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SYNTHESIS OF IMPROVED MOISTURE RESISTANT POLYMERS

BY

M. K. O'RELL

TRW

DEFENSE AND SPACE SYSTEMS GROUP

ONE SPACE PARK · REDONDO BEACH · CALIFORNIA

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA LEWIS RESEARCH CENTER

CONTRACT NAS3-21011

PETER DELVIGS, PROJECT MANAGER

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FOREWORD

This document constitutes the final report for the work accomplished between 24 June 1977 and 24 August 1978 by TRW Defense and Space Systems Group for the National Aeronautics and Space Administration, Lewis Research Center, under Contract NAS3-21011 on Synthesis of Improved Moisture Resistant Polymers. This work was conducted under the technical direction of Dr. Peter Delvigs of the Lewis Research Center, Cleveland, Ohio.

The Chemistry Department of the Chemistry and Chemical Engineering Laboratory was responsible for the work performed on this program. Dr. R. J. Jones, Assistant Manager, Chemistry Department, provided overall program supervision and Mr. M. K. O'Rell was Program Manager. Acknowledgement is made of the technical contributions of Mr. R. W. Vaughan and technical assistance of Mr. J. M. Hom and Mr. J. N. Kennedy.

SUMMARY

The use of difluoromaleimide-capped prepolymers to provide improved moisture resistant polymers was investigated. Six different prepolymer formulations were prepared by two different methods. One of the methods utilized the PMR approach to polyimides and the other method employed the normal condensation route to provide fully imidized prepolymers. Polymer specimens cured at 505K (450°F) exhibited adequate long-term stability in air at 477K (400°F). Moisture absorption studies were conducted on one polymer formulation. Neat polymer specimens exhibited weight gains of up to 2% (w/w) after exposure to 100% relative humidity at 344K (160°F) for 400 hours.

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I. INTRODUCTION

Structural nonmetallic composites have gained wide acceptance in aerospace materials applications. It is expected that composite components will continue to assume an even greater role in future aircraft designs because of the potential improvements in system performance and weight/cost savings offered by these materials. Composites derived from epoxy resin matrices and fibrous reinforcements such as graphite and boron have found the greatest number of applications. However, concern has arisen over the use of epoxy based composites for certain use applications because it has been shown that the high-temperature properties of epoxy based composites are adversely affected by absorbed atmospheric moisture.

The effect of moisture on epoxy resins was first observed by investigators at General Dynamics Corporation under a NASA contract (Reference 1) and property degradation was attributed to absorption of moisture by the epoxy resin matrix. Since the initial discovery of this phenomenon, several other workers have substantiated the effect of absorbed moisture on composite properties at elevated temperature. It has been shown as a result of this work that there are two modes of property degradation:

(1) Initial reversible degradation resulting from plasticization of the epoxy resin matrix by the absorbed moisture

(2) Permanent degradation resulting from micro-cracking in the epoxy resin matrix.

Work performed by the Air Force (Reference 2) showed that the initial degradation can be predicted in neat epoxy resin castings based on standard diffusion models. However, the permanent degradation observed in composites cannot be predicted in a straightforward fashion and is influenced by thermal peaks during exposure (Reference 3). Consequently, it is apparent that in order to provide composite structures that do not undergo severe moisture degradation, the matrix resin must be improved.

Two different approaches may be employed to provide an improved matrix resin. First, the epoxy matrix may be modified to make it more hydrophobic and thereby reduce the influence of moisture. In the second approach, a

matrix resin other than an epoxy is used which has improved moisture resistance. However, to be a viable replacement resin, the new resin system should possess processing requirements similar to those of an epoxy.

The second approach to an improved moisture resistant polymer was investigated in the work described in this final report. The basic resin system investigated was derived from difluoromaleimide capped prepolymers. The imide family of polymers was selected for investigation because of their improved moisture resistance over epoxy resins (Reference 4). In addition, a maleimide resin was selected because of the low cure temperature 477 to 505 K (400 to 450°F) as compared to most condensation and addition curing polyimides.

The polymers evaluated in this study were prepared by two different synthetic approaches. One set of polymers was prepared by the PMR (Polymerization of Monomeric Reactants) approach to polyimides, originally developed by NASA-Lewis personnel, in which the monomers (a diamine and two ester-acids) are mixed in alcohol. At slightly elevated temperatures, the diamine reacts with the ester-acids to form amide-acid linkages and at higher temperatures [>323K (122°F)] the amide-acid is converted to an imide moiety. Subsequent cure of the prepolymer yields the desired polymer.

The second approach employed to prepare polymer samples involved the synthesis of fully imidized prepolymers (same compositions as in the PMR approach), which were subsequently cured to give imide based polymers. The imidized prepolymers were prepared by dehydrating the amide-acid precursors under mild conditions in solvent (as opposed to in the melt as in the first approach). The advantage of the second approach was the elimination of volatile formation during cure.

Six different polymer formulations were prepared during the course of the program. The different formulations were obtained by varying the structure of the dianhydride and diamine. All of the polymer samples prepared during the course of the program were found to possess long-term service capability at 477 K (>400°F) as assessed by isothermal aging. Because of difficulties encountered in monomer and polymer synthesis, only limited moisture absorption data were obtained on one of the six formulations. Humidity aging studies were conducted at 344 K (160°F) at 95% and 100% relative humidity. Weight gains of up to 2% (w/w) were observed. Molding of neat polymer specimens derived from the PMR approach was difficult because of volatile evolution during cure.

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II. TECHNICAL DISCUSSION

The objective of this work was to develop new polyimide matrix resins with improved moisture resistance compared to state-of-the-art epoxy resins. The new resins were to have a cure temperature of less than 533K (500°F) and long-term service capability at >477K (400°F). The approach used to meet these objectives was to use difluoromaleic anhydride as a reactive end-cap in a prepolymer approach to polyimide resins. Six different prepolymer formulations were prepared and cured during the polymer screening activities. Screening of candidate formulations was performed by measuring their thermo-oxidative stabilities by thermogravimetric analysis (TGA) and by long-term isothermal aging at 477 K (400°F). Limited moisture resistance data were obtained on one formulation by aging neat resin samples in 95% and 100% relative humidity environments at 344 K (160°F).

2.1 MONOMER SYNTHESIS

Six different monomers were used to prepare the candidate polymer formulations studied on this program. Specifically, two dianhydrides, three diamines and a reactive end-cap were employed. The structures of these compounds are shown in Figure 1. Selection of these monomers was based on the expectation that they would yield a series of prepolymers with widely varying properties such as solubility, melting point and decomposition temperature. Of the six monomers, 3,3',4,4'-benzo-phenonetetracarboxylic acid dianhydride (BTDA) and 4,4'-methylene dianiline (MDA) are commercially available. A sample of *m,m'*-methylene dianiline prepared by NASA Langley personnel was available because of previous work with the compound. A limited quantity of difluoromaleic anhydride was on hand at TRW DSSG prior to initiation of this program. Consequently, synthetic studies conducted were devoted to the preparation of 2,2-*bis*-[4-(3,4-dicarboxyphenoxy)phenyl] hexafluoropropane dianhydride (BFDA) 2,2-*bis*[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF) and difluoro-maleic anhydride (DFMA). These activities are discussed in the following sections.

2.1.1 Preparation of 2,2-*bis*[4-(3,4-dicarboxyphenoxy)phenyl] hexafluoro-propane dianhydride (BFDA)

The synthesis route employed to prepare BFDA is shown in Figure 2 and is based on previous work performed under company funding. In general,
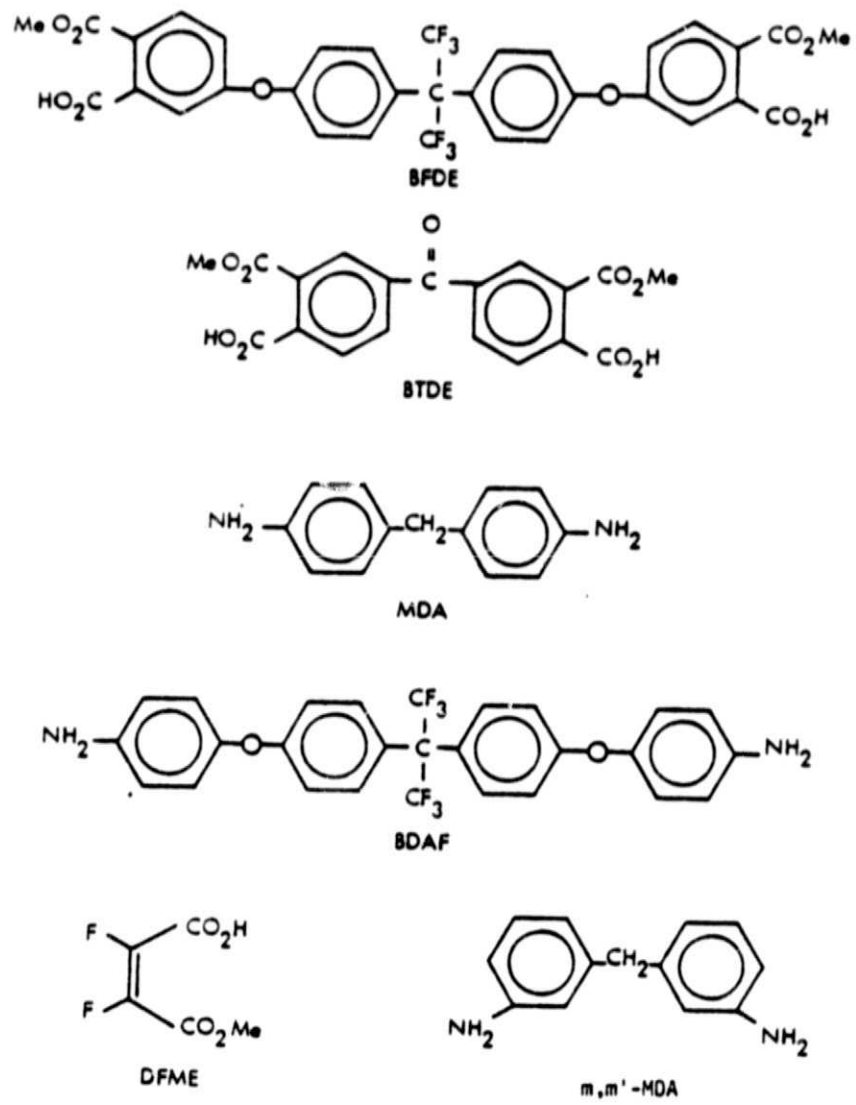
3

Figure 1. Structures of Monomeric Ingredients
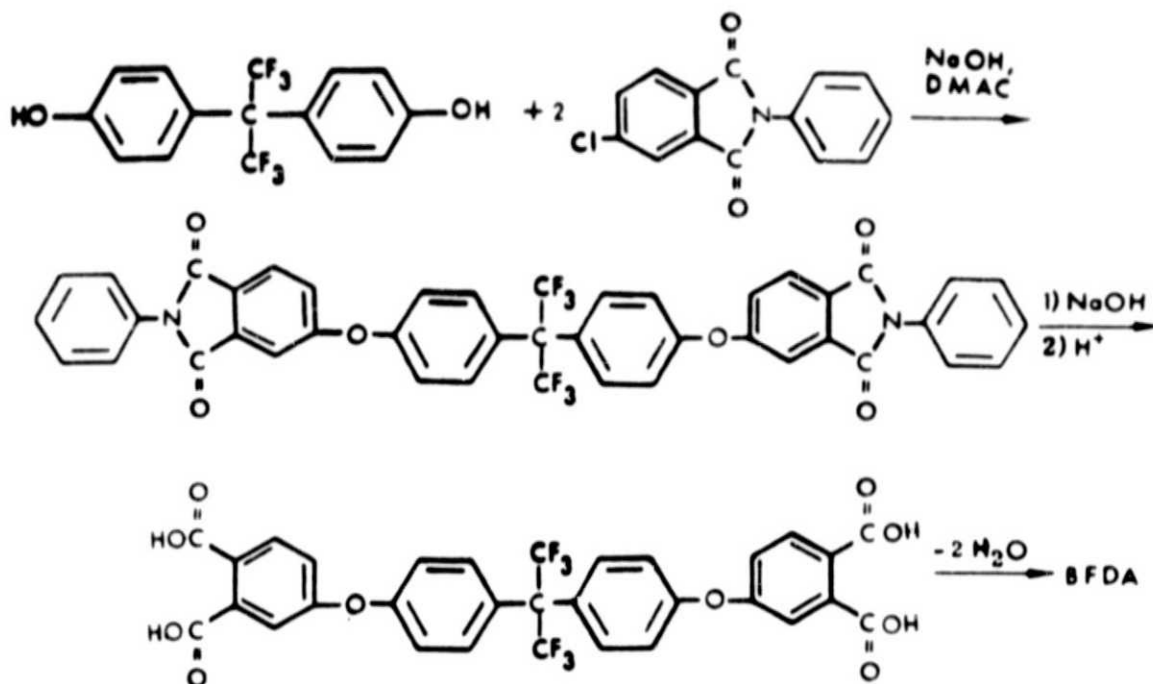
Figure 2. Synthesis Route to BFDA

the synthesis route involves the aromatic nucleophilic displacement of
chloride ion from 4-chloro-N-phenyl phthalimide by a phenoxide followed
by hydrolysis of the imide group under basic conditions to give, upon
acidification, a tetraacid. Dehydration of the tetraacid yields the
desired dianhydride.

The phenol, 2,2-*bis*(4-hydroxyphenyl) hexafluoropropane, was purchased
from Dupont under the trade name of Bisphenol AF. 4-Chloro-N-phenyl-
phthalimide was synthesized from monosodium-4-chlorophthalate and aniline
as described in the Appendix. To perform the displacement reaction, the
phenoxide was prepared by adding sodium hydroxide to a solution of
Bisphenol AF in dimethylacetamide. Water was removed from the solution
by azeotropic distillation with toluene and then the chlorophthalimide
was added. The displacement reaction was conducted at 423K (302°F) for
96 hours and crude *bis*imide was isolated by adding the reaction mixture to
a methanol-water mixture. Purification of the *bis*imide was first attempted
using aqueous acetone as the recrystallization solvent. The product

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obtained was an off-white solid with a broad melting point [417 to 425K (291 to 306°F)]. The melting point of this material was considerably lower than the melting point (482 to 486K) observed for this compound during previous work at TRW. Repeated recrystallization from isopropanol failed to improve the melting point. An acceptable elemental analysis was obtained for the *bis*imide and the depressed melting point was attributed to presence of isomers. The isomers apparently result from isomers present in the Bisphenol AF starting material.

The *bis*imide was hydrolyzed with refluxing aqueous sodium hydroxide. Aniline was removed during the hydrolysis period by steam distillation. Acidification of the hydrolysis mixture afforded the tetraacid in 80% yield. Dehydration of the tetraacid was accomplished by refluxing a mixture of the tetraacid in acetic anhydride.

2.1.2 Preparation of 2,2-*bis*[4-(4-aminophenoxy)phenyl]hexafluoropropane (BDAF)

The synthesis route to 2,2-*bis*[4-(4-aminophenoxy)phenyl]hexafluoropropane was similar to that used to prepare BFDA (Section 2.1.1). As shown in Figure 3, a nucleophilic displacement reaction of chloride from 4-chloronitrobenzene was used to prepare the dinitro precursor of BDAF. The displacement reaction occurs at a much faster rate in this case due to the activation of the chlorine group by the nitro group. Reduction of the dinitro compound to the diamine was accomplished with iron/acid. Experimental details are presented in the Appendix (Section A.2).
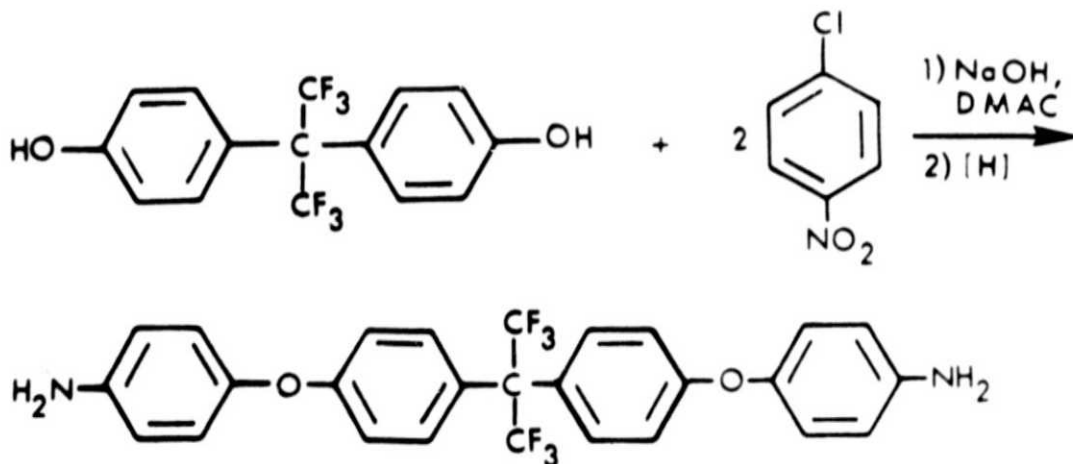

Figure 3. Synthesis Route to 2,2-*bis*[4-(4-aminophenoxy)phenyl]hexafluoropropane

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2.1.3 Preparation of Difluoromaleic Anhydride (DFMA)

A limited supply of difluoromaleic anhydride was already on hand at TRW DSSG prior to initiation of this program. It had been prepared in low yield by a multi-step synthesis scheme (Reference 5). During the course of this program studies were conducted to identify a different synthesis route to this monomer. The route selected for investigation was that of Kobrina, *et al*, (Reference 6) in which pentafluorophenol is oxidized with peracetic acid at elevated temperature.

Repeated experimental runs employing the reported oxidation conditions yielded small amounts (<20% yield) of a substance that appeared to be difluoromaleic acid. The products resulting from these attempts were combined and treated with refluxing trifluoroacetic anhydride. The infrared spectrum of this material was very similar to that of difluoromaleic anhydride. Further purification of the product was not undertaken because of the limited amount (~2 g) of material that would have been isolated and also because of time and funding limitations. It was concluded from these experimental activities that this synthesis scheme has some merit for producing DFMA but that additional experimental work must be conducted to improve the reaction yield.

2.2 POLYMER STUDIES EMPLOYING THE PMR APPROACH

The PMR approach to polyimides was used to prepare the initial polymer samples on this program. The major advantage of this approach is the use of a low boiling alcohol (methanol for these studies) as a solvent which makes solvent removal a very facile process. Use of the PMR technology was thought to be a viable approach with this system because it appeared from previous in-house studies that the amide-acid of difluoromaleic acid was easily converted to the desired maleimide structure under mild conditions. Apparently, this is not the case for maleic anhydride which requires the use of chemical dehydration to give the maleimide.

2.2.1 Prepration of Monomeric Mixtures

The six candidate formulations prepared and evaluated are presented in Table 1. Structures of the monomers referred to in Table 1 are shown in Figure 1. As was discussed earlier, these combinations of ingredients

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Table 1. Candidate PMR Polyimide Systems Studied

Monomeric Reactants	Candidate Systems					
	1	2	3	4	5	6
Aromatic Diacid-Diester						
BFDE	X	X	X			
BTDE				X	X	X
Aromatic Diamine						
MDA	X			X		
BDAF		X			X	
m,m'-MDA			X			X
End-Cap Crosslinker						
DFME	X	X	X	X	X	X

X   indicates that the reactant was used in the formulation

were selected to provide prepolymers possessing different processing characteristics such as melting point, flow properties and gel time.

The six candidate prepolymers that were formulated employed a 2:2:1 molar ratio of end-cap:diamine:diacid-diester, respectively. The general procedure used to prepare the monomeric mixtures is given below. Specific procedures are given in Appendix B. The diester portion of the formulation was prepared by refluxing the appropriate dianhydride in methanol for four hours at a 30% w/w solids loading. Separately, a 30% w/w solids solution in methanol was prepared from the appropriate diamine and DFME. The diester solution and diamine/DFME solution were mixed, then the solvent was allowed to evaporate. Removal of the last traces of solvent was performed *in vacuo* at 313 K to give a dry powder.

2.2.2 Preliminary Cure Studies on PMR Mixtures

Initial characterization of the cure cycle of the PMR mixtures was performed by thermogravimetric analysis. An initial scan was run in nitrogen on the PMR mixture up to a maximum of ∿533 K to identify the thermal

regimes where loss of methanol, water and other volatile matter occurs. The sample then was allowed to cool to room temperature and a second TGA scan was run in air to assess the polymer's thermooxidative stability.

The TGA scan of the monomeric mixture composed of BFDE/2*m*,*m*'-MDA/2DFME is shown in Figure 4 and is representative of the results obtained for the other samples. A 20% (w/w) weight loss was observed over the temperature range of 373 K to 523 K. This temperature range corresponds to the range normally associated with prepolymer formation (methanol loss) and subsequent imidization (water loss). For this particular formulation, the theoretical weight loss for these two reactions is 15% (w/w) and the measured loss was 20% (w/w). The additional weight loss was attributed to residual solvent and absorbed moisture.

As can be seen in Figure 4, the sample obtained after heating the monomeric mixture in nitrogen displayed promising thermooxidative stability. An initial weight loss was observed at 548 K and only a 5% loss was recorded at 713 K.

A brief study was also conducted to determine the temperature at which the onset of cure occurs, in these mixtures. A sample of the monomeric mixture was subjected to Differential Scanning Calorimetry (DSC) analysis to define the cure exotherm. Unfortunately, the volatiles that were created during prepolymer formation masked this region of the DSC scan. Preliminary evidence that cure occurs between 477 K and 505 K was obtained by heating a sample of the mixture on a Fisher-Johns melting point apparatus. A gel was obtained in the temperature range for each of the samples indicating cure was taking place. Based on this preliminary information, it was decided to cure larger samples of the six candidate formulations to permit additional characterization.

Cure of the PMR monomeric mixture was accomplished by a two-step heating process in a forced-air oven. Initial heating was conducted at 423 K for 30 minutes to promote formation of the prepolymer. It was presumed that this temperature would be sufficiently low to prevent cure. Final cure was performed by placing the sample in a 505 K (450°F) oven for one hour. The resultant samples were dark brown foams indicating that evolution of volatiles occurred during the cure cycle.
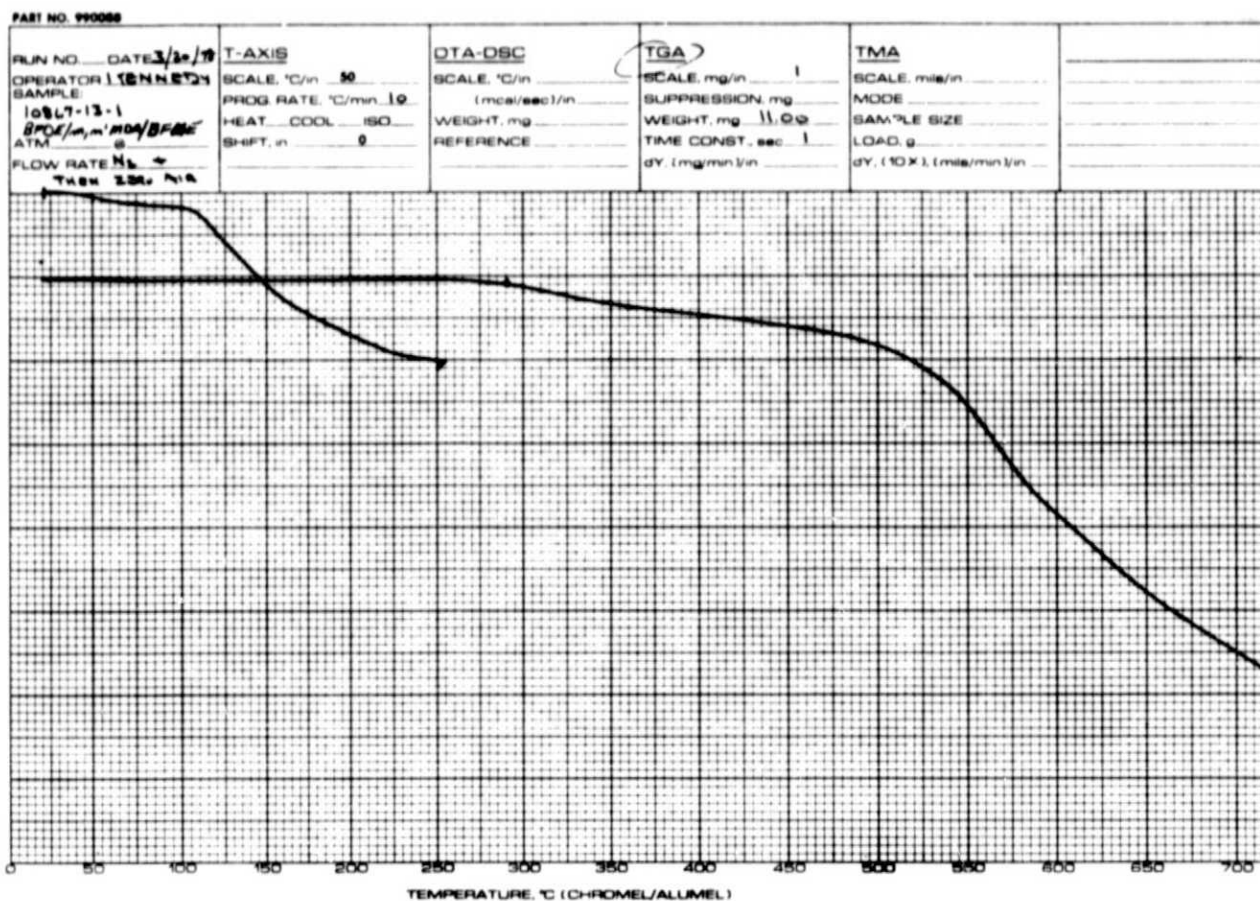
Figure 4. TGA Scan of BFDE/2m,m'-MDA/DFME Monomeric Mixture in Nitrogen and Then in Air

The observed weight losses for the two-step cure are reported in Table 2. These data support the visual observation that volatiles were formed during the heating cycle at 505 K. The infrared spectrum for the BFDE/2MDA/2DPME derived polymer is shown in Figure 5. The solubility data confirm that a high degree of cure (cross-link formation) was obtained. The results of the TGA characterization of these polymers indicated that they possessed sufficient thermo-oxidative stability to meet the program objective. A TGA scan for BFDE/2MDA/2DFME is shown in Figure 6. However, the initial thermo-oxidative properties were inferior to those obtained in prior work conducted on this type of system when the polymers were derived from fully imidized prepolymers that were prepared in solution.

Table 2. Characterization of Cured PMR Candidate Samples[a]

Sample No.	Constituents	Wt. Loss at 423 K, % w/w	Wt. Loss at 505 K,[b] % w/w	Temp. of Initial Wt. Loss in TGA, K	Solubility in DMF
1	BFDE/MDA/DFME	12.1	10.6	533	Insoluble
2	BFDE/m,m'-MDA/DFME	12.0	10.6	523	Insoluble
3	BFDE/BDAF/DFME	12.2	5.0	533	Insoluble
4	BTDE/MDA/DFME	13.3	14.9	523	Insoluble
5	BTDE/m,m'-MDA/DFME	15.0	13.9	578	Insoluble
6	BTDE/BDAF/DFME	13.4	15.6	533	Insoluble

[a] Cured by following cycle: 30 min. at 423 K followed by 60 min. at 505 K.

[b] Based on weight of original monomeric mixture

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OF POOR QUALITY
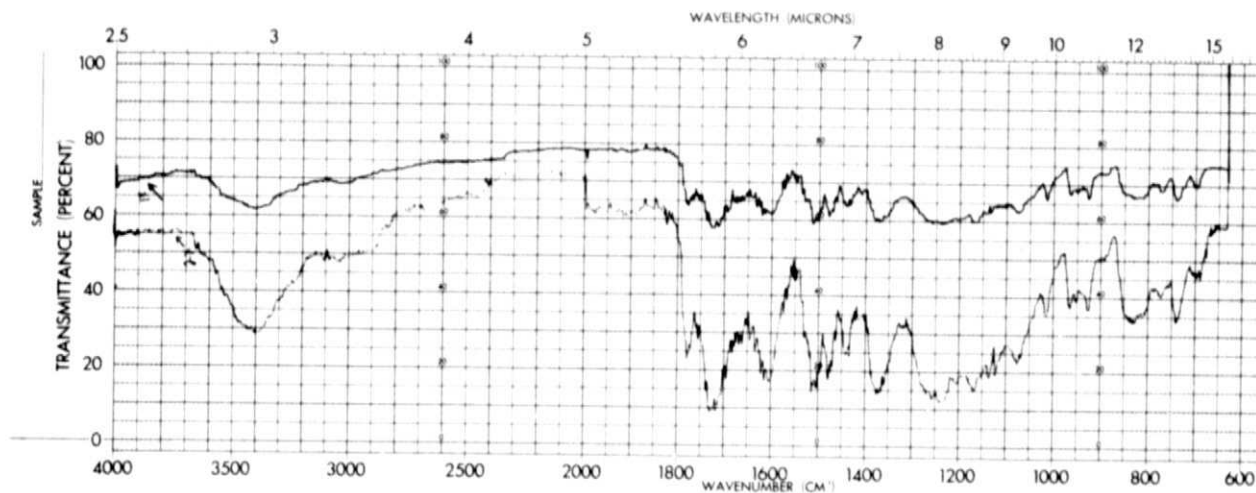
Figure 5. Infrared Spectrum (KBr) of Cured Polymer Derived From BFDE/2MDA/2DFME

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RUN NO. DATE 4/19/78	T-AXIS	DTA-DSC	TGA	TMA
OPERATOR J SENNABAY	SCALE, °C/in 50	SCALE, °C/in	SCALE, mg/in	SCALE, mils/in
SAMPLE: 10867.12-1	PROG. RATE, °C/min 10	(mcal/sec)/in	SUPPRESSION, mg	MODE
BFDE/2MDA/2DFME	HEAT COOL ISO	WEIGHT, mg	WEIGHT, mg 13.50	SAMPLE SIZE
ATM	SHIFT, in 0	REFERENCE	TIME CONST., sec 1	LOAD, g
FLOW RATE ZERO AIR			dY, (mg/min)/in	dY, (10 X), (mils/min)/in

Figure 6. TGA Scan in Air of Cured BFDE/2MDA/2DFME Formulation

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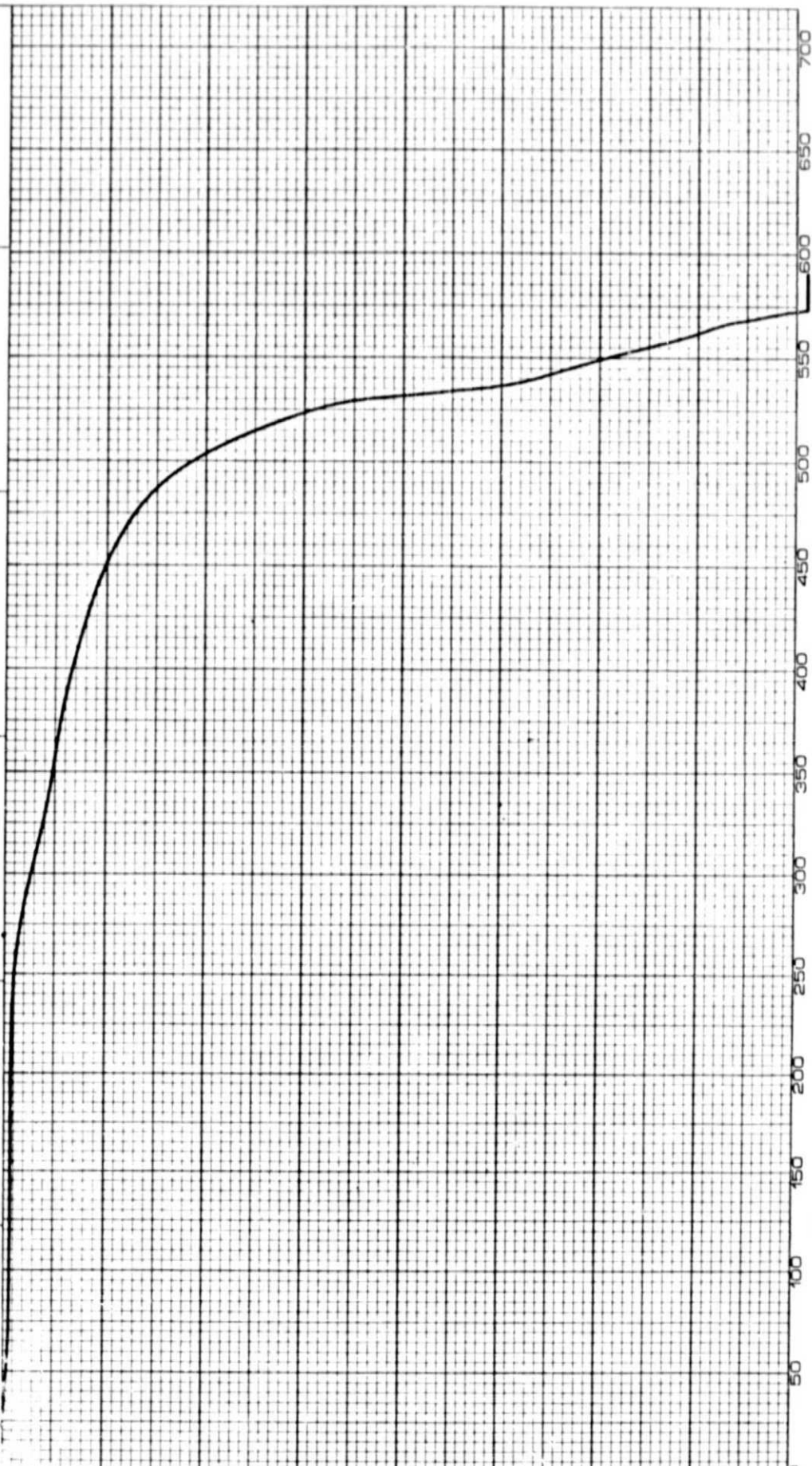A study then was conducted to determine the effect of cure time on the thermo-oxidative properties of the polymers. The BTDE/2MDA/2DFME formulation was employed for this study. A sample of the monomer mixture was heated from ambient to 428 K over a 30-minute period and then maintained at that temperature for 1 hour to promote prepolymer formation. The resultant solids then were heated up to 498 K and held at that temperature for 2, 4 and 6 hours. Analysis of the samples was performed by TGA. The results of this cure study are presented in Table 3. It can be seen from the data that there was additional weight loss as the cure time was increased. Only a slight increase in the temperature at which the initial weight loss in the TGA occurs was obtained. However, the temperature at which 10% by weight of the sample was lost increased significantly. Based on these results, it was concluded that a longer cure time or a postcure would result in polymers with improved thermo-oxidative properties.

Table 3. Effect of Cure Time on PMR Derived BTDE/2MDA/2DFME Formulation

Sample No.	Cure Time,[a] hr	Wt.Loss During Cure % w/w	Temperature of Initial Weight Loss in TGA, K	Temperature of 10% (w/w) Weight Loss in TGA, K
1	2	26.5	518	623
2	4	28.8	533	708
3	6	29.6	533	743

[a] Time at 498 K

2.2.3 Isothermal Aging Results For PMR Derived Polymers

The six candidate polymer samples prepared *via* the PMR approach to polyimides (Section 2.2.2) were characterized for long-term thermo-oxidative stability by isothermal aging at 477 K (400°F) in a forced air oven. The samples were prepared at n = 1 stoichiometry and cured at 505 K for 1 hour. The resultant specimens were powdered prior to aging. The results of the isothermal aging are presented in Table 4. It is evident that all of the candidates possess good long-term thermo-oxidative stability at 477 K. Three of the samples appear to be more stable as based on the weight

Table 4. Results of Isothermal Aging of PMR Derived
Polymers[a]

Sample No. (Formulation)	% Weight Loss					
	68 hr	116 hr	308 hr	550 hr	830 hr	990 hr
1. BFDE/2p,p'-MDA/2DFME	2.3	2.3	3.6	4.3	5.2	5.5
2. BFDE/2m,m'-MDA/2DFME	5.1	5.1	6.2	7.2	8.0	8.3
3. BFDE/2BDAF/2DFME	1.8	1.8	2.7	3.4	3.8	4.1
4. BTDE/2p,p'-MDA/2DFME	5.0	5.0	7.0	7.9	8.5	8.9
5. BTDE/2m,m'MDA/2DFME	4.4	4.4	6.2	7.5	7.8	8.1
6. BTDE/2BDAF/2DFME	2.3	2.3	3.6	4.5	4.9	5.1

[a]400°F, Forced air oven, powdered samples.

loss data. The results are also presented graphically in Figure 7. It
should be noted that after 68 hours the weight losses were almost equal
for all of the samples. The initial losses before 68 hours may have
resulted from additional cure (dehydration) or loss of absorbed water.

2.3 PREPARATION AND CURE OF IMIDIZED PREPOLYMERS

Due to problems encountered in molding neat resin specimens from the
PMR derived prepolymers and because the overall thermo-oxidative properties
of the PMR derived polymers were lower than observed for polymers obtained
from fully imidized prepolymers, it was decided that the six polymer can-
didates should be prepared from imidized prepolymers prepared in solvent.
The samples were prepared as outlined in the following paragraph.

The dianhydride (either BFDA or BTDA) was added to a solution of the
diamine in toluene/DMF and then the amide acid was thermally imidized at
reflux temperature. To the imide/amine was added the end-cap (DFMA) and
this imide/amide-acid compound was imidized with acetic anhydride at $\sim$343 K.
The prepolymer precipitated from solution by adding the reaction mixture
to methanol. The infrared spectrum of the prepolymer composed of BFDA/
2m,m'-MDA/2DFMA is shown in Figure 8. The strong carbonyl bands for the
imide linkage are evident at 1715 cm^{-1} and 1775 cm^{-1} indicating that
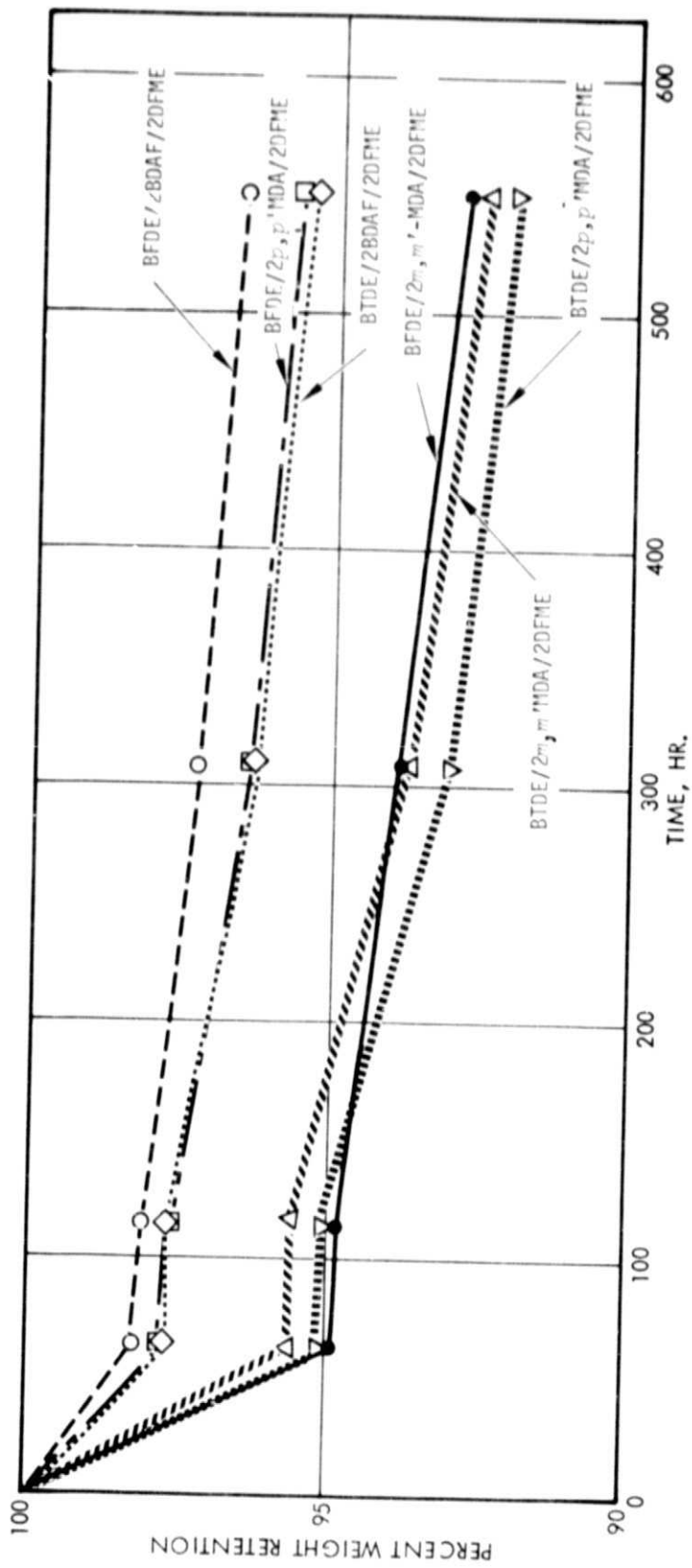imidization occurred.

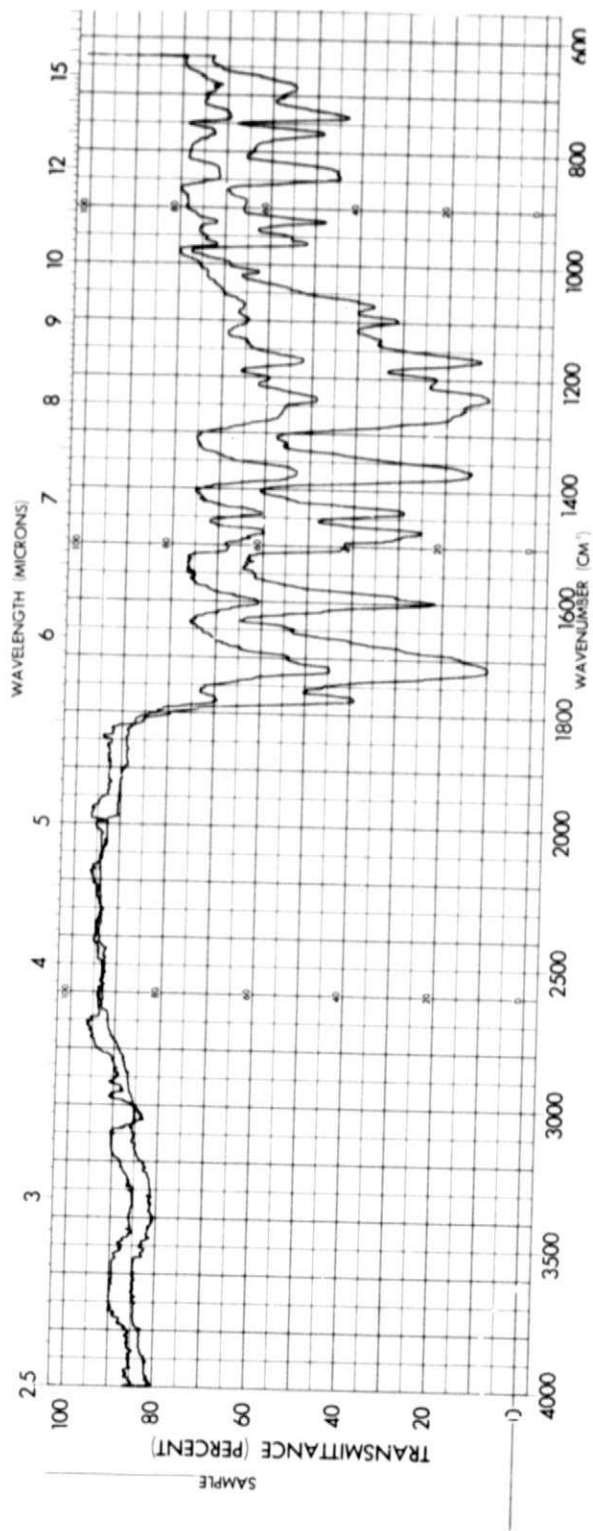Figure 7. Weight Retention of PMR Derived Samples During Isothermal Aging

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Figure 8. Infrared Spectrum (KBr) of BFDA/2m,m'-MDA/2DFMA Prepolymer

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Samples of the prepolymers were characterized by DSC in an attempt to more fully define the prepolymer melting point range and in particular, the cure temperature. As an illustration, the DSC scan of BFDA/2*m,m'*-MDA 2DFMA is shown in Figure 9. The scan shows that the prepolymer melts over a broad temperature range with the maximum of the endotherm occurring at 418 K (293°F). A sharp exotherm representative of cure is not present in the scan but it appears that cure initiates near 473K (392°F). These observations were confirmed on a Fisher-Johns hot-stage. The prepolymer sample was found to be fluid at 418K (293°F) and gelled at 503K (446°F) during heatup.

A screening study also was conducted to assess the solubilities of the prepolymers in various solvents. It was found that the prepolymers were partially soluble in methyl ethyl ketone, acetone and 2-propanol They were not soluble in methanol, ethanol or toluene. Solubility was displayed in tetrahydrofuran and dioxane.

Based on the above results relative to the apparent cure temperatures, samples of the prepolymers were cured at 494K (430°F) for 90 minutes in a forced air oven. The resultant polymer samples were rigid foams indicating that sample outgassing occurred during cure. TGA showed that the samples possessed about the same thermo-oxidative stabilities as observed for the polymers prepared *via* the PMR methodology. That is, the samples lost about 10% weight at 723K (842°F) and the main inflection point is around 783K (950°F).

Isothermal aging studies were performed on these samples at 477K (400°F). Again the samples were powders to permit direct comparison of these results with those obtained for the PMR derived polymer samples. Between the 210-hour and 450-hour weight loss measurements, the oven temperature inadvertently increased to 508 K (455°F). As a result, higher weight losses were observed at 450 hours and at subsequent measurement points. It is noteworthy that three of the samples displayed less than a 10% weight loss even after exposure to the higher temperature.

2.4 MOLDING OF NEAT POLYMER SPECIMENS

A brief study was undertaken to mold neat resin specimens from the PMR monomeric mixtures. The formulation selected for these studies was BFDE/2BDAF/2DFME. Selection of this formulation was based upon the very promising isothermal aging data.

PART NO. 990088

RUN NO. _____ DATE _____	T-AXIS	DTA-DSC	TGA	TMA
OPERATOR _____	SCALE, °C/in **50**	SCALE, °C/in	SCALE, mg/in	SCALE, mils/in
SAMPLE: **BFDA/M.M.¹**	PROG. RATE, °C/min **10**	(mcal/sec)/in **1**	SUPPRESSION, mg	MODE
MDA/DFMA 10867-26	HEAT COOL ISO	WEIGHT, mg **11.2**	WEIGHT, mg	SAMPLE SIZE
ATM _____	SHIFT, in **0**	REFERENCE	TIME CONST., sec	LOAD, g
FLOW RATE, N₂			dY, (mg/min)/in	dY, (10×), (mils/min)/in

TEMPERATURE, °C (CHROMEL/ALUMEL)

Figure 9. DSC Scan of BFDA/2m,m'-MDA/2DFMA Prepolymer

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Table 5. Results of 477K (400°F) Isothermal Aging of
Polymers Prepared From Fully Imidized Prepolymers

Sample No., Formulation	Weight Loss, Percent (w/w)						
	20 hr	60 hr	120 hr	210 hr	450 hr[a]	810 hr	1480 hr
1. BFDA/2p,p'-MDA/2DFMA	0.8	1.3	2.0	2.3	5.9	7.6	9.4
2. BFDA/2m,m'-MDA/2DFMA	1.4	1.9	2.3	2.3	4.9	7.2	8.8
3. BFDA/2BDAF/2DFMA	2.7	3.5	4.1	4.1	8.8	9.6	12.4
4. BTDA/2p,p'-MDA/2DFMA	4.5	5.6	6.0	6.1	12	16.9	20.5
5. BTDA/2m,m'-MDA/2DFMA	5.0	5.8	6.1	6.1	10	13.6	16.7
6. BTDA/2BDAF/2DFMA	2.3	3.2	3.4	3.5	5.9	7.6	9.5

[a] Temperature inadvertently increased to 508 K (455°F) between 210 hr and 450 hr.

The mold used for this work was a 2.54-cm circular mold. The three
processing conditions and the results obtained for each are discussed
below.

A charge of 2.5 g of prepolymer [prepared by heating monomeric mixture
at 423K (302°F) for 25 minutes] was placed in the cold mold and then the
mold was inserted into a preheated press at 477K (400°F). The mold was
closed with 6.9 MPa (1000 psi) pressure and held for 2 minutes. Then the
press was opened and no apparent volatiles were observed. The press was
closed with 6.9 MPa (1000 psi) pressure. Mold temperature reached 422K
(300°F) after 10 minutes, and then the part was bumped twice. The part
was bumped two more times over a 30-minute period while the mold tempera-
ture increased to 455K (360°F). Then pressure was increased to 27.6 MPa
(4000 psi) for 1 hour at 472K (390°F). When removed from the press, the
mold expanded indicating additional volatile formation had occurred. The
mold was returned to the press and cure was extended to 1 hour minimum at
486K (415°F) and 27.6 MPa. The mold was removed hot after the 1-hour cure.
The resultant part was well consolidated except for some small craters on
one face.

In a second attempt to mold a void-free specimen, the mold was pre-
heated to 450K (350°F). The part was bumped repeatedly during heatup to
486K (415°F) and after 1 hour at this temperature the mold was removed
from the press. The mold immediately expanded and a sponge-like specimen
resulted.

To reduce the amount of volatiles formed during the molding operation, the prepolymer was heated at 472K (370°F) for 2 minutes to advance the resin. The resultant prepolymer was loaded into a preheated mold [477K (400°F)] and the mold was placed in a preheated press, platen temperature 505K (450°F). The part was bumped four times during the first 4 minutes and then the pressure was set at 27.6 MPa. The mold temperature was maintained at 486K (415°F) and the pressure was increased to 69 MPa (10,000 psi) after 20 minutes and held for 10 minutes. The press heaters were turned off and the mold was allowed to cool to 366K (200°F) before the mold was removed from the press. In this instance the part was void-free except for one small blister on one face.

2.5 MOISTURE ABSORPTION STUDIES

Moisture absorption studies were conducted on molded neat polymer specimens at 344 K (160°F) at two different relative humidities, 95% and 100%. Fabrication of the molded polymer specimens used in this study was discussed in the preceding section. To conduct the moisture absorption studies, the two acceptable specimens were cut in half to provide identical samples for aging under the two different humidity conditions. Specimen A, the first sample molded, had some very small craters on one surface and specimen B contained a few small void areas near one surface.

The results of the humidity aging studies are shown in Figure 10. (Weight gain is plotted against the square root of time assuming the moisture diffusion process obeys Fick's law). It is evident from Figure 10 that the equilibrium weight gains for the specimens approach 2% w/w. Specimens aged in 100% R.H. show a greater weight gain which is in agreement with previously reported work on moisture absorption (Reference 2) in polymers. Specimen B, aged at 100% R.H., was found to contain some void areas accounting for the somewhat higher absorption value.

The results of these studies indicate that the difluoromaleimide based polymers possess improved moisture resistance over epoxies as assessed by
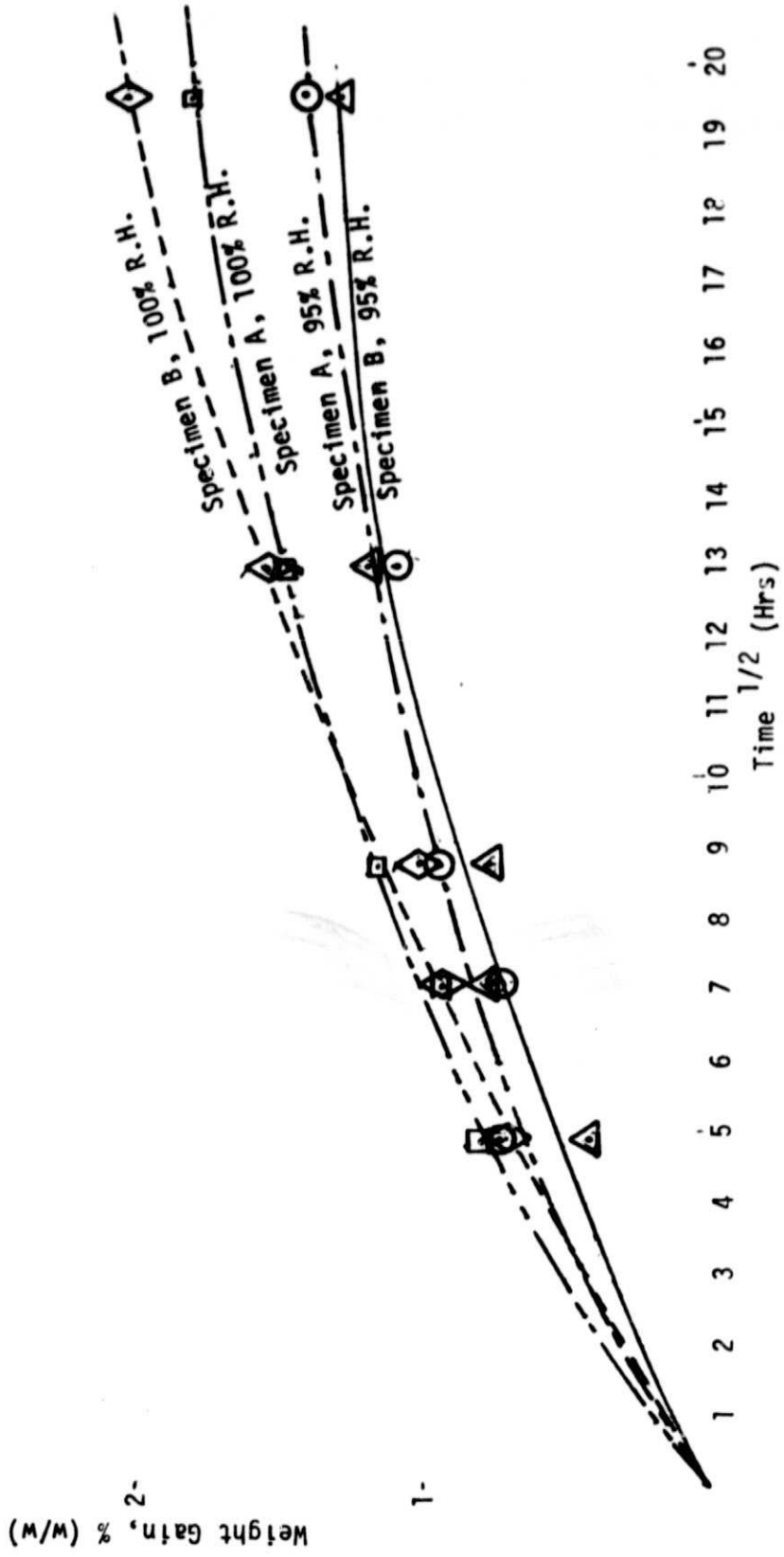
Figure 10. Weight Gain *vs* Time For Different Relative Humidities at 344 K (160°F)

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weight gain studies. The normal weight gain for state-of-the-art epoxies is about 5% w/w under these conditions (Reference 2). However, additional studies are required to fully assess the effects of moisture on the thermo-mechanical properties of the difluoromaleimide derived polymers.

III. CONCLUSIONS AND RECOMMENDATIONS

Summarized below are the conclusions reached during this effort to develop polymers with improved moisture resistance employing difluoromaleimide capped prepolymers. Based on these findings, recommendations are given for further developmental activities.

3.1 CONCLUSIONS

- Polymer studies have shown that the difluoromaleimide derived polymers are suitable for long-term service applications at 477 K (400°F).

- Difluoromaleimide containing imidized prepolymers are soluble in cyclic ethers thereby providing a method for processing these resins into prepreg goods.

- Limited moisture resistance studies showed that these resins possess improved moisture resistance over state-of-the-art epoxies. However, additional studies are required to confirm this conclusion.

3.2 RECOMMENDATIONS

- Additional neat resin studies are recommended to establish the thermomechanical properties of these resins in both dry and wet conditions.

- If the recommended neat resin studies show promise then these resins should be evaluated as matrices in graphite reinforced composites with improved moisture resistance over state-of-the-art epoxies.

- Studies to evaluate new synthesis routes to difluoromaleic anhydride are necessary to provide the monomer in larger, low-cost quantities.

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APPENDIX A

MONOMER SYNTHESIS

A.1 Synthesis of 2,2-*Bis*[4-(3,4-dicarboxyphenoxy)phenyl]hexafluoropropane Dianhydride (BFDA).

Preparation of BFDA was accomplished by the following procedure.

To a 12-1 round bottomed flask equipped with a stirrer, reflux condenser and Dean-Stark trap was added 1338 g of 4-chloromonosodium phthalate and 3.5-1 of xylene. To this slurry was added 600 ml of concentrated HCl and water was removed by azeotropic distillation. After all the water was removed the hot mixture was filtered to remove the sodium chloride and the reddish-brown solution was returned to the flask. To the refluxing solution was added 558 g (6 mole) of aniline diluted with 400 ml of xylene. The water formed by dehydration of the amide acid was removed *via* the Dean-Stark trap. The mixture was refluxed for 4 hours after the last water was removed and then allowed to cool after being placed in a beaker. The precipitate was collected by filtration, washed with 1-1 of xylene and dried *in vacuo* to give 1059 g of imide. Analysis by VPC (OV-17 column) showed the material to contain 80% 4-chloro-N-phenylphthalimide, 2% dichloro-N-phenylphthalimide and 18% N-phenylphthalimide.

To a 3-1 flask equipped with a stirrer, heating mantle, Dean-Stark trap, condenser and nitrogen purge were added 336 g (1.0 mole) of 2,2-*bis*(4-hydroxyphenyl)hexafluoropropane, 1.33 liters DMAC and 750 ml toluene. To the stirred solution was added 80 g (2.0 mole) of sodium hydroxide and then the mixture was heated to reflux. Water was removed *via* the Dean-Stark trap and then the toluene was removed by distillation until the pot temperature reached 428 K. The mixture was allowed to cool to 400 K and then 894 g (2.5 mole) of 4-chloro-N-phenylphthalimide was added. The mixture was heated at 423 K for 96 hours, allowed to cool, then added to 4-1 of 1:1 (V:V) mixture of methanol:water. The yellow precipitate was collected by filtration, washed with 2-1 of water and dried. The crude *bis*imide was recrystallized from aqueous acetone (twice) and isopropanol to give 509 g of off-white powder; mp 417 to 425 K. Infrared spectrum of the *bis*imide is shown in Figure A-1. Anal:Calcd for

$C_{43}H_{24}O_6F_6N_2$:C,66.22; H, 3.11; F, 14.64; O, 12.33; N, 3.60. Found:
C, 66.22; H, 3.04; F, 14.79; N, 3.56.

To a solution of 112 g (2.8 mole) of sodium hydroxide in 450 ml of
water was added 492 g (0.635 mole) of the *bis*imide. The mixture was refluxed
for 48 hours under a nitrogen atmosphere during which time the aniline was
removed by steam distillation. The basic solution was diluted with an equal
volume of water, treated with charcoal, filtered and then acidified with 2 N
nitric acid. The tetraacid was collected by filtration, washed with water to
give a white tacky solid. The tetraacid then was dried *in vacuo* to give
330 g (80%) of off-white material, mp 392 to 397 K.

A mixture of 230 g (0.35 mole) of tetraacid and 460 ml of acetic anhydride
was refluxed for 6 hours under a nitrogen atmosphere and then allowed to cool.
The dianhydride which precipitated was collected by filtration and dried *in
vacuo* to give 100 g (46%) of dianhydride as colorless solid; mp 501 to 503 K.
The filtrate was reduced in volume and a second crop (26 g) of dianhydride
was obtained. Recrystallization of the combined crops from a hexane/toluene
mixture yielded 115 g (53%) of BFDA, mp 501 to 503 K. The infrared spectrum
for BFDA is shown in Figure A-2. Anal. Calcd. for $C_{31}H_{14}O_8F_6$:C,59.25;
H, 2.25; O, 20.37; F, 18.14. Found: C, 58.68; H, 2.34; N, 0.05; F, 18.52.

A.2 Synthesis of 2,2-*Bis*[4-(4-aminophenoxy)phenyl] hexafluoropropane (BDAF).

The diamine was prepared by the reduction of the corresponding dinitro
compound. Preparation of the dinitro compound and its reduction is decribed
below.

To a 2-1 rb flask equipped with a stirrer, nitrogen inlet, Dean-Stark
trap and condenser were added 80.7 g (0.24 mole) of 2,2-*bis*(4-hydroxyphenyl)
hexafluoropropane, 460 ml of dimethylacetamide, 180 ml of toluene 21.6 g
(0.54 mole) of sodium hydroxide and 9 ml of water. The mixture was heated
to reflux and the water was removed by azeotropic distillation until the
pot temperature reached 423 K. To the solution of disodium salt was added
94.5 g (0.6 mole) of 4-chloronitrobenzene and the mixture was heated at
423 K for 24 hours. The mixture was allowed to cool to room temperature
and was added to 4-1 of water. The resulting yellow precipitate was collected
by filtration and washed with water. Recrystallization afforded 126 g of

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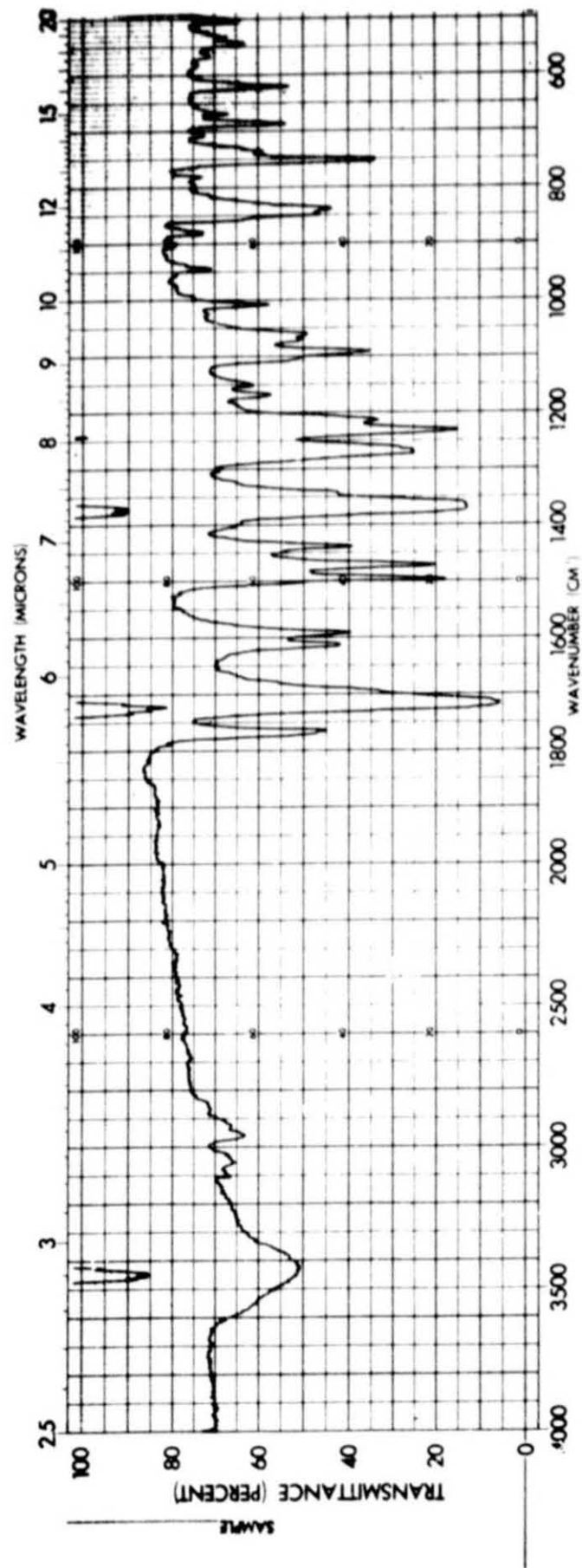
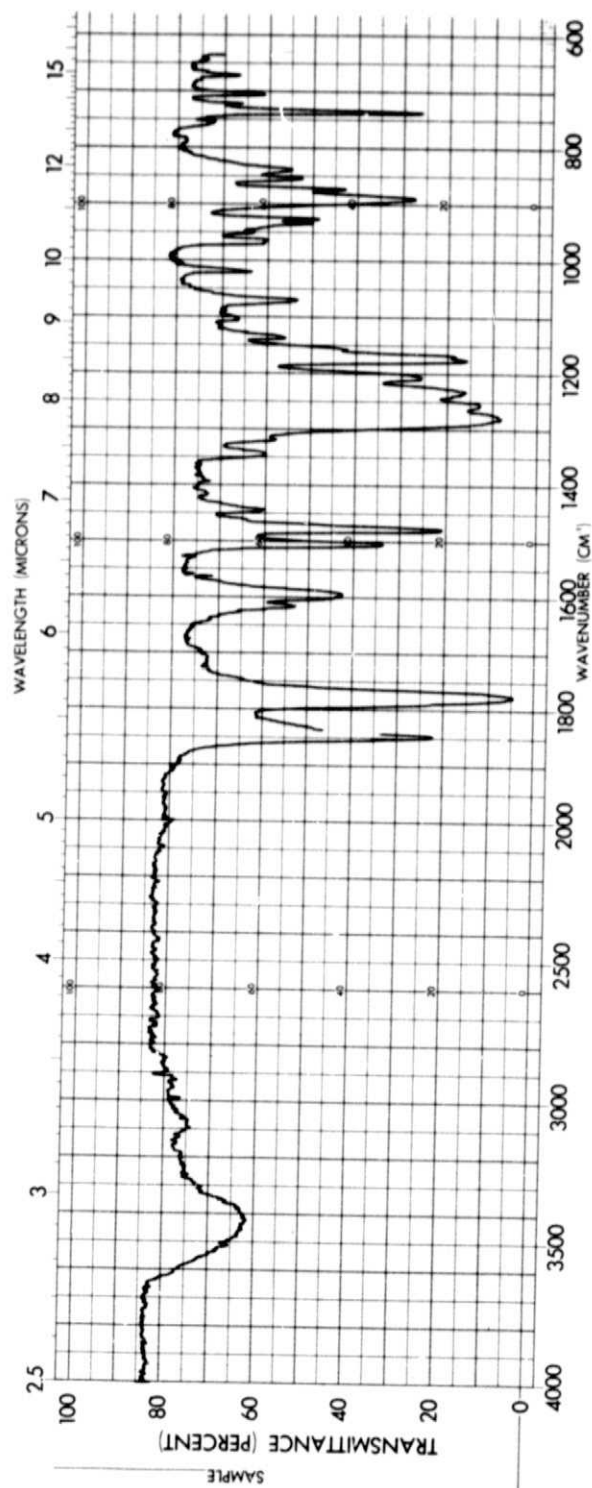Figure A-1. Infrared Spectrum (KBr) of *Bisimide*

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Figure A-2. Infrared Spectrum (KBr) of *Bis*[4-(3,4-dicarboxyphenoxy)phenyl] perfluoroisopropylidene Dianhydride (BFDA)

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2,2-*bis*[4-(4-nitrophenoxy)phenyl] hexafluoropropane; mp 431 to 433 K. The infrared spectrum of the dinitro compound is shown in Figure A-3.

A mixture of 104 g (0.18 mole) 2,2-*bis*[4-(4-nitrophenoxy)phenyl] hexafluoropropane, 80.6 g (1.44 mole) powdered iron, and 180 ml of ethanol were added to a 500 ml three-necked flask. The mixture was heated to reflux and then 1.26 ml (54 mmole) of hydrochloric acid in 50 ml of ethanol was added dropwise with vigorous stirring. The mixture was refluxed for 2 hours, then made alkaline to litmus by adding alcoholic potassium hydroxide. The mixture was filtered hot and the filter cake was boiled twice with fresh ethanol to remove all of the amine. The filtrate was cooled and 2500 ml of concentrated hydrochloric acid was added. The resulting amine hydrochloride was collected by filtration and washed with ethanol. The di-hydrochloride was dissolved in water (1000 ml) and then 5% (w/v) sodium hydroxide was added until the mixture was alkaline to litmus. The insoluble diamine was collected by filtration and then recrystallized from ethanol to give 54 g of nearly colorless needles; mp 422 to 425 K. Anal. Calcd. for $C_{27}H_{20}N_2O_2F_6$; C, 62.55; H, 3.89; N, 5.40; O, 6.17; F, 21.99. Found: C, 62.43; H, 3.94; N, 5.27. The infrared spectrum is shown in Figure A-4.

A.3 Synthesis of Difluoromaleic Anhydride

The procedure employed was basically that of Kobrina, *et al* (Reference 6).

To a three-necked flask equipped with a magnetic stirrer, condenser, thermometer and addition funnel was added 50 ml of 40% peracetic acid. The peracetic acid was heated to 333 K and then 18.4 g (0.1 mole) of penta-fluorophenol was added over a 20-minute period. (The normally solid penta-fluorophenol was added as a liquid by heating the addition funnel to ~308 K with a heat gun). The temperature of the reaction mixture was increased to ~343 K and maintained at that temperature for 3 hours. (A large exotherm was not observed as reported by the authors). After the 3 hours of heating at 343 K the mixture was cooled and allowed to stand for 18 hours. The mixture was extracted for 60 hours with carbon tetrachloride to remove unreacted pentafluorophenol. The aqueous phase was separated from the carbon tetrachloride and the water and acetic acid were removed at reduced
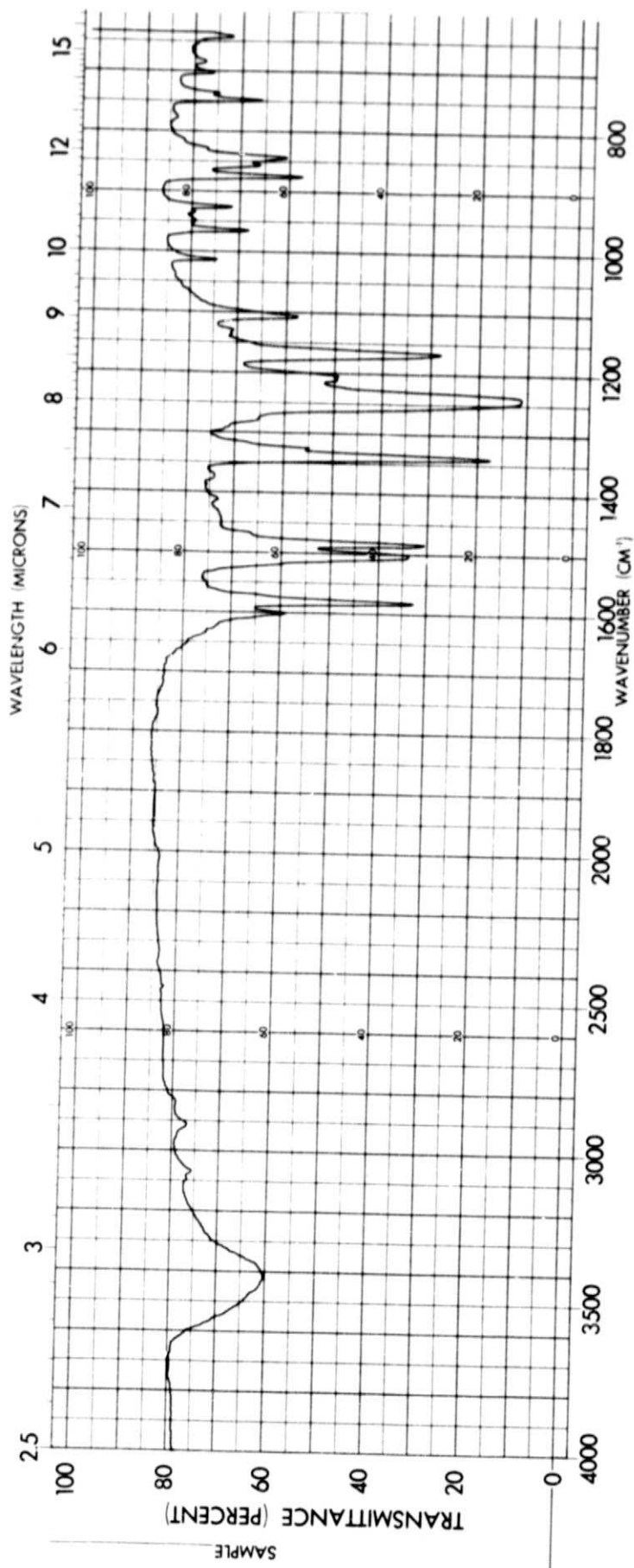
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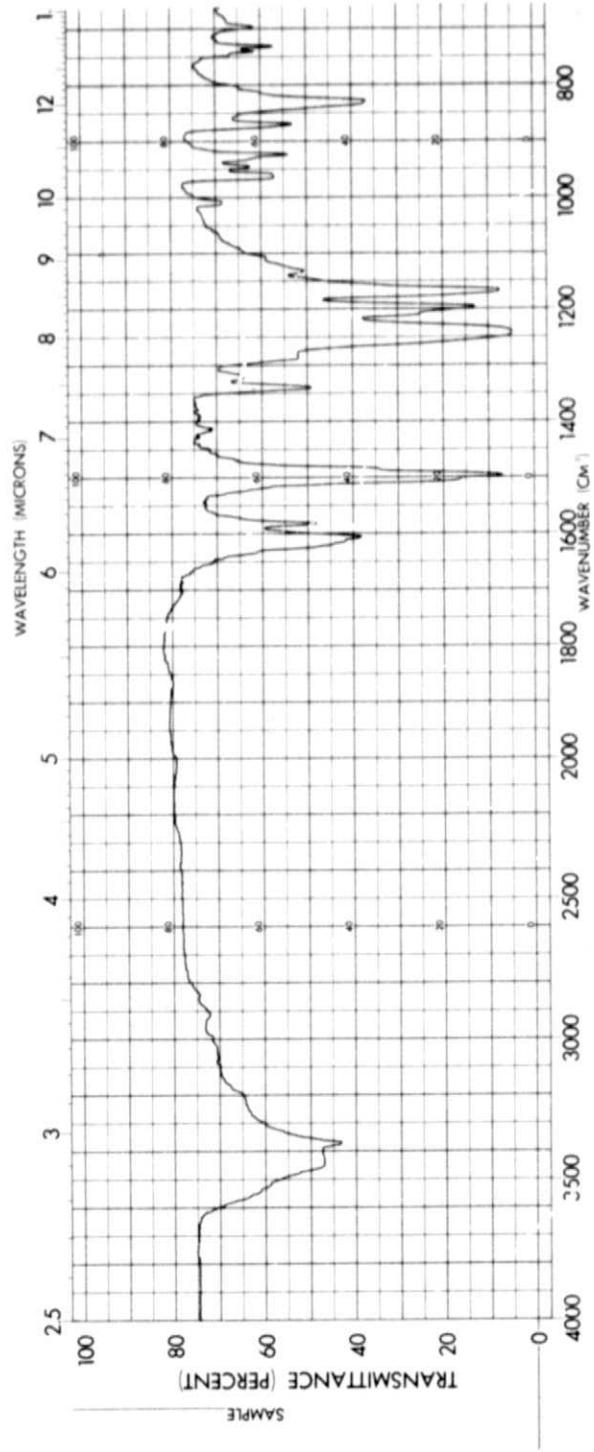Figure A-3. Infrared Spectrum of 2,2'-*Bis*[4-(4-nitrophenoxyphenyl] hexafluoropropane

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Figure A-4. Infrared Spectrum (KBr) of 2,2-*Bis*[4-(4-aminophenoxy)phenyl]
hexafluoropropane

pressure. The residue was extracted with ether, the ethereal solution was treated with activated charcoal and filtered. Removal of ether at reduced pressure gave 0.9 g of solid acid. Additional oxidation runs produced 1.0 g and 1.4 g of acid. The collective oxidation products were dehydrated in 20 ml of refluxing trifluoroacetic anhydride (24 hours at reflux). Trifluoroacetic anhydride and trifluoroacetic acid were removed at reduced pressure on a roto evaporator to give 2.3 g of slightly yellow liquid which crystallized upon cooling to 273 K. The infrared spectrum (Figure A-5) of this compound was in good agreement with the spectrum of difluoromaleic anhydride. No further purification of this material was conducted because of its limited supply. A supply of purified difluoromaleic anhydride already on hand was employed for the polymer preparation and evaluation studies.
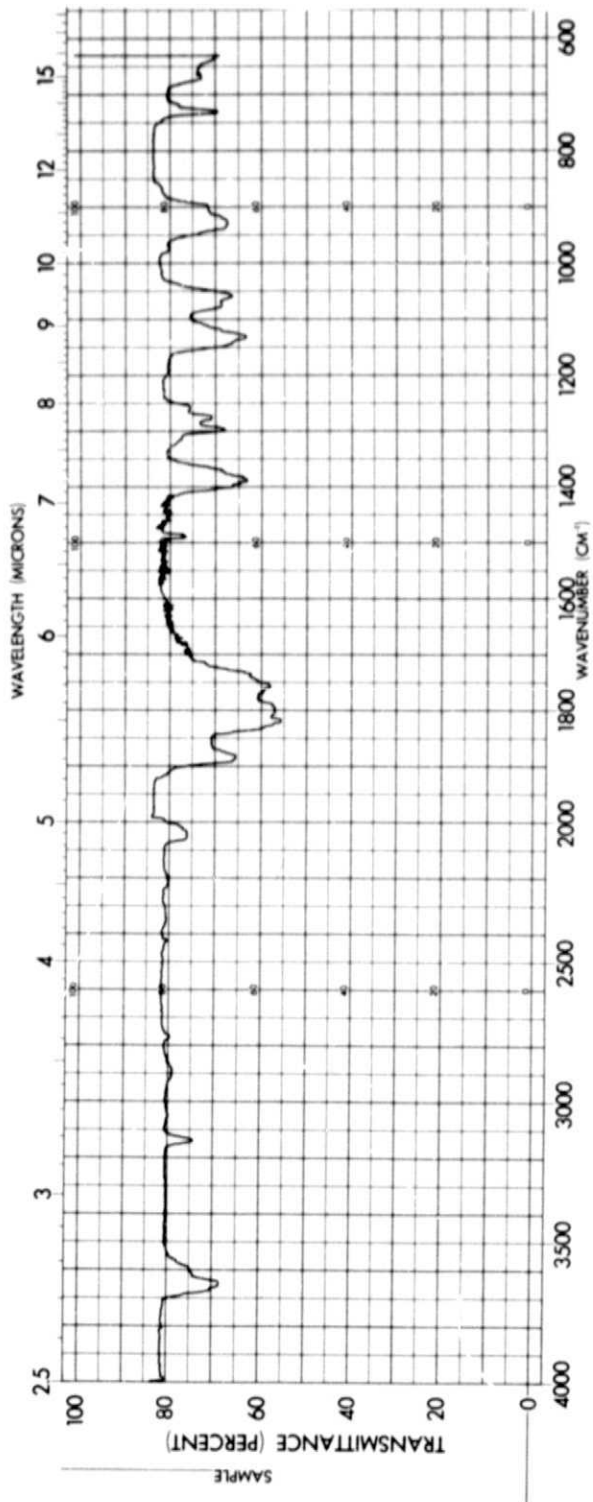
Figure A-5. Infrared Spectrum of Difluoromaleic Anhydride

APPENDIX B.
PREPARATION OF PMR MONOMERIC INGREDIENTS AND POLYMERS

B.1 Preparation of the Monomethyl Ester of Difluoromaleic Acid (DFME)

A mixture of 5.0 g of difluoromaleic anhydride and 25 ml of methanol (dried over 3A mole sieves) was refluxed for 4 hours to give a clear solution. The methanol was removed at reduced pressure to give a colorless crystalline material; mp 360 to 363 K. The infrared spectrum of the compound (Figure B-1) confirms formation of the ester-acid.

B.2 Preparation of a PMR Solution

An example of the procedure used to prepare the PMR mixture is given below.

A mixture of 0.943 g (1.5 mole) of BFDA and 2.2 g of methanol was refluxed for 4 hours to give a pale yellow solution. Separately, 0.595 g (3.0 mmole) of MDA was dissolved in 2.55 g of methanol and then 0.499 g (3.0 mmole) of the monomethyl ester of difluoromaleic acid was added to yield a pale yellow solution. The BTDE solution was allowed to cool and then the MDA/ester acid solution was added to the diester solution. The mixture was stirred for 5 minutes and then was allowed to stand overnight. The solvent was allowed to evaporate and then the remaining methanol was removed *in vacuo* at ~313 K to give 2 g of pale yellow solid.

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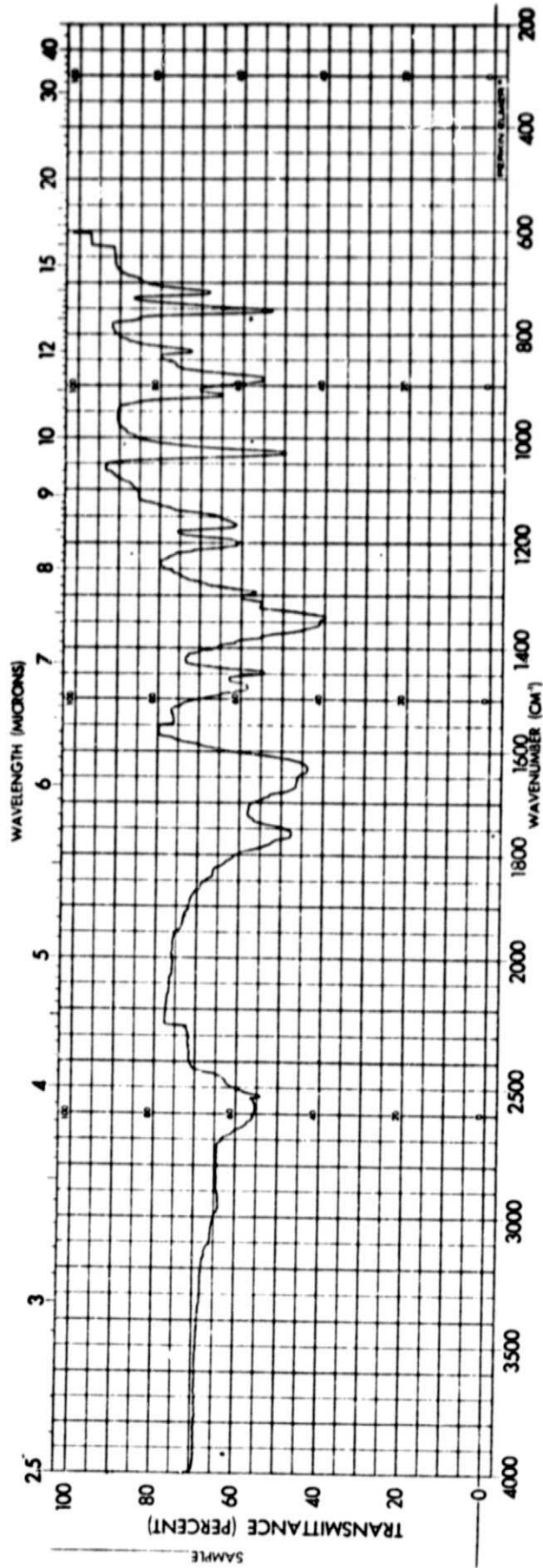removed *in vacuo* at ∿313 K to give 2 g of pale yellow solid.

Figure B-1. Infrared Spectrum (KBr) of the Monomethyl Ester of Difluoromaleic Acid

APPENDIX C.

PREPARATION OF IMIDIZED PREPOLYMERS

The experimental procedure used to prepare the imidized prepolymers is described below.

To a stirred solution of 1.19 g (6.0 mmole) of *m,m'*-MDA in a 20 ml mixture of toluene/DMF (80:20 by volume) under a nitrogen atmosphere was added 1.89 g (3.0 mmole) of BFDA portionwise over a 2-minute period. After stirring for 1 hour the mixture was heated to reflux and water was removed *via* a Dean-Stark trap. After refluxing for 6 hours, the mixture was cooled and then a solution of 0.80 g (6.0 mmole) of difluoromaleic anhydride in 2 ml of toluene was added to the amine/imide solution. After stirring for 30 minutes, 1.5 g of acetic anhydride and 0.05 g of sodium acetate were added and the mixture was heated to 343 K and maintained at that temperature for 6 hours. The reaction mixture then was added to 200 ml of cold methanol and the precipitated prepolymer was collected by filtration, washed with methanol and dried.

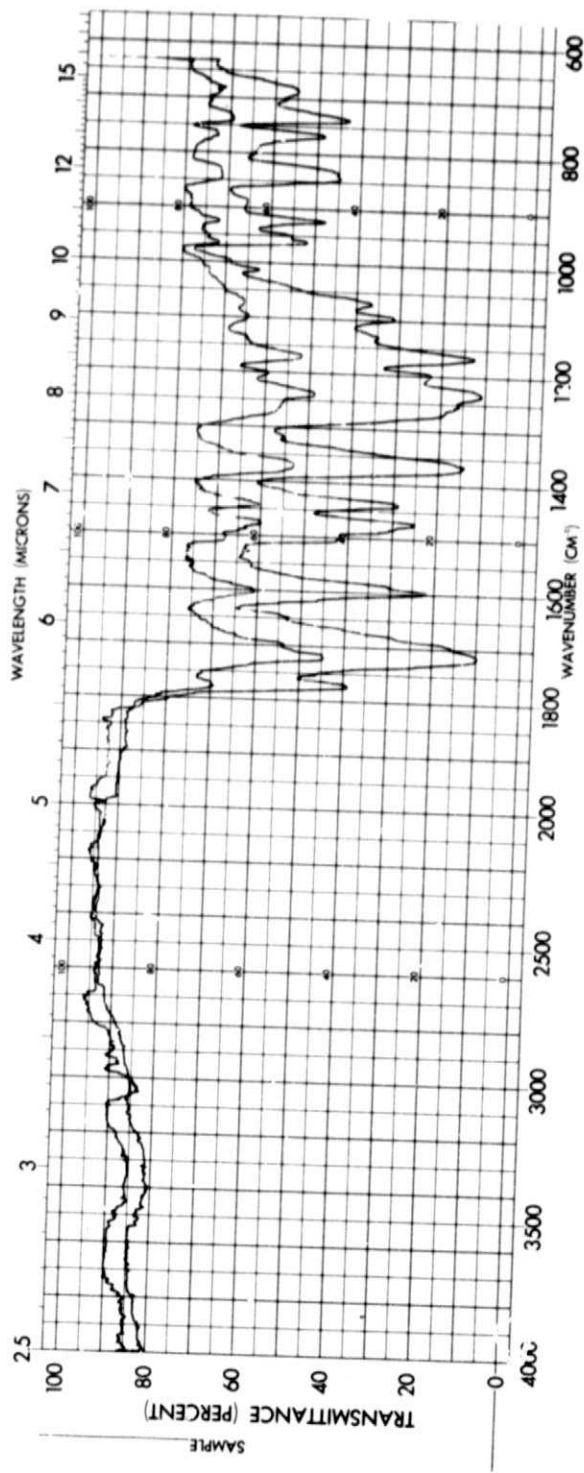The infrared spectrum of this prepolymer is shown in Figure C-1.

Figure C-1. Infrared Spectrum of BFDA/2m,m'-MDA/2DFMA Imidized Prepolymer

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