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RESEARCH GRANT NGR 47-002-041

First Annual Report

THE NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NON-METALLIC MATERIALS BRANCH, MATERIALS DIVISION

Langley Research Center

Hampton, Virginia

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TITLE OF RESEARCH: "ISOMER EFFECTS ON POLYIMIDE PROPERTIES"

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ABSTRACT: The polymerization of 2,4'-Methylene-dianiline [2,4'-MDA] with Benzophenone tetracarboxylic acid dianhydride [BTDA] yields high molecular weight polyamic acid. Polyimide is formed when films of the polyamic acid are cured between 200 - 300 °C. A lower molecular weight polyamic acid is obtained from 2,2'-MDA with BTDA, but it appears that a lowering of the reaction temperature will yield high molecular weight polymer. Evaluation of these polymers is underway. Continued efforts to synthesize 2,3'-MDA and 2,3'-Diaminobenzophenone have met with little success.

B. L. Stump

B. L. Stump, Principal Investigator

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I. Introduction

A study of the effect of structural modifications on the properties of thermally-stable polyimides has continued. The activity during this report period has been focused both on monomer synthesis and on polymerization studies. The ultimate goal is a polyimide with either an unusually low glass transition temperature or with some solvent solubility. The processability of this polyimide would be improved markedly over currently available materials.

II. Discussion

A. Monomer Syntheses

The monomers 2,4'-methylenedianiline, 2,4'-diaminobenzophenone, 2,2'-methylenedianiline and 2,2'-diaminobenzophenone have been successfully synthesized. In addition to the interest in these monomers as precursors of polyimides with unique properties, the monomers have been supplied for additional studies to various researchers either at or connected with the Non-Metallic Materials Branch at Langley Research Center:

1. Samples of these monomers have been furnished Dr. Terry St. Clair for use in adhesives studies.
2. Samples of these monomers have been provided Mr. Phillip Young for use in liquid chromatography studies.
3. Samples of these monomers have been supplied to Dr. Norman Johnston for transmittal to Dr. Mason at VPI & SU, who is engaged in a study of the variation in pK values with structure for diamines.

Polymerization studies with these monomers are discussed in separate sections below.

Attempts to prepare a large batch of 2,3'-dinitrobenzophenone have not been successful. The nitration was carried out as outlined in the experimental section of this report. The product melted over a wide range and was probably a mixture of the 2,2'-; 2,3'-; and the 2,4'-dinitrobenzophenone isomers. Staedel [1] reported a mixture of products (15% 2,2'-; 85% 2,3'-; and 1% 2,4'-), which he separated by fractional crystallization. In the present investigation it appears that the fraction of 2,3'- formed is smaller than that reported by Staedel, and crystallization has not resulted in a pure product. Since attempts to crystallize the 2,3'-diaminobenzophenone were unsuccessful (as reported in the preceding report, March 15, 1973), it may be that the first samples prepared of this compound were also not pure.

Three approaches are being taken to the problem. Work is continuing on the present batch of material to take advantage of the differences in solubility of the isomers. A solubility analysis [2] will be run to determine the number of components present in the system. Secondly, starting materials have been prepared and o-nitrobenzophenone will be nitrated in small batches under varying conditions. A variety of nitrating reagents will be tried if needed to produce the 2,3'-isomer. In the third approach, the mixed dinitro-isomers will be reduced to methylenedianiline derivatives with the hope that these derivatives will be more easily separated. A Wolf-Kishner reduction following the procedure of Grundon, Henbest, and Scott [3] has been run successfully with benzophenone. A small amount of the mixed dinitrobenzophenones hydrazones has been prepared, and it will be reduced according to the procedure described for the benzophenone.

B. Polymerization Studies with 2,4'-Methylenedianiline

The polymerization of the title compound [2,4'-MDA] with 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride [BTDA] has been investigated extensively. Polymerizations have generally been carried out in dry serum bottles equipped with stoppers and magnetic stirring bars. The diamine was dissolved in dimethylacetamide [DMAc] which had been distilled *in vacuo* from calcium hydride at about 100 °C/80 torr and stored under nitrogen. Crystalline dianhydride [which had been sublimed at 215 °C/1 torr] was added as a single batch in a quantity equimolar to the diamine. Between 2 and 4 minutes was usually required for the dianhydride to dissolve completely. Samples of the reaction solution were removed and inherent viscosities at concentrations of 0.5% by weight in DMAc at 35 °C were determined.

The results obtained from a series of reactions using 15% solids, where the viscosity-time relationship was explored, are summarized in Figure I. As has been noted in polymer systems similar to this one, *e.g.* 4,4'-diaminobenzophenone with BTDA [4], the highest viscosity is observed within a 24 hour reaction period. The polyamic acid apparently degrades as stirring is continued at room temperature. It is not surprising that the higher molecular weight, *i.e.* higher viscosity, was achieved with 2,4'-MDA that had been sublimed, except for the fact that the differential thermal analysis curves, Figure II, for the sublimed and recrystallized diamine suggested that the recrystallized sample was purer.

Another experiment was carried out on a 15% solids solution of BTDA and 2,4'-MDA in DMAc, and the reaction system was kept in the temperature range of 1 - 2 °C. A viscosity determination was made after 24 hours reaction time and the inherent viscosity was found to be 0.63, essentially the same value found in the preceeding series of experiments. The reaction mixture was left

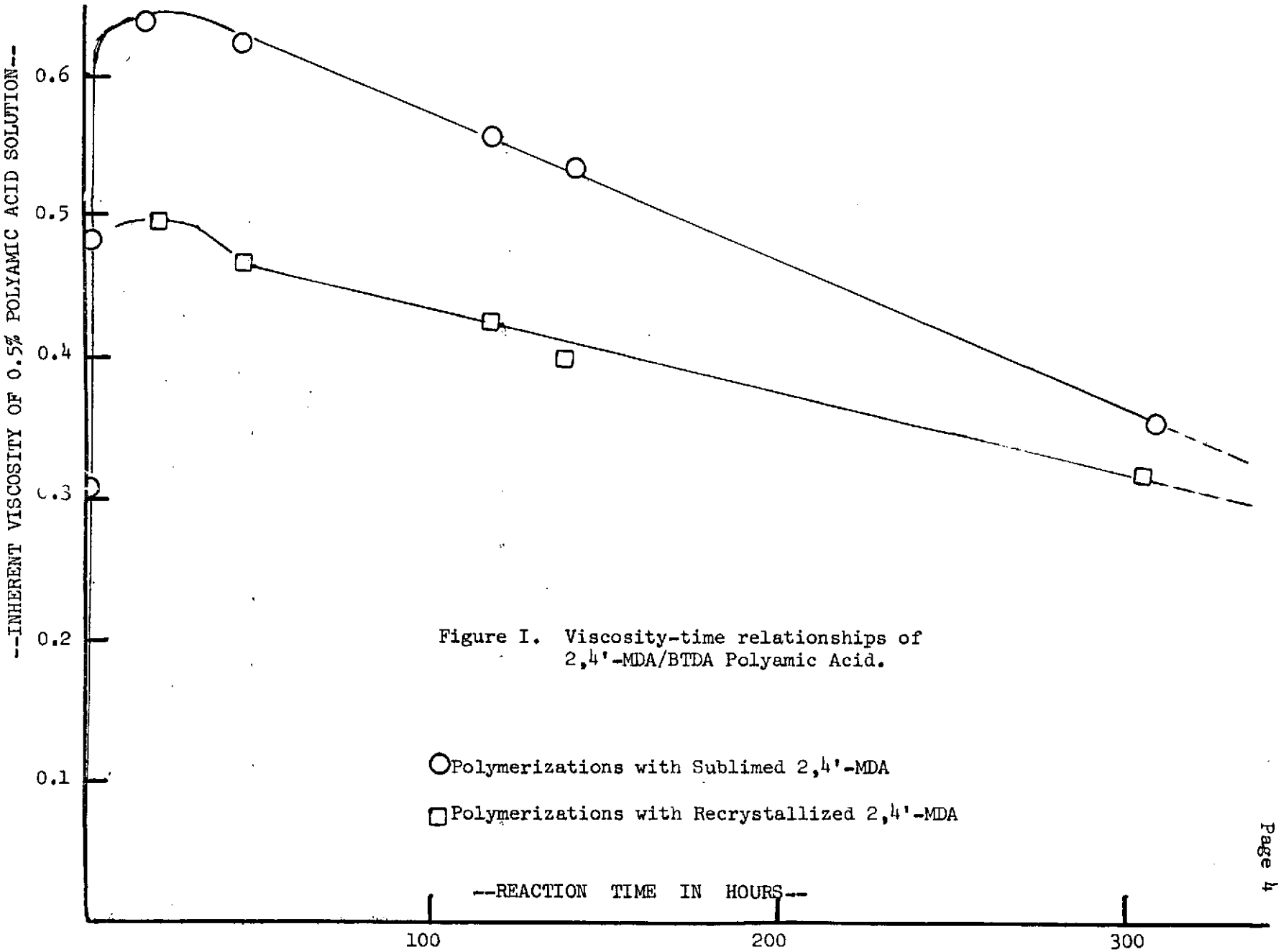


Figure I. Viscosity-time relationships of 2,4'-MDA/BTDA Polyamic Acid.

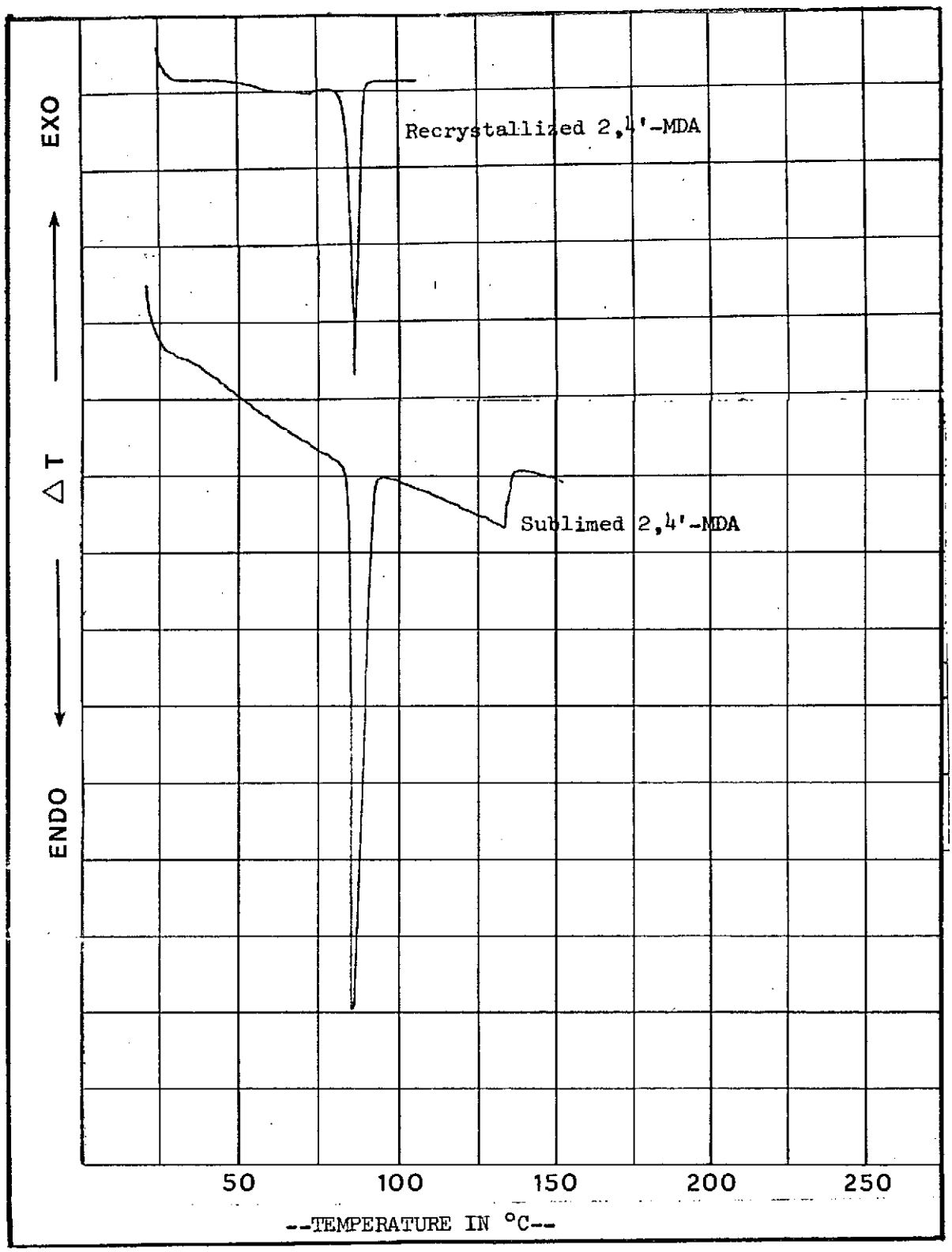


Figure II. DTA curves for recrystallized and sublimed 2,4'-MDA in air at 10 °/min. heating rate.

stirring at 1 - 2 °C for several days and a second viscosity determination was made. After 96 hours reaction time the inherent viscosity was found still to be 0.63. The polyamic acid apparently does not degrade when stirred and/or stored at this low temperature.

Another series of experiments was carried out using BTDA and 2,4'-MDA in DMAc, in which the effect of percent solids on polymer molecular weight was determined. The reactions were carried out at 1 - 2 °C and the results are summarized in Table I. It is apparent that the highest molecular

TABLE I

EFFECT OF PERCENT SOLIDS ON MOLECULAR WEIGHT
FOR 2,4'-MDA/BTDA POLYAMIC ACID

Experiment #	Percent Solids	Reaction Time	Inherent Viscosity
29 A	10	117.5 hours	0.3910
29 B	15	28.0 hours	0.643
29 C	20	24.0 hours	0.464*
29 D	25	22.0 hours	0.645

*A second determination of the viscosity for sample 29 C was made after 192 hours of reaction time and the viscosity was found to be 0.476.

weights are achieved at a 15% solids (or higher) level; no improvement in molecular weight was found by going to 20 or 25 percent solids. The unusually low viscosity found for the 20 percent solids reaction mixture is not considered to be significant but simply reflects some unfortunate circumstance for that particular reaction, i.e. presence of an impurity in the monomer or water in the solvent. In fact, from a later experiment with 2,4'-

MDA and BTDA at the 20 percent solids level in DMAc, polymer with an inherent viscosity of 0.537 was obtained, and this experiment included holding the reaction temperature at about 0 °C for the first three hours.

Attempts to evaluate the physical properties of films from the polyamic acid of 2,4'-MDA and BTDA which have been heat cured to polyimide have not been successful. The films obtained from an oven cure in an atmosphere of air and heating for one hour each at the three temperatures 100 °C, 200 °C, and 300 °C were brittle. It was possible to obtain a thermomechanical analysis on a sample of the film, Figure III, and the glass transition temperature was found to be 272 °C. In addition, the infrared spectrum of a small sample of film was obtained and is shown as Figure IV. Further evaluation of the physical properties of this polyimide will be carried out when an oven that can maintain a nitrogen atmosphere at high temperatures becomes available at Langley Research Center.

C. Polymerization Studies with 2,2'-Methylenedianiline

Two samples of the monomer 2,2'-methylenedianiline [2,2'-MDA] have been used:

> G-044 is sublimed 2,2'-methylenedianiline, which showed a reasonably sharp endotherm centered at 134 °C, beginning at about 129 °C. See Figure V.
>
> G-043RX is recrystallized 2,2'-methylenedianiline, which showed a sharp endotherm at 134 °C, beginning at about 131 °C.

It appears the recrystallized material is of better quality than the sublimed material. Initial polymerization studies tend to confirm this. Reactions carried out at room temperature in DMAc with BTDA produced polymer solutions with higher inherent viscosity values using the recrystallized monomer, as can be seen from the data shown in Table II. Unfortunately, it appears from

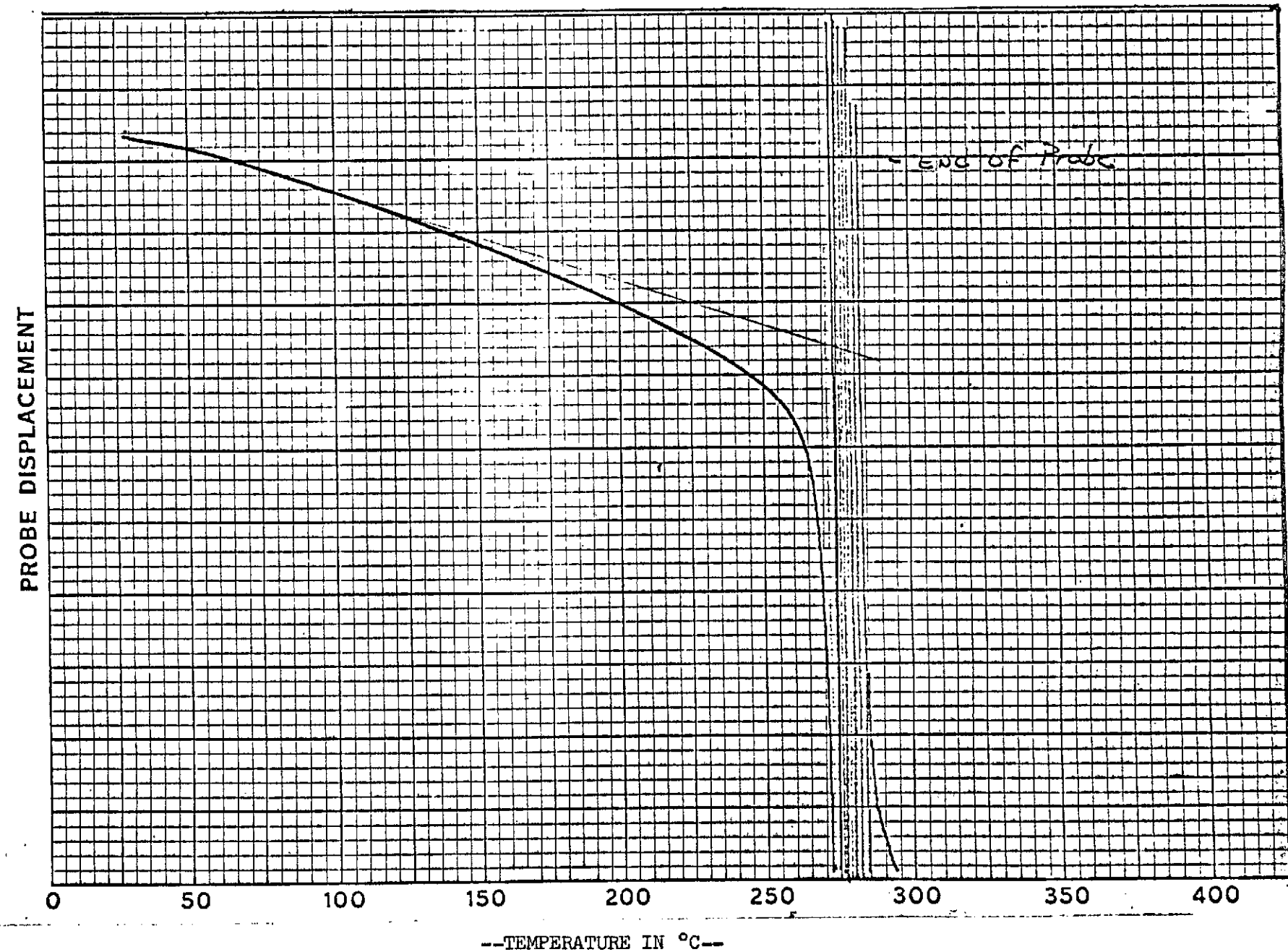


Figure III. Thermomechanical analysis of 2,4'-MDA/BTDA polyimide.

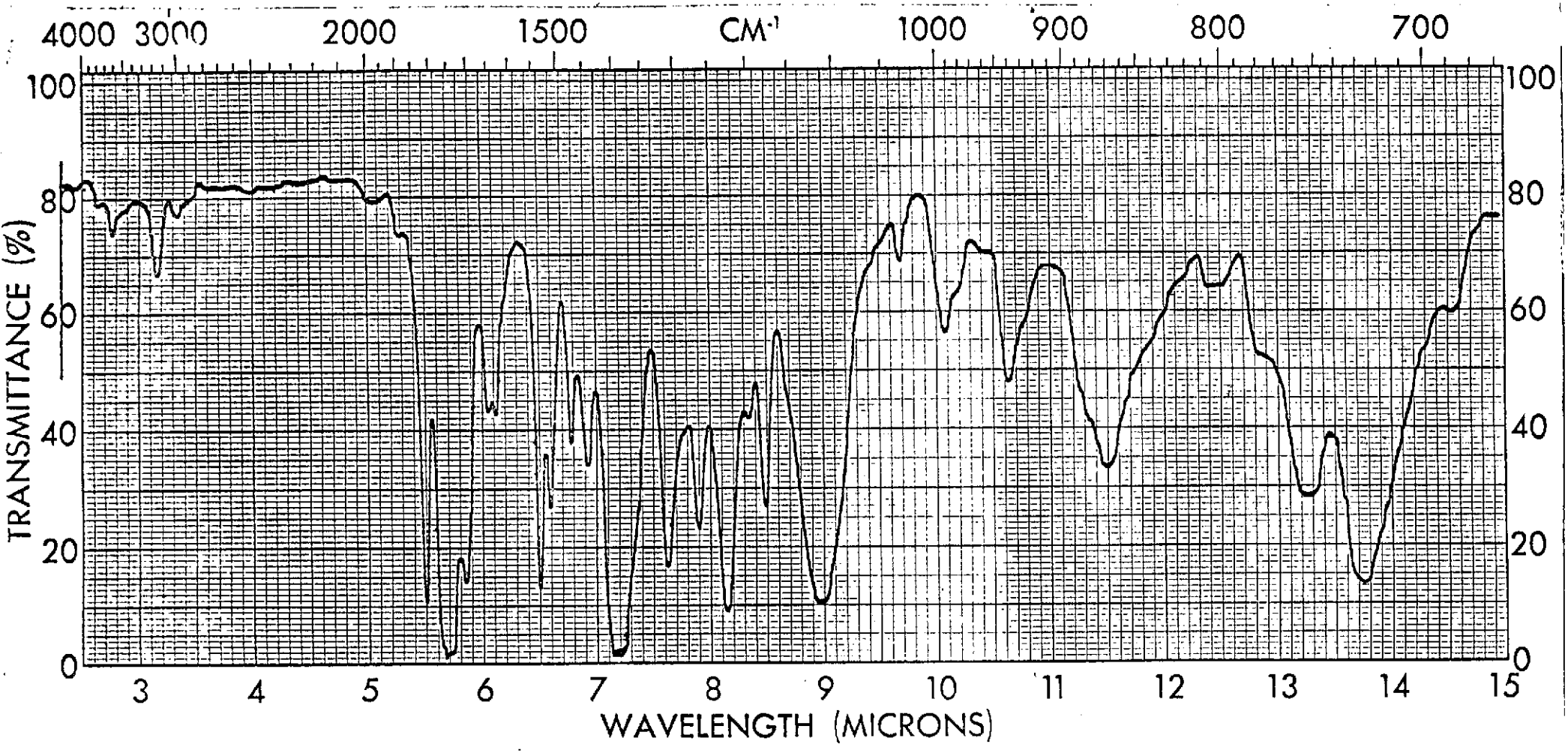


Figure IV. Infrared spectrum of 2,4'-MDA/BTDA polyimide film.

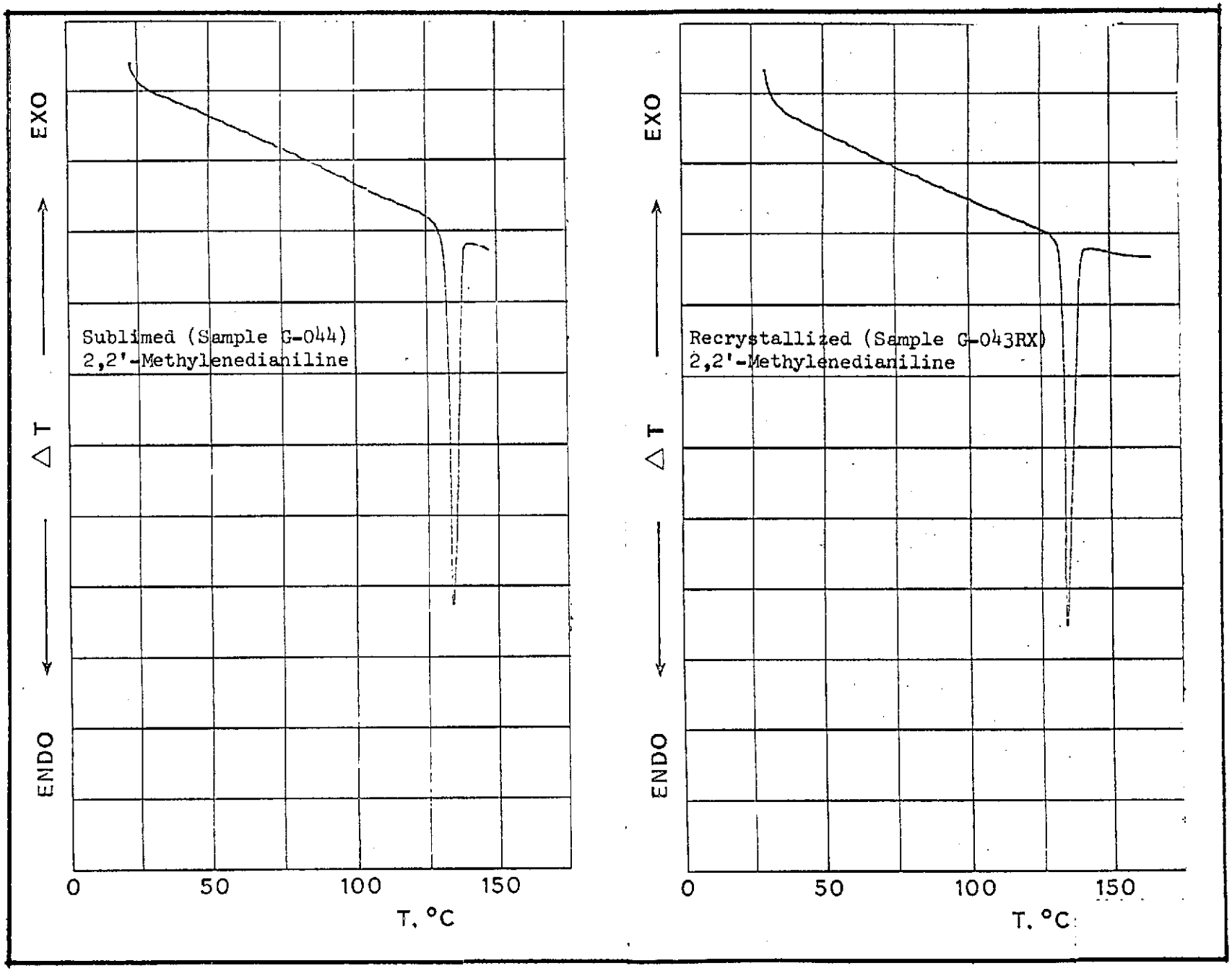


Figure V. DTA curves for recrystallized and sublimed 2,2'-MDA in air at 10 °/min. heating rate.

the results obtained in these reactions that not very high molecular weight polymer is obtainable from this monomer, at least under the conditions employed in these experiments.

TABLE II

POLYAMIC ACID FROM 2,2'-MDA WITH BTDA

Monomer	Percent Solids	Reaction Time	Inherent Viscosity
Sublimed 2,2'-MDA (G-044)	20	163.5 hours	0.144
		427.0 hours	0.1193
Recrystallized 2,2'-MDA (G-043RX)	20	143.3 hours	0.135
		263.3 hours	0.155

Since 2,4'-MDA polymerizes readily with BTDA to give high molecular weight polymer (inherent viscosity about 0.65), steric factors would not appear to explain the low molecular weights being obtained with 2,2'-MDA. The question was raised as to whether the ortho-amino groups were too reactive, with too many polymer chains being initiated too early in the course of the reaction? This would lead to a rapid depletion of the 2,2'-MDA and a low molecular weight polymer would result. To explore this possibility, an experiment was carried out in which a 20 percent solids solution of 2,2'-MDA and BTDA in DMAc was stirred magnetically and kept at about 0 °C for the first six hours of reaction time. A viscosity determination was made after 4.5 hours of reaction time and the inherent viscosity was found to be 0.1898. After six hours of reaction time at 0 °C, the reaction mixture was allowed to warm

to room temperature and stirring was continued. After a total of 28 hours of reaction time, the inherent viscosity was found to be 0.2188. A later experiment using the same reaction system but stirring at 0 °C for five hours, storing at about 0 °C for 16.75 hours, and stirring at 0 °C for 5 additional hours gave a polymer solution with inherent viscosity of 0.2736. Additional stirring and storage at 0 °C failed to produce an increase in viscosity, which is in line with the previously-made observation that maximum molecular weight is achieved in these systems in the first 24 hours of reaction time.

One additional experiment was carried out in which a 15 percent solids solution of 2,2'-MDA and BTDA in DMAc was stirred magnetically in the refrigerator (1 - 2 °C) for a total of 24 hours. The inherent viscosity was determined to be 0.1999. Thus, three observations can be made:

1.) The maximum molecular weight is probably achieved in the first 24 hours of reaction time, regardless of the temperature of the reaction.

2.) The monomer 2,2'-MDA gives higher molecular weight product when polymerized at low temperatures (about 0 °C).

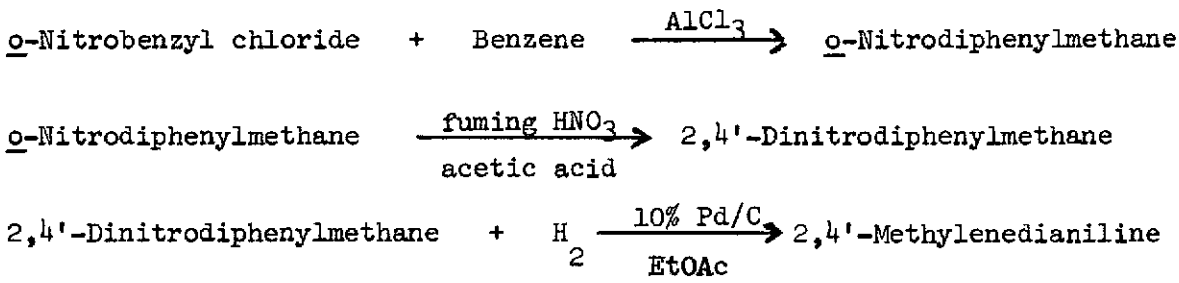
3.) The molecular weight obtained is greater at the 20 percent solids level than at the 15 percent solids level.

Additional polymerization studies of this monomer are planned to establish those reaction conditions which give the highest molecular weight. Physical properties of films of the polymer will then be investigated.

III. Experimental

A. 2,4'-Methylenedianiline

The synthesis of this monomer has been repeated several times according to the reaction scheme:



Experimental details were given in an earlier report [Stump, Summer of 1972 Report]. This monomer has been used extensively in polymerization studies, which are described in Part II-B of this report. In addition, the monomer has been furnished to several different persons for study, and this information was summarized in the Discussion.

Intermediates formed in the total synthesis of 2,4'-methylenedianiline have also been useful. o-Nitrodiphenylmethane has been used in nitration studies in an attempt both to synthesize 2,3'-dinitrodiphenylmethane and 2,2'-dinitrodiphenylmethane. 2,4'-Dinitrodiphenylmethane has been oxidized in CrO_3/HOAc to form 2,4'-dinitrobenzophenone, which has been hydrogenated to obtain 2,4'-diaminobenzophenone.

Attempts to polymerize 2,4'-diaminobenzophenone with BTDA or with PMDA have not given encouraging results. The infrared spectrum of 2,4'-diaminobenzophenone shows evidence of hydrogen bonding between the ortho-amino group and the carbonyl oxygen, and it is not surprising that the monomer fails to polymerize.

B. 2,3'-Dinitrobenzophenone

A mixture of 160 ml of concentrated H_2SO_4 and 120 ml of fuming HNO_3 (90%) was placed in a 500 ml 3-neck round-bottom flask fitted with a thermometer, condenser with drying tube, and a powder funnel. After cooling the mixture in an ice bath, there was added in small portions 5.4 grams of (0.023 mole) of o-nitrobenzophenone. The solution became red as the solid was added. After about an hour the color faded and after an additional three hours the reaction mixture was poured over 100 ml of crushed ice. The white solid was filtered and washed with distilled water. The crude product was recrystallized from toluene to yield 3.6 g of a white solid which melted at 120 - 124 °C. The literature melting point is 126 °C [1]. Analysis for $C_{13}H_8N_2O_5$: Theory, C, 57.56; H, 2.91; N, 10.31; Found, C, 57.36; H, 2.96; N, 10.31. The ir spectrum was obtained using a KBr pellet: ν_{max}: 1650 cm^{-1} (ketone, C=O); ν_{max}: 1600, 1520, and 1345 cm^{-1} ($-NO_2$). The nmr spectrum showed only aromatic hydrogens.

An additional 12.0 g of o-nitrobenzophenone was nitrated according to the procedure above. A total of 12.4 g of solid was recovered (m.p. 150 - 180 °C). The product was recrystallized from toluene with 0.1 g Norit-A. The air dried crystals were collected and recrystallized a second time from toluene, dried overnight in a vacuum oven, and found to melt between 135 - 150 °C. These crystals were further recrystallized from glacial acetic acid, and long yellow needles melting between 120 - 180 °C were obtained.

The filtrate from the original recrystallization was put on the flash evaporator and taken to dryness. The solid which was received was recrystallized from toluene and then melted between 110 - 125 °C, although there was present in the sample some higher melting material. Further attempts to recrystallize this sample did not improve the product. DTA's

are being run on the various fractions in an attempt to further identify possible isomers. Ir spectra show no significant differences.

Since recrystallization attempts did not appear to be suitable for purification, solvents for thin layer chromatography were investigated, but no success was realized. No separation of the fractions could be effected on the plates.

Sublimation was also tried as a means of purification. With a bath temperature of 110 °C, at 0.05 torr a fraction was recovered which melted between 119 - 126 °C. However, the rate of deposition was too slow to be practical. Increasing the bath temperature to 115 - 118 °C produced a sublimate at a reasonable rate but the melting point was 116 - 175 °C.

C. 2,3'-Diaminobenzophenone

The reduction of the 2,3'-dinitrobenzophenone was carried out catalytically using a Parr low-pressure hydrogenator:

Method A. 2,3'-Dinitrobenzophenone (1.08 g, 0.00367 mole) was suspended in 50 ml of ethyl acetate with 0.10 g of Matheson Coleman and Bell 10% Pd/C and pressured with 50 psig of H_2. After 3 hours the hydrogenation was stopped as the sample had taken up the calculated amount of H_2. After filtering to remove the catalyst the ethyl acetate was removed in a flash evaporator. A yellow oil remained in the flask. Staedel [1] reported recrystallizing this compound from ethanol. This was tried with negative results. To date all attempts to crystallize this material have failed.

Method B. 2,3'-Dinitrobenzophenone (1.0 g, 0.00367 mole) was suspended in 50 ml of ethyl acetate with 0.10 g of 10% Pd/C and 1.0 g of $MgSO_4$ as a drying agent. The hydrogenation bottle was pressured with

50 psig of H_2. After 40 minutes 95% of the calculated amount of hydrogen had been taken up. The reaction was continued for a total of three hours. The pressure did not drop below the calculated amount for reduction of the two nitro groups. The solution was filtered and the solvent was removed in the flash evaporator. Attempts to crystallize the residue from ethanol failed. A dilute solution was left standing for several days, and from the dark color which developed it was concluded that the material had decomposed.

D. 4,4'-Diamino-2,2'-dinitrodiphenylmethane Di(hydrogen sulfate)

Potassium nitrate (25 g) was added during 45 minutes to a vigorously stirred solution of 4,4'-diaminodiphenylmethane (25 g, 0.126 mole, Baker Chemical Company, Practical) in sulfuric acid (d 1.84, 250 ml). The temperature was maintained between 0 and 5 °C during the addition and for 1 hour afterwards. The mixture was poured over 1 kg of crushed ice, partially neutralized with aqueous ammonia (d 0.88, 400 ml), and cooled to 15 °C. The resulting precipitate was crystallized from 2N H_2SO_4 to give 37.13 g of the salt, m.p. 216 (decomp). The reported melting point is 228 (decomp) [6].

E. 2,2'-Dinitrodiphenylmethane

The product salt (from part D above), 37 g, was added to a solution of 34.0 g of $NaNO_2$ in 315 ml of H_2SO_4 (d 1.84) with vigorous stirring. The temperature was maintained below 15 °C with an ice bath. After the addition of the salt was complete, about 1.5 hours, glacial acetic acid (463 ml) was added dropwise while still maintaining the temperature at 15 °C. After 2 hours the solution was poured into a 4-liter beaker containing absolute ethanol (934 ml) and Cu_2O (134 g). The solution was stirred vigorously with a magnetic stirrer and refluxed at 70 °C for 30 minutes and filtered while still

hot to remove cuprous oxide. The filtrate was cooled and poured over 3 liters of ice and stored in the refrigerator over the weekend. The precipitate which formed was filtered and dried in a vacuum dessicator. The dry residue was dissolved in benzene and poured through a column of alumina (50 g, Alcoa F-1, 60 - 100 mesh). The first yellow band was eluted with benzene. The eluate was distilled once (Fraction A, b.p. 150 - 165°, Fraction B, b.p. 169 - 175 °C, 0.05 torr). As the distillation continued the distillate became discolored and it was evident that the product was decomposing. The two fractions were recrystallized from methanol. Fraction A gave a solid which melted at 84 °C, while Fraction B gave a solid which melted at 80 °C; the reported melting point is 84 - 85 °C. An ir spectrum was obtained using a KBr pellet; ν_{max} 1500, 1320 cm^{-1} ($-NO_2$). An nmr spectrum in deuterated acetone showed resonance at δ 4.6 and 8.1 to 7.0. The areas of the two bands were in the ratio of 2:8.

F. 2,2'-Diaminodiphenylmethane

The reduction of 2,2'-dinitrodiphenylmethane (1.0 g, 0.0038 mole) was carried out in a Parr low-pressure hydrogenator in ethyl acetate (50 ml) with 0.1 g of Matheson Coleman and Bell 10% Pd/C with an initial 50 psig of H_2. After one and one-half hours the calculated 0.0228 mole of H_2 had been taken up and the solution was filtered to remove the catalyst. The ethyl acetate was stripped off in a flash evaporator. The yellow solid remaining was recrystallized from methanol. The first fraction (0.45 g), which consisted of yellow needles, melted at 132 - 133 °C, in agreement with the value reported by Partridge and Vipond [6], m.p. 132 - 134 °C. Analysis for $C_{13}H_{14}N_2$: Theory C, 78.84; H, 7.02; N, 14.30; Found, C, 78.75; H, 7.11; N, 14.31. The ir spectrum was obtained using a KBr pellet: ν_{max} 3440,3490 (NH stretch),

ν_{max} 1600, 1560 (NH bend), ν_{max} 1290, 1270, 1250 (C-N). An nmr in deuterated acetone showed δ 3.7 ($-CH_2-$), δ 4.4 ($-NH_2$), δ 6.5 - 7.2 (aromatic protons) in the ratio 2:4:9 (Calculated 2:4:8).

Ten grams of the 2,2'-diaminodiphenylmethane was prepared by the above methods. Part of the sample (1.5 g) was purified by sublimation under vacuum (110 °C, 0.05 torr). Sublimation proceeded very slowly. Since decomposition was suspected from the color of the sample, 5 grams was recrystallized a second time from methanol. DTA analyses gave a melting point range of 129 - 134 °C for the sublimed sample and 131 - 134 °C for the recrystallized material [See Figure V].

G. 2,2'-Dinitrobenzophenone

Glacial acetic acid (20 ml) and CrO_3 (0.7 g, 0.0135 mole) were placed in a 50 ml round-bottom flask and cooled in an ice bath. 2,2'-Dinitrodiphenylmethane (1.0 g, 0.0038 mole) was added slowly with stirring. After the addition of the solid was complete the temperature of the reaction mixture was raised and the solution was refluxed for four hours and allowed to stand overnight at room temperature. The solution was poured into 200 ml of ice and the white solid was filtered and washed with distilled water. The crude product was recrystallized from toluene, m.p. 184 °C, Literature m.p. 190 - 191 °C [6]. Analysis for $C_{13}H_8N_2O_5$: Theory, C, 57.40; H, 2.89; N, 10.27; Found, C, 57.36; H, 2.96; N, 10.29. An ir spectrum in KBr gave ν_{max} 1670 (-C=O), ν_{max} 1500, 1340 ($-NO_2$). The sample was too insoluble in acetone, chloroform, and methanol to run an nmr. A suitable solvent is being sought.

H. Attempted Preparation of 2,3'-Dinitrodiphenylmethane

The method of Thorpe and Wildman [7] was adapted. Sulfuric acid (d 1.84, 100 ml) and nitrobenzene (15 g, 0.121 mole) were placed in a 500 ml round-bottom 3-neck flask fitted with a thermometer, condenser with drying tube, and a magnetic stirring bar, and the flask was chilled in an ice bath. o-Nitrobenzyl alcohol (5 g, 0.0326 mole) was added slowly with stirring and continued cooling. The yellow solution became red after about one hour. The reaction mixture was stirred at room temperature for 12 hours and placed in the refrigerator overnight. The reaction mixture was then poured into 200 ml of ice. A dark red solid precipitated out and was removed by suction filtration. In previous reactions it had been found that this material was soluble in ethanol and melted at a temperature greater than 400 °C.

The aqueous solution was extracted four times with benzene and the combined benzene layers were extracted as follows: 2 times with 5% NaOH, 2 times with 5% HCl, 2 times with $NaHCO_3$ (aqueous saturated), and 4 times with water. The red color of the solution decreased markedly with the NaOH extraction. The benzene layer was reduced in volume with the flash evaporator and dried over Na_2SO_4. The remaining liquid was distilled under reduced pressure (0.26 torr), b.p. 27 °C. An ir spectrum of the neat liquid was identical with nitrobenzene's spectrum.

No melting point has been reported in the literature for this compound.

I. Attempted Preparation of 2,3'-Dinitrodifluorodiphenylmethane

The method of Mathey and Bensoam [8] was followed. A solution of 2,3'-dinitrobenzophenone (1.0215 g, 0.00375 mole) in methylene chloride

was placed in a 25 ml round-bottom flask. The flask was capped with a septum containing one large and two small bore syringe needles, one for flushing with nitrogen, one for product-gas exit, and one for the addition of the reagent. After cooling the reaction mixture to - 15 °C in a methanol-ice bath, Fluoreze-M (4.7 ml, PFC) was added dropwise with a syringe. The solution was stirred with bubbling nitrogen for 2.75 hours while the temperature was allowed to rise to 25 °C. Sodium fluoride (0.5 g) was added, then Al_2O_3 (0.5 g). The solution was stirred for 15 minutes; it appeared quite blue in color.

The solvent was removed in a flash evaporator. Since there was insufficient material to distill, even if the reaction had been successful, ethanol and bone charcoal were added to the residue and the solution was filtered. The filtrate and the residue were deep blue in color. Because of the intense color it was impossible to tell if any oil was present, or organic solid, even when the solvent was stripped off on the evaporator. Before this reaction is attempted again, a pilot run will be made with benzophenone to become familiar with the reaction.

J. 2,3'-Dinitrobenzophenonehydrazone [Tentative identification]

2,3'-Dinitrobenzophenone (m.p. 135 - 181 °C) was mixed with 3 ml of hydrazine hydrate (95%) and about 8 ml of absolute ethanol was added to make a solution at the temperature of reflux. The reaction mixture turned red but the color faded to pale yellow. After refluxing for 4 hours the solution was cooled and the yellow solid which precipitated was collected, washed in ethanol and dried in a vacuum. A yield of 15% of material melting at 225 - 229 °C was obtained. Mass spec analysis indicated peaks consistent

with the assignment of dinitrobenzophenone hydrazone. Addition of water to the reaction mixture failed to produce any additional precipitate. Benzophenone reacted under similar conditions gave a 70% yield of hydrazone. It is interesting to note that the melting point range of the derivative is sharp, whereas the starting material covered a wide range.

K. Wolf-Kishner Reduction Pilot Run

Following the method of Grundon, Henbest, and Scott [3], benzophenone hydrazone (6.9 g) was dissolved in dry toluene (120 ml) in a flask flushed with dry nitrogen. Solid potassium t-butoxide (3.0 g) was added and the reaction mixture was refluxed for four hours. The solution was allowed to cool overnight at room temperature, and it was then poured into water (100 ml). The two layers which formed were separated in a separatory funnel and the water layer was washed twice with ether. The combined ether and toluene layers were evaporated in a flash evaporator. The yellow precipitate which formed was filtered, washed and dried. It melted at 161 - 162 °C, which agrees with the literature melting point of 161 °C for benzophenone azine [3].

The filtrate was distilled under vacuum. The distillate (b.p. 104 °C/ ca. 1 torr) had a slight pink cast but the infrared spectrum has been used to identify the material as methylenedianiline, the desired product. The yield was not calculated as the entire sample was not distilled.

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