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FINAL TECHNICAL REPORT

NASA Grant NSG-1064

"Synthesis of Aromatic Secondary Diamines"

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INTRODUCTION

Due to chain stiffness and intermolecular hydrogen bonding between amide groups, wholly aromatic polyamides [1-4] have been noted for their high melting points, good thermal stability, difficult processability, and limited solubility in organic solvents. The thermoplastic processing of these polymers has been greatly hindered because they lack any softening or melting tendencies at routine processing temperatures, which often coincide with polymer decomposition temperatures. [5] One method for improving the processability and solubility of aromatic polyamides has been to vary the structural backbone of the polymer. Efforts have been made to lower the glass transition temperatures (T_g) by introducing flexibilizing groups between phenyl rings. [6] Recently Takatsuka et al. reported an increase in the solubility of aromatic polyamides due to methyl-substituted phenylene linkages. [7]

The current study concerns the preparation of wholly aromatic polyamides of type II from secondary aromatic diamines of type I and aromatic diacid chlorides as illustrated in Reaction Scheme 1. Polyamides II thus lack amide hydrogens, and this structural feature should produce a lowering of their T_g's and improved solubility. Previous work on aliphatic polyamides has shown that N-alkylation eliminates intermolecular hydrogen bonding thereby converting rigid, insoluble, highly crystalline polymers into soft, flexible, more soluble materials

with lower melting temperatures. [8]   In some cases the N-methyl-
ation of aliphatic polyamides has not only lowered melting points
but destroyed crystallinity altogether.[9] In the present investi-
gation, the effect of N-methyl substitution in aromatic polyamides
has been studied with regard to T_g, crystallinity, thermal
stability and solubility.

<div align="center">Reaction Scheme 1</div>
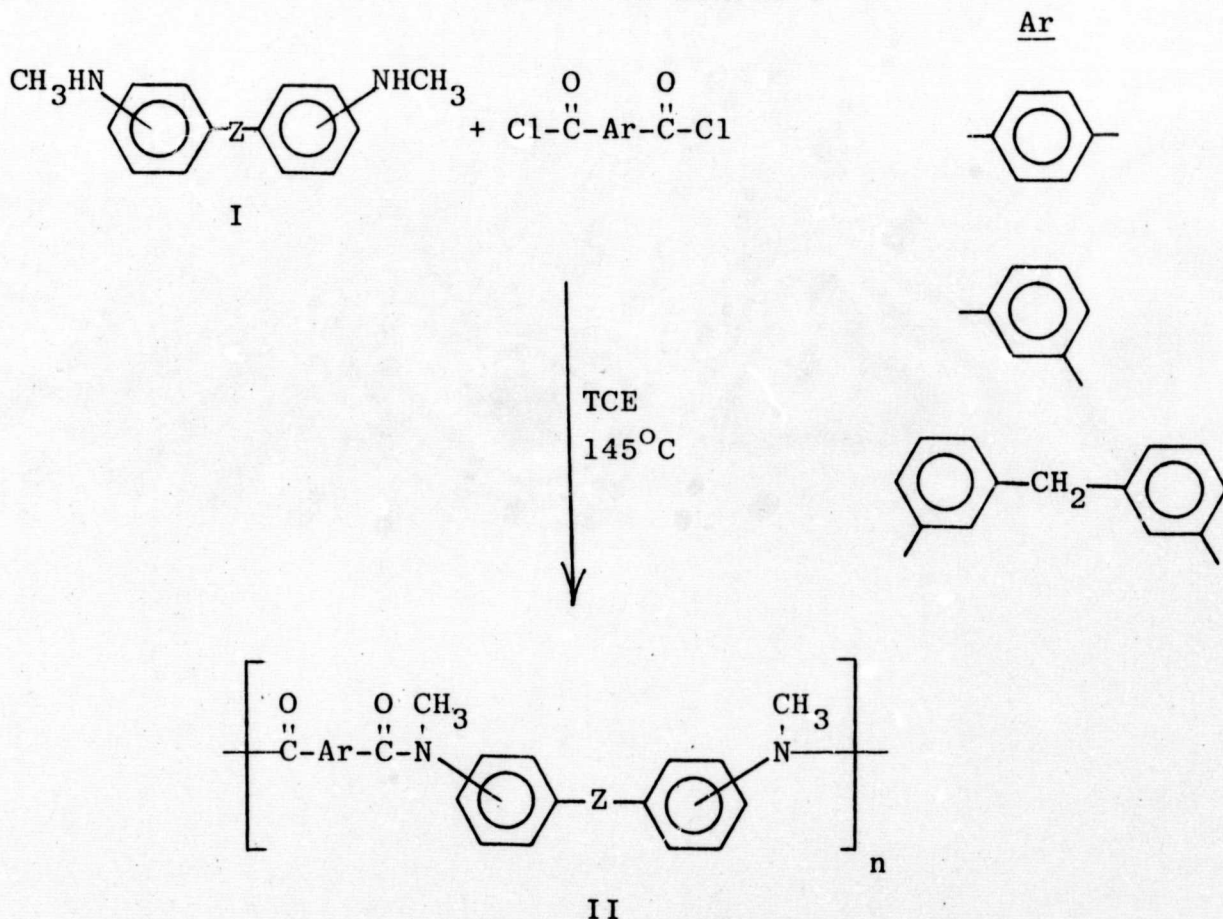
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EXPERIMENTAL

Materials

Commercial isophthaloyl dichloride was distilled and then recrystallized from hexane, mp 43-44°C. Monomer grade terephthaloyl dichloride, mp 83-84°C, and 3,3'-diphenylmethane dicarboxylic acid dichloride,[10] mp 110°C were purified by vacuum sublimation at 80°C and 108°C, respectively.

The N-methylated diamines (Ia-d) used in this study were prepared from the corresponding primary amines (IIIa-d)[11] as shown in Reaction Scheme 2. 4,4'-Bis(methylamino)diphenylmethane (Ia) was more conveniently prepared from the condensation of N-methylaniline with formaldehyde in 73% yield.[12]

Polymerization solvents s-tetrachloroethane (TCE) and N,N-dimethylacetamide (DMAC) were distilled from calcium hydride and stored over 4 $\overset{o}{A}$ molecular sieves.

3,3'-Bis(methanesulfonamido)diphenylmethane (IVb). 3,3'-Diaminodiphenylmethane (IIIb), (10.00 g, 0.0504 mole) was dissolved in 150 ml of dry pyridine and the resulting solution was cooled to 10°C in an ice bath. Methanesulfonyl chloride (12.71 g, 0.111 mole) was added to the solution dropwise over a period of 0.5 hr while the temperature was maintained at 10-15°C. The solution was allowed to warm to 25°C over 1.5 hr, heated at 90°C for 2 hr, and then poured into a vigorously stirred ice-concentrated hydrochloric acid slurry. The product, which precipitated as a tan solid, was filtered, dried, and recrystallized from

N-METHYL SUBSTITUTED AROMATIC POLYAMIDES*

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Synopsis

A series of N-methyl substituted aromatic polyamides der-
ived from the secondary aromatic diamines, 4,4'-bis(methylamino)-
diphenylmethane, 3,3'-bis(methylamino)diphenylmethane, 4,4'-bis-
(methylamino)benzophenone or 3,3'-bis(methylamino)benzophenone
and isophthaloyl dichloride, terphthaloyl dichloride or 3,3'-
diphenylmethane dicarboxylic acid dichloride was prepared by
high temperature solution polymerization in s-tetrachloroethane.
Compared to analogous unsubstituted and partially N-methylated
aromatic polyamides, the full N-methylated polyamides exhibited
significantly lower glass transition temperatures (T_g), reduced
crystallinity, improved thermal stability and good solubility in
chlorinated solvents.

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ethyl acetate-hexane to give 15.18 g (85%) of IVb as nearly colorless crystals, mp 161-162°C. ^{1}HNMR (DMSO-d$_6$); 9.68 δ (2H, s, amide), 7.08 δ (8H, m, phenyl), 3.90 δ (2H, s, methylene), and 2.98 δ (6H, s, sulfonamide methyl).

ANAL. Calcd for C$_{15}$H$_{16}$N$_2$O$_5$S$_2$: C, 50.83%; H, 5.11%; N, 7.91%.

Found: C, 50.55%; H, 4.99%; N, 7.63%.

4,4'-Bis(methanesulfonamido)benzophenone (IVc). Using the same procedure as described for IVb, this compound was prepared from 4,4'-diaminobenzophenone (IIIc), (19.50 g, 0.0920 mole) in 79% yield, mp 280-281°C from 2-methoxyethanol. ^{1}HNMR (DMSO-d$_6$); 10.44 δ (2H, s, amide), 7.57 δ (8H, m, phenyl), and 3.15 δ (6H, s, sulfonamide methyl).

ANAL. Calcd for C$_{15}$H$_{16}$N$_2$O$_5$S$_2$: C, 48.90%; H, 4.38%; N, 7.60%.

Found: C, 49.23%; H, 4.40%; N, 7.58%.

3,3'-Bis(methanesulfonamido)benzophenone (IVd). This com- This compound was prepared in 71% yield from 10.00 g (0.0472 mole) of 3,3'-diaminobenzophenone (IIId), mp 199-200°C for methanol. ^{1}HNMR (DMSO-d$_6$); 10.06 δ (2H, s, amide), 7.56 δ (8H, m, phenyl), and 3.08 δ (8H, m, phenyl), and 3.08 δ (6H, s, sulfonamide methyl).

ANAL. Calcd for C$_{15}$H$_{16}$N$_2$O$_5$S$_2$: C, 48.90%; H, 4.38%; N, 7.60%.

Found: C, 48.94%; H, 4.39%; N, 7.94%.

3,3'-Bis(N-methylmethanesulfonamido)diphenylmethane (Vb).

Sulfonamide IVb (48.45 g, 0.137 mole) was dissolved in 200 ml of hexamethylphosphoramide (HMPA) and powdered potassium hydroxide (30.66 g, 0.547 mole) was added. The mixture was heated to $90^{\circ}C$ during which time the potassium hydroxide dissolved. Up-on cooling to $25^{\circ}C$ the sulfonamide salt precipitated, but gradually dissolved as methyl iodide (77.74 g, 0.547 mole) was added dropwise over a period of 0.5 hr. After the addition was complete the mixture was heated at $60^{\circ}C$ for 1 hr, cooled to $25^{\circ}C$, and the product was then precipitated by pouring into an ice-water slurry in a blender. The air dried, light tan-colored solid weighed 51.5 g (98%), mp 103.5-105$^{\circ}C$. Recrystallization from benzene-hexane using neutral Norite afforded 48.5 g (93%) of Vb as nearly colorless crystals, mp 105-106$^{\circ}C$. ^{1}HNMR (CDCl$_3$); 7.16 δ (8H, m, phenyl), 4.00 δ (2H, s, methylene), 3.32 δ (6H, s, N-methyl), and 2.84 δ (6H, s, sulfonamide methyl).

ANAL. Calcd. for $C_{17}H_{22}N_2O_4S_2$: C, 53.38%; H, 5.80%; N, 7.32 %.

Found: C, 53.65%; H, 5.80%; N, 7.56%.

4,4'-Bis(N-methylmethanesulfonamido)benzophenone (Vc).

This compound was prepared following the procedure for Vb from sulfonamide IVc (36.8 g, 0.100 mole) to give 38.1 g (96%) of Vc as colorless crystals, mp 158-159$^{\circ}C$ from ethyl acetate-hexane. ^{1}HNMR (CDCl$_3$); 7.70 δ (8H, m, phenyl), 3.40 δ (6H, s, N-methyl), and 2.94 δ (6H, s, sulfonamide methyl).

ANAL. Calcd for $C_{17}H_{20}N_2O_5S_2$: C, 51.50%; H, 5.08%; N, 7.07%.

Found: C, 51.55%; H, 5.11%; N, 7.37%.

3,3'-Bis(N-methylmethanesulfonamido)benzophenone (Vd).
Following the previous procedure, this compound was prepared
from sulfonamide IVd (57.40 g, 0.156 mole) in 92% yield, mp
208-209°C from diglyme. ^{1}HNMR (DMSO-d$_6$); 7.80 δ (8H, m, phenyl),
3.34 δ (6H, 5, N-methyl), and 3.04 δ (6H, s, sulfonamide methyl).
ANAL. Calcd for C$_{17}$H$_{20}$N$_2$O$_5$S$_2$: C, 51.50%; H, 5.08%; N, 7.07%.

Found: C, 51.23%; H, 4.97%; N, 7.04%.

3,3'-Bis(methylamino)diphenylmethane (Ib). Bis-N-methyl-
sulfonamide Vb (10.00 g, 0.0261 mole) was dissolved in 100 ml
of a 60:40 (v/v) acetic acid-concentrated-sulfuric acid mixture.
The solution was stirred at 50°C for 24 hr, poured into 500 ml
of an ice-water slurry and sodium hydroxide added until the pH
of the solution was 9.0. The oily diamine was extracted with
chloroform and the solution dried over anhydrous magnesium
sulfate. The chloroform was removed on a rotary evaporator and
the tan oily residue distilled. The fraction distilling at 168°C
(0.05 mm) was collected as a nearly colorless oil, 4.02 g (68%).
^{1}H NMR (CDCl$_3$); 6.72 δ (8H, m, phenyl), 3.74 δ (2H, s, methylene).
3.44 δ (2H, s, amino), and 2.60 δ (6H, s, N-methyl)
ANAL. Calcd for C$_{15}$H$_{18}$N$_2$: C, 79.60%; H, 8.03%; N, 12.38%.

Found: C, 79.33%; H, 7.88%; N, 12.66%.

4,4'-Bis(methylamino)benzophenone (Ic). Following the pro-
cedure for diamine Ib, this compound was prepared from bis-N-
methylsulfonamide Vc (1.00 g, 0.00253 mole) in 82% yield, mp
130-131°C from benzene-hexane (lit.[13] mp 130°C). ^{1}HNMR (CDCl$_3$);

7.26 δ (8H, m, phenyl), 4.36 δ (2H, 2, amino), 2.98 δ (6H, s, N-methyl).

ANAL. Calcd for $C_{15}H_{16}N_2O$: C, 74.98%; H, 6.71%; N, 11.85%.

Found: C, 74.63%; H, 6.63%; N, 11.77%.

3,3'-Bis(methylamino)benzophenone (Id). This compound was obtained as described above from bis-N-methylsulfonamide Vd (7.80 g, 0.0204 mole) as a yellow viscous oil, which was distilled at 239-241° (0.30 mm); yield 3.13 g (64%). ^{1}HNMR (CDCl$_3$); 7.40 δ(8H, m, phenyl), 3.80 δ (2H, s, amino), and 2.78 δ (6H, s, N-methyl).

ANAL. Calcd for $C_{15}H_{16}N_2O$: C, 74.98%; H, 6.71%; N, 11.85%.

Found: C, 75.27%; H, 6.89%; N, 11.54%.

Polymers

The following procedure is representative of that used for the preparation of N-methylated polyamides IIa-e (Table I). Polymer yields were essentially quantitative in all cases.

Polyamide (IIb) from 4,4'-bis(methylamino)diphenylmethane (Ia) and isophthaloyl dichloride. s-Tetrachloroethane (30 ml) was added to a stirred mixture of diamine Ia (4.52 g, 0.020 mole) and isophthaloyl dichloride (4.06 g, 0.020 mole) contained in a 50 ml resin kettle under a flow of dry nitrogen. The resulting solution was then heated at 110°C for 1 hr, and at 145°C for 2 hr. The viscous, yellow solution was cooled to 30°C, diluted with 20 ml of chloroform and the polymer was precipitated as a white, fibrous solid by pouring slowly into hexane in a blender.

After washing several times with hexane, the polymer was air dried and then dried _in vacuo_ at 150°C for 12 hr to yield 7.10 g (99%) of IIb.

Copolymer VII from 4,4'-bis(methylamino)diphenylmethane (Ia), 4,4'-diaminodiphenylmethane (IIIa) and isophthaloyl dichloride. Diamine Ia (2.26 g, 0.0100 mole), diamine IIIa (1.98 g, 0.0100 mole) and isophthaloyl dichloride (4.06 g, 0.0200 mole) were weighed into a 50 ml resin kettle and 30 ml of TCE was added. A light tan precipitate formed almost immediately after initial dissolution of the monomers and persisted throughout the polymerization reaction. The mixture was heated gradually to 145°C and maintained at that temperature for 21 hr, after which time the mixture was watery and hydrogen chloride evolution had ceased. The cooled mixture was precipitated into hexane in a blender and the granular polymer was filtered, washed with hexane, and dried _in vacuo_ at 150°C for 14 hr. The yeild was 5.3 g (77%).

Preparation of Films

Films of the N-methyl-substituted polyamides IIa-e were made from 7% (w/w) chloroform solutions of the polymers. The film of unsubstituted polyamide VI was prepared from a 7% DMAc solution. Solutions were doctored onto soda-lime glass plates in an enclosed dust-free area at a relative humidity of 10-20%. A blade gap of 15 mil was washed to ensure a final film thickness of approximately 1 mil. A 4 mil blade gap was used to produce thinner films for

infrared analysis. The cast solutions were dried in air for 2 hr at room temperature until tack-free. The films were then heated in a forced air oven for 1 hr each at $100^{\circ}C$ and $200^{\circ}C$. The properties of the cured films are summarized in Table II.
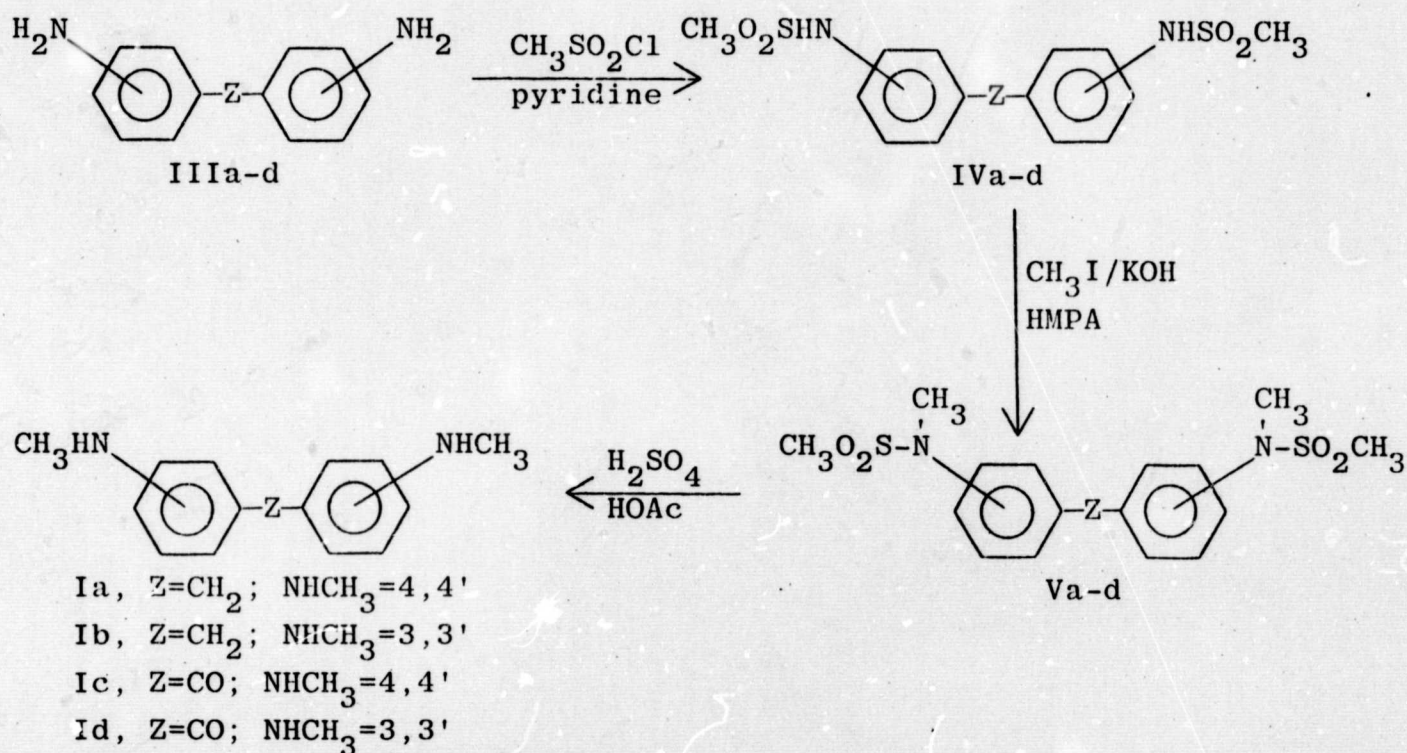
Characterization of Polymers

Inherent viscosities of the polyamide solutions were determined at 0.5% in chloroform or DMAc at $35^{\circ}C$ (Table II). Infrared spectra of the polyamide films were obtained on a Digilab FTS-15 IR in a nitrogen atmosphere.

Elemental analyses of the polymers were performed on polyamide powders by Galbraith Laboratories, Knoxville, Tennessee (Table II). Solubilities of films cured to $200^{\circ}C$ were obtained at 2% (w/w) at room temperature in chloroform, TCE, DMAc, N,N-dimethylformamide (DMF), and N-methylpyrrolidone (NMP)(Table II). Glass transition temperatures (Tg) of polyamide films or powders were determined by differential scanning calorimetry (DSC) on a DuPont Model 990 Thermal Analyzer with the Standard DSC cell attachment in a nitrogen atmosphere at $20^{\circ}C/min$. Torsional braid analyses[14] (TBA) were performed under nitrogen at a heating rate of $3^{\circ}C/min$ on glass fiber braids which had been coated with 7% chloroform or DMAc polymer solutions and preheated to $250^{\circ}C$ in nitrogen. Thermogravimetric analyses of films IIa-IIe, VI, and powder VII were performed in a nitrogen atmosphere using a Perkin Elmer TGS-2 Thermogravimetric System and a heating rate of $2.5^{\circ}C/min$.

RESULTS AND DISCUSSION

Monomer Synthesis

The N,N'-dimethyl aromatic diamines (Ia-d) were synthesized in overall yields of 42-62% from their respective unmethylated analogs (IIIa-d) by conversion of the latter to the corresponding methanesulfonamides or trifluoroacetamides followed by N-methylation and subsequent amide hydrolysis as shown in Reaction Scheme 2. The trifluoroacetamide route,[15] proved to be less desirable than the methanesulfonamide procedure, owing to premature cleavage of the trifluoroacetyl group and subsequent polymethylation during the alkylation step.

Reaction Scheme 2

$$\text{H}_2\text{N} - \bigcirc - Z - \bigcirc - \text{NH}_2 \quad \xrightarrow[\text{pyridine}]{\text{CH}_3\text{SO}_2\text{Cl}} \quad \text{CH}_3\text{O}_2\text{SHN} - \bigcirc - Z - \bigcirc - \text{NHSO}_2\text{CH}_3$$

IIIa-d → IVa-d

$\downarrow$ CH$_3$I/KOH HMPA

Va-d

CH$_3$O$_2$S-N(CH$_3$) - ◯ - Z - ◯ - N(CH$_3$)-SO$_2$CH$_3$

$\xleftarrow[\text{HOAc}]{\text{H}_2\text{SO}_4}$

CH$_3$HN - ◯ - Z - ◯ - NHCH$_3$

Ia, Z=CH$_2$; NHCH$_3$=4,4'
Ib, Z=CH$_2$; NHCH$_3$=3,3'
Ic, Z=CO; NHCH$_3$=4,4'
Id, Z=CO; NHCH$_3$=3,3'

Polymer Synthesis

Since preliminary studies using low temperature solution and interfacial methods consistently resulted in low molecular weight polymer, the N-methylated polyamides IIa-e were prepared by high temperature solution polymerization at concentrations of 15% solids (w/w). Although several different solvents including nitrobenzene, DMAC, hexamethylphosphoramide, chloroform and TCE were used in the polymerization studies, only the latter solvent afforded polyamides with $\eta_{inh} \gtreqless 0.35$, which could be case into flexible films. Unfortunately, all polymers derived from the 3,3'-substituted diamines (Ib and Id) had very low solution viscosities, due presumably to the presence of small amounts (<5% by HPLC) of persistent impurities in the diamines which could not be removed by vacuum distillation. Consequently, these polymers were not investigated further.

In order to more clearly evaluate the effect of N-methylation on the thermal and solubility properties of aromatic polyamides, the unmethylated analog VI of the completely methylated polyamide IIb was prepared by low temperature solution polymerization in DMAC according to a literature procedure.[16] Likewise, the partially N-methylated copolymer VII, derived from diamine IIIb and diamine Ia (1:1) and isophthaloyl dichloride, was prepared for further comparison.

Infrared spectra of both the unsubstituted polyamide VI and partially methylated copolymer VII displayed a broad absorption peak centered at 3300 cm^{-1} due to hydrogen-bonded NH groups. This peak was absent in spectra of polyamides IIa-e. Spectra of VI and VII contained three additional peaks attributable to Amide I, II and III bands[17] at 1650 cm^{-1} (C=O stretch), 1530 cm^{-1} (CNH), and 1250 cm^{-1} (CNH) respectively. Only the Amide I band at 1650 cm^{-1} was present in spectra of the N-methylated polymers IIa-e. A peak of medium intensity at 1435 cm^{-1} in the spectra of the latter was thought to be due to N-CH_3 deformation, since this peak was absent or very weak in the spectra of polymers VI and VII.

Thermal Properties

Melt and T_g characterization. T_g values of the polyamides determined in an inert environment are listed in Table I. In almost every case, the values determined by TBA, a thermomechanical technique, closely agreed with those obtained by the enthalpy changes of DSC. The Tg values obtained by DSC were questionable for those films that had been pretreated in air, and showed evidence of decomposition (films IIc, VI and VII). The TBA method gave more reliable values for these polymers since the braids were pretreated in a dry nitrogen atmosphere. However, when polyamide IIc was pretreated at 200^OC in nitrogen rather than air, presumably oxidation of the methylene groups was minimized and its T_g (129^OC) by DSC was almost identical to that found by TBA (130^OC).

The T_g data in Table I clearly demonstrate that incorporation of methyl groups in place of amide hydrogens proved to be a successful approach for significantly lowering the T_g values of these polymers. For example, the T_g of polymer IIb (162^OC) was over 100^OC lower than that of its unsubstituted analog, polymer VI (280^OC). Likewise, the softening temperature of polymer IIa was found to be much lower than that of its unsubstituted analog, which has been reported at $>360^O$C.[2] The T_g values of the N-methylated polyamides were further reduced by varying the molecular structure of the diacid chloride monomers and thereby introducing more flexibilizing groups. In the series of polymers IIa-IIc containing the diphenylmethane moiety in the

diamine portion, the T_g's ranged from $179^{\circ}C$ for IIa derived from the rigid terephthaloyl monomer, to a minimum of $129^{\circ}C$ for polymer IIc derived from the more flexible diphenylmethane diacid chloride. A similar ($\Delta T_g = 27^{\circ}-32^{\circ}C$) was noted in the values of polymers IId and IIe prepared from substituted benzophenone diamines. Copolymer VII, in which theoretically one-half of the amide nitrogens are methylated, exhibited a T_g ($210^{\circ}C$) midway between that of the unsubstituted polymer VI ($281^{\circ}C$) and the completely N-methylated polymer IIb ($159^{\circ}C$). It is also interesting to note that the polyamides containing the $-CH_2-$ moiety in the amine portion of the repeat unit had T_g values $26^{\circ}-28^{\circ}C$ lower than those made with the $-CO-$ moiety (IIb vs IId and IIc vs IIe). Similar variations in T_g have been observed with aromatic polyimides[11] and unsubstituted aromatic polyamides[6] containing related $-CH_2-$ and $-CO-$ Z-group substitution.

Hill and Walker[9] found that partial N-methylation reduced crystallinity in aliphatic polyamides, and that 100% N-methylation eliminated crystallinity altogether. They reasoned that N-alkylation facilitated separation of polymer chains causing both linear and lateral disorder, thus inhibiting crystallization. This same phenomenon was observed in the present work. Of the five N-methylated polyamide films studied, all were amorphous except those of polyamides IIa and IIb which showed evidence of semicrystalline behavior when cast from 7% chloroform solutions. DSC scans illustrating this behavior for polyamide IIa are reproduced in Figure 1. The melt endotherm at $306^{\circ}C$ in the first DSC curve indicates at least a low degree of crystallinity;

however, a second DSC scan after the film had been melted and quenched in liquid nitrogen showed that the polymer film had become completely amorphous with a T_g of $179^{\circ}C$. The TBA spectrum of this same polymer, Figure 2, showed a more intense T_g damping peak on cooling ($174^{\circ}C$) than on heating ($181^{\circ}C$). These observations indicate that the crystalline character of the material disappears after a melt/quench operation. Similar behavior has been noted for semicrystalline polyimides.[18] Unsubstituted polyamide VI was thought to be partly crystalline due to opaqueness of the polymer film. Unfortunately, melting points by DSC for VI or for copolymer VII were difficult to ascertain due to decomposition of the samples at temperatures around $300^{\circ}C$. The TBA spectrum of the polyamide VI suggested a melt at $380^{\circ}C$, compared to a previously reported value of $350^{\circ}C$.[3] Another source, however, reported difficulty in characterizing this polymer because it underwent decomposition at $360^{\circ}C$.[19]

Thermal Stability. Thermogravimetric analysis (TGA) of polyamides pretreated at $200^{\circ}C$ in air are presented in Figure 3. Polymer decomposition temperatures (PDT) shown in parentheses were obtained as the intersection of tangents drawn to the zero and maximum weight loss portions of the TGA curves. Polyamide VI, which contains no methyl substitution, displayed the lowest thermal stability with a PDT of $480^{\circ}C$. Partial substitution of the amide hydrogens with methyl groups (copolymer VII) increased the PDT by $15^{\circ}C$. Full N-methyl substitution as in polyamide IIb raised the PDT to $535^{\circ}C$. In contrast to our findings, a recent

study on wholly aromatic polyamides containing either terephaloyl or isophthaloyl linkages showed that methyl substitution on the phenylene rings of the polymer chain lowered thermal stability.[7]

Solubility of N-Methylated Polyamides

Room temperature solubilities of the subject polyamides in a variety of chlorinated and amide solvents are presented in Table II. The solubilities of IIa-e and VI and powdered copolymer VIII, all preheated to 200°C in air, were determined at 2% concentrations (w/w). With the exception of polyamide IIc, all of the N-methylated polymers were readily soluble in both chlorinated and amide solvents. However, a film of IIc was rendered completely soluble by preheating it in a nitrogen atmosphere, thereby minimizing the possibility for air-induced crosslinking of the methylene groups. Other authors have reported the effect of oxidative crosslinking on solubility for both aromatic polyamides[19] and polyimides[20] containing methylene groups in the diamine portions of the molecular chains. In the present study, however, only the solubility of polyamide IIc containing methylene linkages in both the diamine and diacid chloride segments was significantly altered by oxidation.

Polyamides VI and VII, unlike their N-methylated analogs, were totally insoluble in TCE or chloroform, and only polyamide VI showed solubility in amide solvents. Improvement in the solubility of polyamides after removal of intermolecular hydrogen-bonding forces by N-alkylation has been previously noted.

Thus, by replacing one-half of the N-hydrogens with methyl groups, Preston was able to improve solubility of wholly aromatic ordered copolymers in DMAc.[21] Similarly, Shashoua and Earekson found such remarkable solubility associated with N-alkylated partially aromatic polyamides that they had difficulty finding a non-solvent for their materials.[20]

Effect of Solvent on Polyamide Properties

Difficulty in removing all traces of solvent from N-substituted polyamides has been reported by Khar'kov, et al.[23] in a study of polymers substituted with hydroxyethyl and cyanoethyl groups. In the present study, a cure temperature of at least $200^\circ C$ for one hr was necessary to remove solvent from the N-substituted polyamide films prepared in TCE and cast from chloroform solutions. Early in this investigation a drying temperature of $100^\circ C$ was used in order to prevent thermal decomposition of the films. However, DSC and TBA spectra of these pretreated films yielded unusually low T_g values and an extra unidentified peak at $90^\circ C$. However, when the films were cured at $200^\circ C$ prior to DSC or at $250^\circ C$ prior to TBA measurements, plasticization by solvent was eliminated and the T_g data became reproducible. The plasticizing solvent was not chloroform as originally suspected but, was identified by FT infrared as TCE, the polymerization medium. Apparently pretreatment of the polyamide films overnight in a vacuum oven at $150^\circ C$ had not been sufficient to remove it. The amount of TCE remaining in films heated only at $100^\circ C$ for one hr was estimated by TGA to

be around 10% by weight. The remarkable ability of this solvent
to remain bound to polymer chains well above its boiling point
of $146^{\circ}C$ has been observed previously with polyphenylquinoxa-
lines.[24]

Acknowledgement
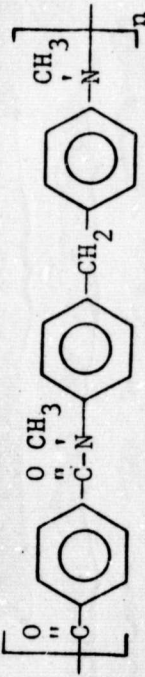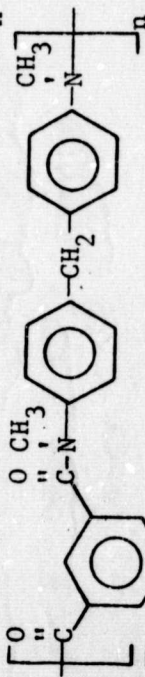
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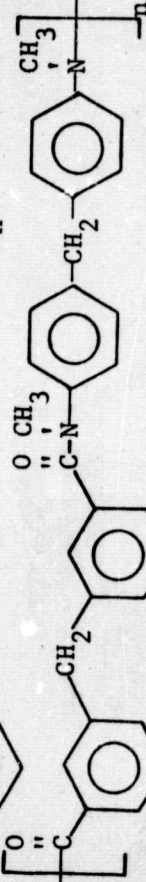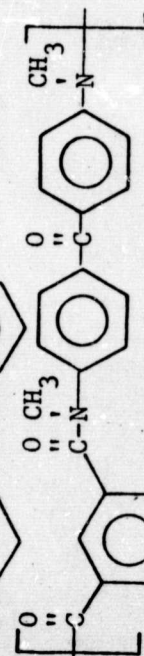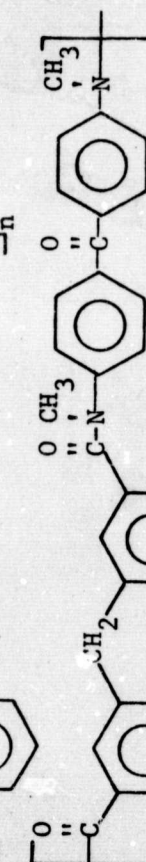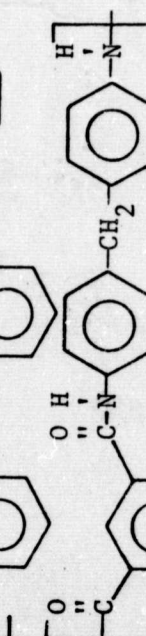2. R. A. Dine- Hart, B. J. C. Moore, and W. W. Wright, J. Polym. Sci. B, 2, 369 (1964).

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TABLE I. GLASS TRANSITION TEMPERATURES OF POLYAMIDES

Polymer No.	Polyamide Structure	DSC T_g (°C)[a]	TBA T_g (°C)[b]
IIa	*(chemical structure)*	179 (T_m = 306)	181 (T_m = 308) 174 on cooling
IIb	*(chemical structure)*	162 (T_m = 345)	159 (T_m = 340)
IIc	*(chemical structure)*	154 (decomp.) 129 (film cured in N_2)	130
IId	*(chemical structure)*	184	185
IIe	*(chemical structure)*	157	153 158 on cooling
VI	*(chemical structure)*	255 (decomp.) 280 after cooling	257 (T_m = 380) 281 on cooling
VII	1:1 Copolymer (IIb and VI) Unsubstituted Polymer	179 (decomp.)[c]	210

[a] DSC scans at 20°C/min in nitrogen were obtained from films preheated to 200°C in air.

[b] TBA spectra at 3°C/min in nitrogen were obtained from braids preheated to 250°C in nitrogen.

[c] Film unattainable, DSC was run on powder preheated to 200°C in air.

TABLE II. ELEMENTAL ANALYSES AND PHYSICAL PROPERTIES OF POLYAMIDES

Polymer No.		Elemental Analysis			η_{inh}	Film Characteristics (Preheated at 200°C)	Solubility
		C	H	N			
IIa	Calcd.	77.51	5.66	7.86	0.56 CHCl$_3$	Pale Yellow-Colorless Brittle	a
	Found	77.27	5.67	7.72			
IIb		77.51	5.66	7.86	0.68 CHCl$_3$	Pale Yellow-Colorless Brittle (N$_2$/Colorless, Flexible)	a
		77.27	5.70	7.78			
IIc		80.69	5.87	6.27	0.42 CHCl$_3$	P. Yellow Brittle (N$_2$/colorless, Flexible)	a
		80.42	5.75	6.12			
IId		74.58	4.90	7.56	0.35 CHCl$_3$	Colorless Flexible	a
		74.31	4.92	7.38			
IIe		78.24	5.25	6.08	0.36 CHCl$_3$	P. Yellow Flexible	a
		78.05	5.25	5.99			
VI		76.81	4.91	8.53	0.80 DMAc	Yellow Opaque	b
		75.53	4.96	8.97			
VII		77.17	5.30	8.18	insol.	Brown Powder	c
		75.45	5.30	8.00			

a = soluble in CHCl$_3$, TCE, DMAc, DMF, NMP

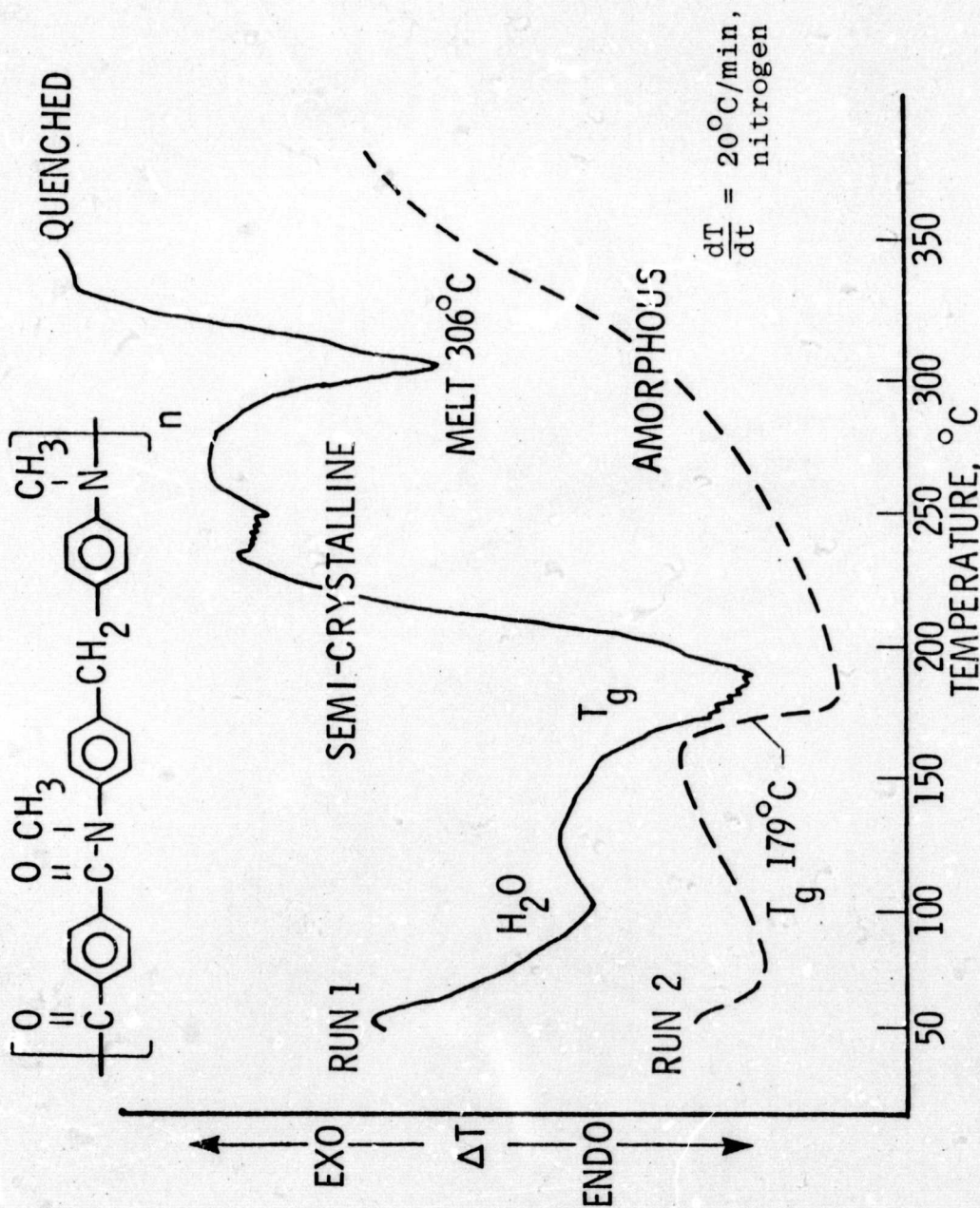b = insoluble in CHCl$_3$, TCE; soluble in DMAC, DMF, NMP

c = insoluble in CHCl$_3$, TCE; partially soluble in DMAc, DMF, NMP

Figure 1

DSC Scan of Polyamide IIa Film
Preheated in Air at 200°C.

- 26 -

Figure 2

Torsional Braid Analysis of Polyamide IIa;

Braid Preheated in Nitrogen to 250$^{\text{O}}$C

- 28 -
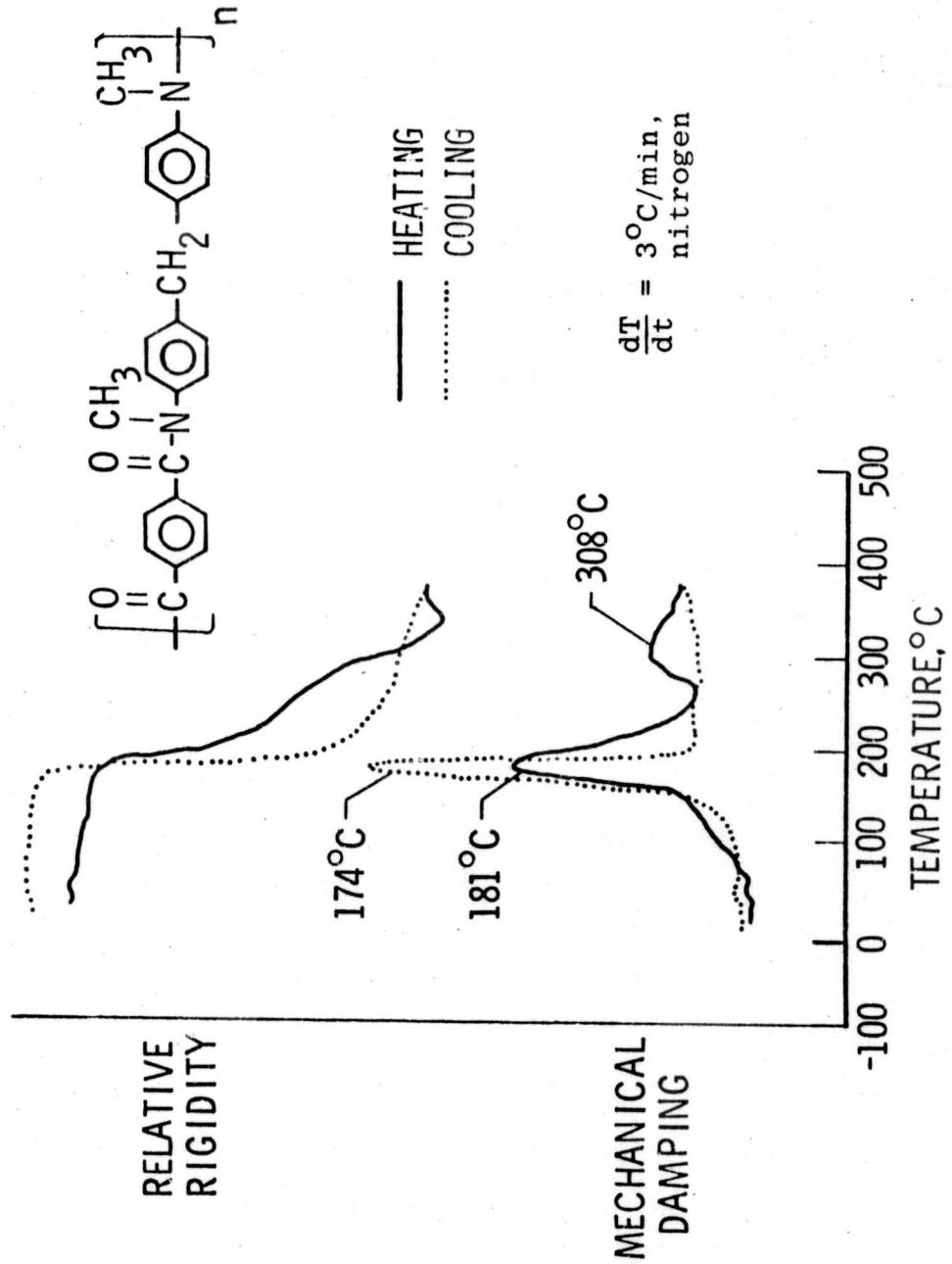
Figure 3

Dynamic TGA Spectra of Polyamides Preheated to 200°C in Air

Polymer Decomposition Temperature, (PDT)

$\partial T / \partial t = 2.5°C/min.$ in air

COPOLYMER VII (495°C)

IIc (500°C)
IId (508°C)
IIa (515°C)
IIe (537°C)
IIb (535°C)

UNSUBSTITUTED VI (480°C)

% WEIGHT LOSS

TEMPERATURE, °C

RELATIVE RIGIDITY

MECHANICAL DAMPING

174°C

181°C

308°C

—— HEATING
········ COOLING

$\dfrac{dT}{dt} = 3°C/min.,$ nitrogen

-100   0   100   200   300   400   500
TEMPERATURE, °C

QUENCHED

MELT 306°C

SEMI-CRYSTALLINE

AMORPHOUS

T_g

H_2O

T_g 179°C

RUN 1

RUN 2

EXO

ΔT

ENDO

$$\frac{dT}{dt} = 20°C/min.,$$
nitrogen

TEMPERATURE, °C

50   100   150   200   250   300   350

$$\left[\begin{array}{c} O \\ \| \\ C \end{array} \text{—} \begin{array}{c} O \\ \| \\ C \end{array} \text{—} \begin{array}{c} CH_3 \\ | \\ N \end{array} \text{—} CH_2 \text{—} \begin{array}{c} CH_3 \\ | \\ N \end{array} \right]_n$$

COPOLYMER VII (495°C)

IIc (500°C)
IId (508°C)
IIa (515°C)
IIe (537°C)
IIb (535°C)

UNSUBSTITUTED VI
(480°C)

Polymer Decomposition Temperature, (PDT)

$\partial T/\partial t = 2.5°C/min.$ in air

TEMPERATURE, °C

% WEIGHT LOSS