone of the diamine has been lengthened through the addition of an additional aromatic ring. 6F-MDA, BIS-M, and BIS-P have also replaced

the methylene bridge between the rings with bulkier groups to disrupt the planarity of the molecule.

The difficulty with substituting another diamine for MDA is threefold. First, any differences in reactivity to imidization will be reflected in changes to the cure cycle. A less reactive diamine may require higher processing temperatures, longer hold times, or both. Second, the effect of the diamine on the melt viscosity of the resin will affect the amount of pressure needed to produce a fully consolidated composite sample. If the required pressure exceeds that which is obtainable in commonly available autoclaves (about 1.38 MPa, or 200 psi), the adoption of the material by industrial users is unlikely. Finally, the cured polymer must show at least comparable thermal stability and mechanical properties to the MDA-containing formulation. While determining the effects of diamine substitution on the performance of the processed polymer is important, this work focused on the first step to replacing MDA: the differences in reactivity relative to MDA.

Five diamines which represent promising candidates for replacing MDA were selected for this study. These diamines were: 1,4-Bis(4-aminobenzyl)benzene (BAX)(4), 1-(4-aminobenzoyl)-4-(4-aminobenzyl)benzene (CO-BAX)(5), 4,4'-(1,4-phenylenediisopropylidene)bisaniiline (BIS-P) (6), 4,4'-(1,3-phenylenediisopropylidene)bisaniiline (BIS-M) (7), and 4,4'-(hexafluoroisopropylidene)dianiline (6F) (8). An additional diamine, 4,4'-diaminobenzophenone (DABP) (9) was added as a model of the carbonyl end of CO-BAX.

Determining the relative reactivity of diamines to imidization should be a relatively straightforward process, involving the measurement of the rate of the reaction

for each of the diamines and comparing it to the rate with MDA. Unfortunately, this is often a difficult and time-consuming process, a process not suited to the rapid screening of candidates to provide guidance to the process of creating time-temperature profiles used in processing.

It is well known that the electronic environment of an atom will affect its NMR resonance frequency, since the electrons partially shield the nucleus from the magnetic field. It was believed that the same electronic differences that lead to differences in NMR resonances should also affect the reactivity of the amine nitrogen. If this is the case, there should be some correlation between the position of an amine's ^{15}N NMR resonance line and its reactivity to imidization. This would provide the simple screening process that is desired.

Examination of the ^{15}N spectra of the subject diamines (Table 1) shows some interesting information. The nitrogen in BAX, which has simple methylene bridges between the aromatic rings, had a very similar chemical shift to those in MDA, as did BIS-P and BIS-M, in which the bridging carbons are dimethyl substituted. In 6F-MDA, where the bridging carbons are substituted with CF_3 groups there is a substantial shift of -4.72 ppm in the nitrogen resonance relative to MDA. It is not unreasonable to expect that the CF_3 groups will affect the electron density on the nitrogen causing such a shift. Co-BAX is interesting in that it shows two ^{15}N resonances, evidently due to the presence of the carbonyl bridge between two of the rings. (Co-BAX was originally included because, at least in the initial synthetic scheme, it is a precursor to BAX and it would be more economical to produce in bulk than BAX). One of the Co-BAX nitrogens is very similar in chemical shift to MDA, while the other has a shift of -14.46 ppm relative to MDA, which is greater than those in 6F-MDA.

In all of these cases, samples were prepared by mixing approximately equimolar amounts of the diamine with nadic anhydride, to produce the amide. It should be noted that while equimolar amounts were used, the amines are bifunctional, so there is only enough anhydride to react with half of the available amine. It was hoped that the result would be primarily the mono-amide but, as it does not seem to affect the results, no real effort was made to determine if this was the case.

In each case where the amide has been formed, the new amide nitrogen peak appears higher in chemical shift than that of the amine, and there remains a prominent peak due to unreacted amine. In the case of diamines with only two phenyl rings, the residual peak is actually two very closely spaced peaks. This suggests that reaction with an amine at one end of these small diamines induces a slight change in the chemical shift of the unreacted amine at the other end. The appearance of the doubled amine peak does not occur with the longer chain diamines, leading to the speculation that the extra ring may serve to insulate one end from the effects of a reaction at the other.

The two nitrogens in Co-BAX react somewhat differently from the rest when combined with nadic anhydride. The amine resonance at -322.68 ppm disappears into the baseline noise, while the peak at -308.95 ppm remains. The amide peak is at -248.01 ppm. It is reasonable to assume from the amine chemical shifts that the peak at -233.68 comes from the nitrogen on the aromatic ring nearest the methylene bridge, as it is very close to the shift of the nitrogens in MDA. From this information, it appears that the carbonyl bridge makes the adjacent nitrogen considerably less reactive, as reaction to the amide appears to occur almost exclusively on the “methylene nitrogen”.

Because, based on these initial observations, it appeared that Co-BAX would always react first from the methylene end, an additional diamine, DABP, was added to

the study to serve as a model for the carbonyl end of Co-BAX. At -312.09 ppm the ^{15}N chemical shift of DABP is similar to that of the carbonyl end of Co-BAX

Based on the amide ^{15}N shifts and the observed behavior of Co-BAX with nadic anhydride, it is assumed that 6F-MDA, DABP, and the carbonyl end of Co-BAX will be less reactive than MDA, while BAX, BIS-M, BIS-P, and the methylene end of Co-BAX will be comparable in reactivity with MDA.

In order to test this assumption, a series of reactions were carried out that involved mixing approximately equimolar amounts of each diamine with nadic anhydride, heating the mixture at 150 °C, and withdrawing samples at intervals to be examined by ^{13}C NMR spectroscopy.

^{13}C NMR was selected for this analysis for practical reasons. In the ^{13}C spectra the carbonyl carbons are readily visible, and spectra could be obtained in a reasonable time even with the use of gated decoupling for Nuclear Overhauser Effect suppression. In comparison, ^{15}N spectra took approximately 16 hours per sample. ^1H spectra could be obtained even more rapidly than ^{13}C spectra, but while the spectra for each diamine were different, it was not clear which feature in the ^1H spectrum could best be used to track the progress of the reaction.

The initial attempt to measure the relative rates was done in a mixture of dimethyl sulfoxide (DMSO) and its deuterium labeled analogue, $\text{d}_6\text{-DMSO}$, used to allow a field lock in the NMR instrument. These samples intermittently suffered from solubility issues, allowing the products to occasionally precipitate before their relative concentrations could be measured.

In order to improve the solubility of the reaction products, DMSO was replaced by N-methyl-2-pyrrolidone as the primary solvent. Field lock in the NMR was provided

by the use of a coaxial internal reference tube filled with d_6 -DMSO. While this procedure solved the solubility problems, the reaction rates of all of the diamines initially appeared to be the same. It was subsequently determined that the NMP was not sufficiently dry for this purpose, and was rapidly converting the nadic anhydride to the nadic diacid. The identical rates for all diamines indicated that some other slow process was dominating the reaction. It was postulated that the conversion from diacid to anhydride, which is necessary for reaction with the amine, was the slow step which dominated the rates of all of the other reactions. To combat the difficulties caused by the production of the diacid, subsequent reactions were undertaken using precautions to exclude water from the external environment, and to remove water created during the reaction itself.

Monitoring the progress of the reaction was done by identifying the carbonyl resonances corresponding to the amide, acid, and imide in the ^{13}C spectrum and integrating. In all cases there was an initial peak near 170 ppm that disappeared over the course of the reaction, while two peaks, one near 176 ppm and one near 178 ppm, appeared. The peak near 170 ppm decreased with time, while the peak near 176 ppm increased. The peak near 178 ppm increased to a low level and remained roughly steady throughout the series of experiments.

In order to make sense of this data, the species responsible for each of these NMR peaks had to be identified. Based on the shape of the curve, the resonance near 176 ppm was thought to represent the carbonyl carbons in the imide. As a verification of this belief the spectrum of a sample of N-[4-(4-Aminobenzyl)phenyl]-5-norbornene-2,3-dicarboximide (**10**) (the product of the imidization of a single molecule of NA with MDA) was acquired. Under conditions similar to those used in the kinetics experiments (dry NMP solvent, locked and referenced to d_6 -DMSO in a stem coaxial tube) the imide

carbonyl peaks from (**10**) appeared at 176.4 ppm. Based on these spectra, the peak at approximately 176 ppm was identified as the imide carbonyl carbons.

Nadic anhydride under the same conditions showed two peaks, a prominent one at 172.6 ppm and a smaller peak at 173.1 ppm. Water was added to this sample in the hope that a substantial part of the anhydride would be hydrolyzed to diacid. The resulting spectra showed almost no difference in the relative height or chemical shift of these two peaks. There was, however, a definite shoulder that appeared on the nearby peak due to the NMP carbonyl, at about 173.9 ppm. Due to the interference of the solvent peak, this experiment was repeated using d_6 -DMSO as the solvent instead of NMP. In DMSO, the main carbonyl peak was observed at 172.3 ppm, with a much smaller peak at 173.3 ppm. Upon addition of water the most prominent peak appears at 173.6 ppm, with a substantial peak at 174.9 ppm. These peaks do not appear in the kinetics spectra, although the peak at 173.6 ppm would overlap with the solvent peak and may be masked by it.

In order to determine the chemical shifts of the diacid, the ^{13}C NMR spectrum of a sample of 5-nobornene-2-endo, 3-exo-dicarboxylic acid was obtained. (**11**). The carbonyl region of the spectrum shows two peaks, at 174.0 and the other at 175.2 ppm.

A full kinetics run was performed in DMSO using the same precautions as were used for runs in NMP. This produced a much clearer picture of the carbonyl resonances, allowing a fairly confident set of assignments to be made. In this case, a peak near 176 ppm grows in over the course of the experiment. This is the imide carbonyl peak, as has been previously described. Another peak, this time at 150 ppm grows in, but plateaus rather than continuing to grow with time. This is the carbonyl carbons in the diacid, shifted in frequency compared to the same peaks in NMP. Of more interest are the two peaks at 170 and 173.5 ppm. Throughout the experiment, until they disappear into the

baseline, these peaks track each other. They remain essentially equal in area throughout the experiment. We had tentatively identified the peak at 170 ppm as arising from the amide-acid based on the experiments done in NMP, although it would not be expected that the amide and acid carbonyls would have the same chemical shift. The experiment in DMSO reveals the additional amide-acid peak that is obscured by the large NMP carbonyl peak.

With this information, the concentration of each of the important carbonyl-containing species can be calculated. Since all of the acid, ester, and imide carbonyls come from the same source, namely the nadic anhydride, it is clear that the sum of the concentrations of all of the carbonyl-containing species must equal the initial concentration of NA.

The integral data is normalized, i.e. the sum of all of the peaks selected for integration sums to 100. If the measured areas of the integrals of the peaks at 170, 176, and 178 ppm are denoted by I_{170} , I_{176} , and I_{178} , respectively, the concentration of each species can be calculated. It is important to note that because the resonance peak at 170 ppm represents only half of the carbonyl carbons in the amide-acid (the other half being obscured by the solvent peak) it is necessary to double the integral of that peak to capture the true integral of amide-acid.

$$I_{TOTAL} = 2(I_{170}) + I_{176} + I_{178} \quad (1)$$

Normalizing with the total integral and multiplying by the initial concentration of anhydride ($C_{ANHYDRIDE}$) allows the calculation of the concentrations of each species:

$$C_{AMIDE} = \left(\frac{2(I_{170})}{I_{TOTAL}} \right) C_{ANHYDRIDE} \quad (2)$$

$$C_{ACID} = \left(\frac{I_{178}}{I_{TOTAL}} \right) C_{ANHYDRIDE} \quad (3)$$

$$C_{IMIDE} = \left(\frac{I_{176}}{I_{TOTAL}} \right) C_{ANHYDRIDE} \quad (4)$$

Once the calculation of the concentrations is complete, a plot of concentration vs. time can be created for each species. Based on the shape of the curves (an example set of curves is shown in Figure 1) the data appears to indicate two irreversible reactions occurring in parallel [7], which is consistent with the two most likely reactions of the amide-acid, namely closure to form the imide and reversion to the diacid. While it is known that the diacid will reconvert to the anhydride, which will then immediately react with diamine, if this reaction rate is much smaller than the rates of the other two reactions it could be treated as being effectively irreversible. In no case was evidence of anhydride seen in any of the spectra taken once a sample had been heated. To test the assumption that no appreciable reversion of the imide to amide-acid or diacid occurs, a sample of **10** was prepared under typical reaction conditions. After heating for 80 minutes, no changes were seen in the carbonyl region of the ^{13}C spectrum.

Following the disappearance of the amide-acid with time should result in a straight line whose slope is the sum of the reaction rates leading to the imide and diacid. Plotting the concentration of the imide vs. the diacid should result in a straight line whose slope is the reaction rate for production of imide divided by the reaction rate for the production of the diacid. In the reactions studied, this latter plot did not yield a straight line, and a plot of the disappearance of amide-acid indicates that the order of the reaction changes during the course of an experiment.

A number of other researchers have noted and studied the reaction kinetics of imide formation [8-12]. There seems to be some agreement that the imidization reaction

from the amide-acid proceeds through an initial fast step and a later slower step, although there are differing views on the cause of this difference. Since the closure of the amide-acid to the imide is an intermolecular reaction, it has been argued that it should be first-order, and the initial stage of the reaction appears to be reasonably describable as a first-order reaction. For the purpose of developing a screening method for determining the relative reaction rates of diamines to imidization, analysis has been limited to this initial region.

For each dataset, the first four time / imide concentration points were plotted and a linear regression performed. The slope of the regression line was obtained, and the slopes for each diamine were averaged (Table 2).

When the averaged slopes for each diamine are compared, it becomes clear that the only diamines whose reactivity is significantly different from MDA are Co-BAX, 6F-MDA, and DABP. This conclusion is even clearer when the ^{15}N chemical shifts are plotted against the average slope. (Figure 2). A question arises concerning how to properly analyze Co-BAX. Since Co-BAX has amines with substantially different ^{15}N chemical shifts, which resonance to associate the rate with is not clear. If the assumption is made that the nitrogen nearest the methylene linkage is the one that reacts preferentially, it should show a rate that is similar to MDA. If the nitrogen nearest the carbonyl linkage were to react preferentially, one would expect a rate similar to DABP. It is interesting to note that the actual rate measured for Co-BAX is between these extremes, implying that both nitrogen atoms are involved in the reaction. In fact, if the chemical shifts of the two Co-BAX nitrogens are averaged, as was done for Figure 2, The Co-BAX rate/chemical shift correlation falls into line with the other rates.

Conclusions

Based on the correlation of the results of the kinetics data with the ^{15}N chemical shifts of the study diamines, it appears that ^{15}N NMR is a viable screening technique to determine the relative reactivity to imidization of a multi-ring aromatic diamine. Use of this technique represents a considerable savings in time and effort over a conventional kinetics study. Since the amine nitrogens have at least one proton attached, observing the ^{15}N chemical shifts by indirect methods should be possible, and should result in even greater time savings.

Because of the relative similarity of the chemical structures of the study diamines extension of this technique to arbitrary amines should be done with care, although the principle should be sound, as molecular features which change the electron density on the amine nitrogen should also affect its reactivity. In particular, none of the subject diamines were substituted on the phenyl rings, so the effect of such substitution on the rate / chemical shift correlation is unknown.

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Table 1 ¹⁵N Chemical Shifts for study diamines and their amides

Diamine	Amine	Amine Shift	Amide	Amide Shift
MDA (1)	-323.41	0.00	-248.08	0.00
BAX (4)	-323.03	-0.38	-248.10	0.02
Co-BAXa (5)	-322.68	-0.73	-248.01	-0.07
Co-BAXb (5)	-308.95	-14.46		
BIS-P (6)	-323.54	0.13	-248.24	0.16
BIS-M (7)	-323.50	0.09	-248.71	0.63
6F-MDA (8)	-318.69	-4.72	-247.62	-0.46
DABP (9)	-312.09	-11.32	-245.78	-2.30

Table 2 Slope Data for all Kinetics Experiments with averages.

Diamine	Run Number	Slope	Average Slope
MDA	3	1.62406E-05	1.9828E-05
	5	1.82275E-05	
	7	2.50159E-05	
DABP	4	7.77142E-06	7.53702E-06
	6	6.63351E-06	
	8	8.20613E-06	
6F-MDA	11	1.38987E-05	1.59468E-05
	18	1.65916E-05	
	21	8.42144E-06	
	22	2.48755E-05	
BAX	9	1.26485E-05	1.9803E-05
	15	1.56093E-05	
	16	2.31215E-05	
	30	2.78327E-05	
CoBAX	10	1.33925E-05	1.25836E-05
	19	1.15955E-05	
	24	1.27628E-05	
BIS-M	13	2.13952E-05	1.90541E-05
	20	1.00522E-05	
	23	2.57149E-05	
BIS-P	12	1.21086E-05	1.92119E-05
	14	2.1258E-05	
	17	1.63847E-05	
	31	2.70964E-05	

Figure Captions

Figure 1 – Typical concentration vs time curve for amide, imide, and diacid peaks

Figure 2 Correlation of Chemical Shift with Reaction Rate for the Study Diamines

Concentration vs time for amide, imide, and diacid peaks
Run 5 (MDA)

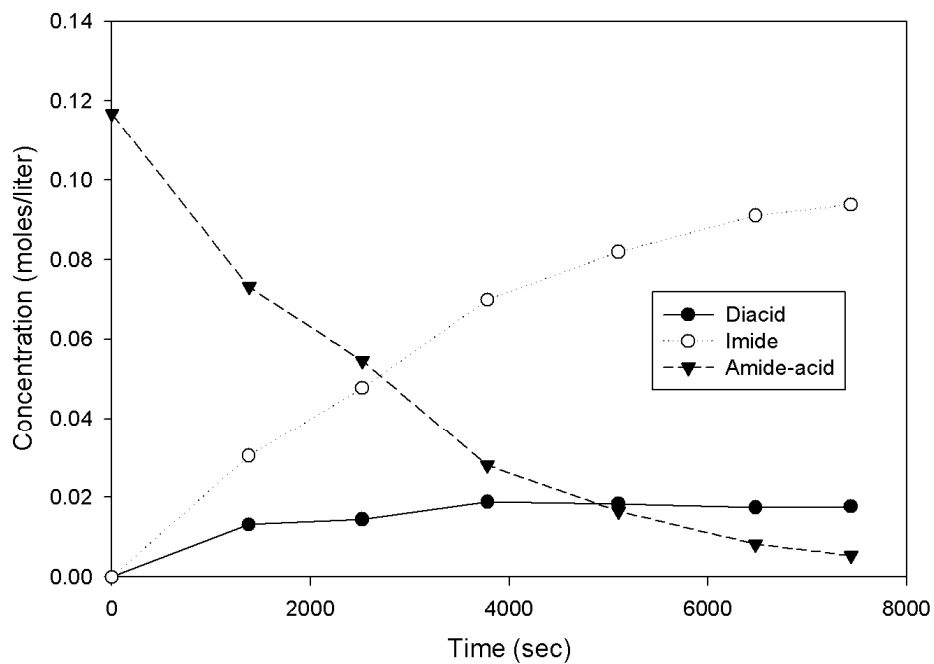


Figure 1

Chemical Shift vs. Imidization Rate for all Diamines
Using Averaged Chemical Shift for CoBAX

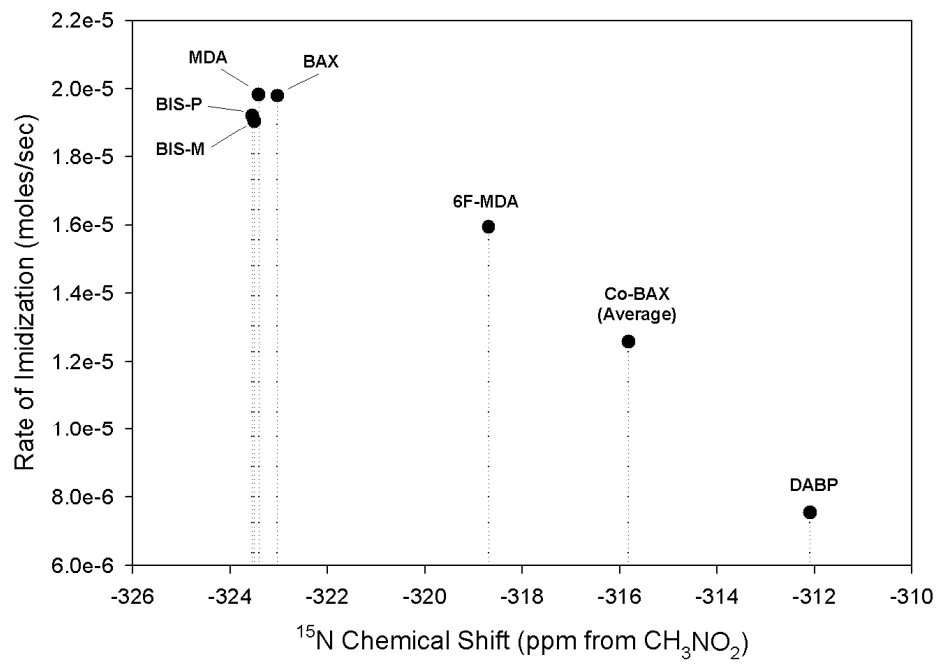
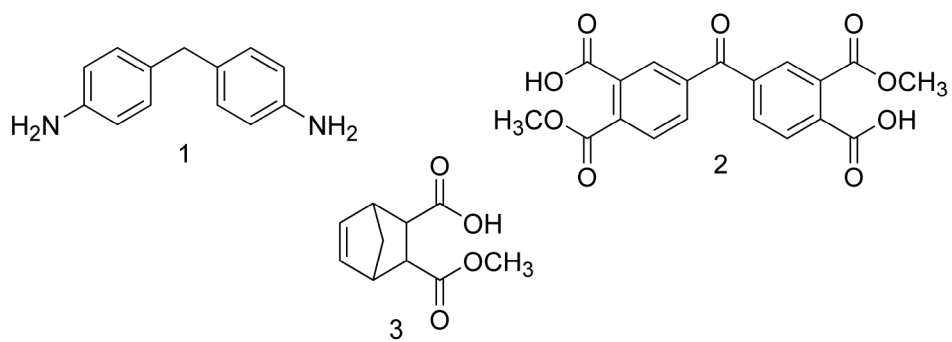


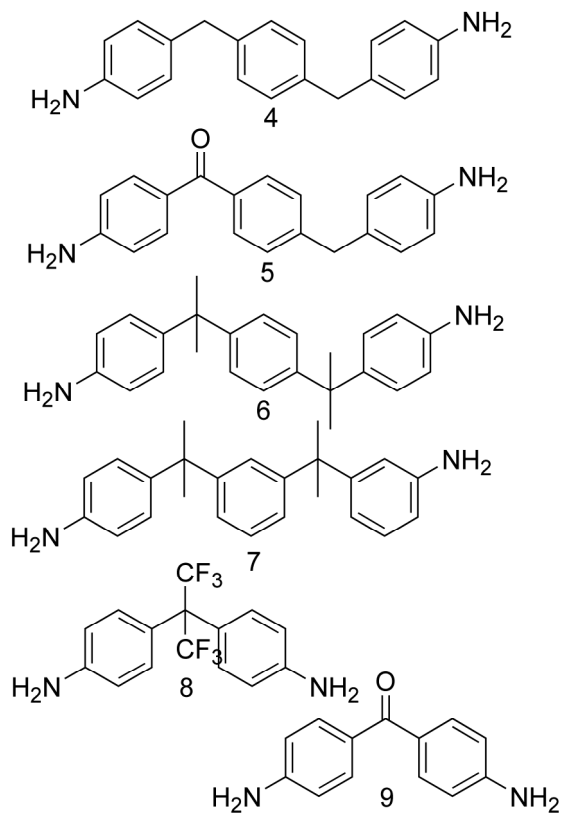
Figure 2

Chemical Structure Diagrams

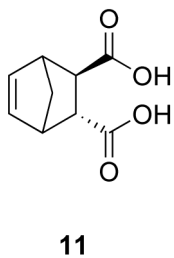
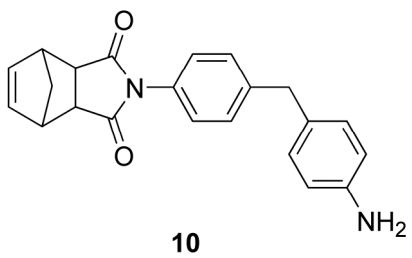
- 1: PMR-15 monomers
- 2: Study Diamines
- 3 Additional Structures



PMR-15 Monomers



Study diamines



Additional Structures