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A STUDY OF THERMAL TRANSITIONS IN A NEW SEMICRYSTALLINE
THERMOPLASTIC POLYIMIDE

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INTRODUCTION

Polyimides have become preeminent as technologically and commercially viable materials for thermally stable heteroaromatic applications due to their versatility, processability and high level of thermooxidative stability (1). They have historically been regarded as an amorphous class of high temperature polymers. The synthesis of new polyimide monomers having certain longer connecting groups between the diamine and dianhydride termini has led to the appearance of a new class of high performance materials called semicrystalline polyimides. Some of these new polyimide monomers contain aromatic ketone and ether groups similar to those incorporated in semicrystalline polymers like polyetheretherketone (PEEK) or polyetherketoneketone (PEKK) (2). Several examples of wholly aromatic, semicrystalline polyimides have appeared (See reference 3 and others therein.).

An example of a semicrystalline polyimide developed in this laboratory is crystalline LARC-TPI (3,3',4,4'-benzophenonetetracarboxylic dianhydride - 3,3'-diaminobenzophenone), (BTDA-3,3'-DABP). This material was prepared by

chemically imidizing the poly(amic acid) of BTDA-3,3'-DABP in acetic anhydride and triethylamine (4). One report on this material has indicated that it can be induced into crystallinity from the amorphous state with N-methyl-2-pyrrolidinone (NMP) at elevated temperatures. This new material form shows multiple melting endotherms by differential scanning calorimetry (DSC) (5).

Several potential benefits for developing semicrystalline polyimides include enhanced solvent and caustic chemical resistance, higher tensile strength and modulus, enhanced thermooxidative stability below the melting point and enhanced melt processability, especially when heated to the melting point.

The role of solvent molecules during the crystallization of polyetheretherketones (PEEK) and polyetherketoneketones (PEKK) as well as in the imidization of poly(amic acids) has recently been reported (6-8). Matheson, et al. (6) have reported that solvent effects cannot be simply equated to a suppression of the glass transition temperature, T_g. They postulate that solvent is preferentially absorbed into polymer regions prone to crystallize because of local stresses, conformational arrangements, etc., and that these regions can vary from point to point within a sample. They further state that this model of stress - induced crystallization of thermoplastics is "rather generally valid for thermoplastic materials" (6). Because of increased dilution of the imide ring from the backbone with aromatic ether and ketone segments, one may increasingly regard semicrystalline polyimides as imide-modified semicrystalline PEEK and PEKK polymers.

Brekner and Feger have studied the mechanism of imidization in a model di(amic acid) and poly(amic acid) and found them to behave similarly (7,8). The presence of solvent was found to markedly influence the imidization. Thus, they proposed complexation between the amic acid and the solvent, NMP. Two

distinct loss steps were observed during decomplexation (heating), one for the 1 to 4 initial complex break-up and another for the 1 to 2 complex of pyromellitic dianhydride-aniline di(amic acid) (PMDA-aniline diamic acid/NMP).

Using GC/mass spectrometry they isolated two imidization fractions from this di(amic acid) model. One contained aniline, water and PMDA. The second contained the mixed imide anhydride and a small amount of the bisimide.

This finding supports the thermal imidization studies of Young and Chang (9), who observed a lowering of molecular weight during poly(amic acid) cure before the ultimate molecular weight as a polyimide was achieved. This appeared to be due to initial breakdown of amide linkages in the poly(amic acid) to form shorter amine and anhydride-terminated macromolecules. These chains are postulated to extend at high temperature to the fully-cured polyimide.

Furthermore, Brekner and Feger present an imidization model of a solid (solvent free) di(amic acid) of high reactivity (low selectivity) which can either lose water and imidize to the thermodynamically stable imide or lose aniline to regenerate the anhydride. The anhydride formation is reversible and the equilibrium strongly favors the amic acid. Some anhydride remains because of the escape of aniline from the system.

The objective of this paper is to report a structure-property study of a new semicrystalline thermoplastic polyimide, prepared from 4,4'-isophthaloyldiphthalic anhydride (Figure 1) and 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (Figure 2), designated IDPA-1,3-BABB (Figure 3). We have made an analysis of the multiple DSC transitions seen after various stages of cure, from N,N-dimethylacetamide (DMAc)-laden poly(amic acid) film through a solvent-free film cured to 350°C. The semicrystallinity of some polyimides has probably gone undetected because they were taken through a standard 300°C cure, thus missing lower temperature crystallization and melting transitions. Our

approach was to study thermally treated poly(amic acids) staged to various temperatures by DSC, thermomechanical analysis (TMA) and thermogravimetric analysis (TGA) before and after methylene chloride extraction. We hope to expand and elaborate the Brekner and Feger Model for thermal imidization, as well as discuss the multiple crystallization and melting behavior of this new polyimide. DSC is a dynamic analysis giving an ongoing view of thermal events as well as those built into the polymer during prior thermal staging. Therefore, one must carefully look at the disappearance of a particular DSC transition with increasing cure conditions in order to make accurate interpretations, i.e., look backwards rather than forwards.

EXPERIMENTAL

Details of the preparation of 4,4'-isophthaloyldiphthalic anhydride (IDPA) (Figure 1) have been reported (10,11). The diamine, 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BABB) (Figure 2) was an experimental sample also prepared in this laboratory by Dr. Steve Havens and has been reported (3). The DMAc was obtained from Fluka Chemical Corp.;* the methylene chloride (CH_2Cl_2) from Mallinckrodt;* and the tetrahydrofuran (THF) from Burdick and Jackson Laboratories, Inc.* All were used as received.

<u>Polymer Synthesis</u>

Polymerizations were conducted at 20% solids in DMAc. 1,3-BABB was dissolved in the DMAc in a serum bottle and stirred with a magnetic stirrer.

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*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.

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IDPA was added on an equimolar basis to the dissolved diamine and the solution was allowed to stir at room temperature (RT) overnight. The polymerization in THF was carried out in a similar fashion. The poly(amic acid) was cast on a soda lime glass plate, lightly treated with Frekote 33, at approximately 20 mil wet thickness and dried at RT to tack free film in a dust proof, low humidity chamber. Films were cured to varying temperatures for times as indicated in forced air and/or vacuum ovens. Cooled films were readily removed from the plates with a razor blade unless otherwise indicated. Films for methylene chloride extraction were prepared as indicated, removed from the glass plate, steeped in a dish of methylene chloride and stirred. They were then blotted dry and cured as indicated.

Characterization Methodology

Inherent viscosities (η_{inh}, dl/g) were determined for the poly(amic acid) solutions in DMAc at 0.5% (wt./vol.) and 35°C. DSC was performed using either a DuPont 990 Thermal Analyzer at a scan rate of 20°C/min and a sensitivity of 0.5 (mcal/sec)/in or a DuPont 1090 Thermal Analyzer at a scan rate of 20°C/min.

Films were characterized as "creasable" when they could withstand a 180° fold followed by a 360° fold with a finger crease; "brittle" films snapped or tore at the crease line. Films were also described as transparent, translucent or opaque based on their appearance to light transmission.

Crystallinity information was obtained via Wide Angle X-ray Scattering (WAXS) and polarized light microscopy. WAXS was performed on a Philips APD 3600, XRG 3100 at 45 kV and 40 mA using copper radiation with a flat sample holder and a graphite monochromator. The intensity, measured for a 1 second time increment every 0.01 degree (2θ), was recorded on a hard disc for the angular range: 5.0°-40.0° (2θ). The light microscope (Reichert Nr. 309072)

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was operated using a Sorensen Xe lamp supply XLS1 equipped with a polarized analyzing lens.

Dynamic thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGS-2 thermogravimetric system at a programmed heating rate of 2.5°C/min from 25°C to 550°C.

TMA was performed on a DuPont 943 thermomechanical analyzer used in conjunction with a DuPont 9900 computer/thermal analyzer at a scan rate of 5°C/min from RT through T_g with 2.0 g added weight or from RT to break with no added weight.

Film tensile properties at 25° and 200°C were obtained on an Instron Universal Testing Instrument with a Model 4068 infrared parabolic clamshell radiant heating chamber. Mechanical tests were performed according to ASTM D882.

WAXS data was analyzed by the Hermans-Weidinger Method (12) for percent crystallinity. Because this method depends only on the existence of the proportionality between the experimentally measured crystalline intensity, I_c and the crystalline fraction and between the amorphous intensity, I_a and the amorphous fraction, two intensity factors are neglected, namely the polarization factor and the correction for incoherent scattering.

RESULTS AND DISCUSSION

The preparation of the IDPA monomer is outlined in Figure 1; its synthesis, polymerization and initial characterization have been reported in preliminary form (10,11). o-Xylene was condensed with isophthaloyldichloride and anhydrous aluminum chloride in a Friedel-Crafts reaction. The resulting tetramethyldiketone was oxidized with nitric acid in a liquid phase pressure

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reactor to afford the tetracarboxylic acid. Nitration of the initially activated o-xylyl rings was minimized by incremental addition of the conc. HNO_3 under pressure at elevated temperature, allowing oxidation to proceed in preference to nitration. Formation of the dianhydride was attained by slurrying the tetracarboxylic acid in acetic anhydride - toluene at reflux. The product remained insoluble in the reaction solvents and the impurities dissolved in the filtrate. The overall yield of polymer grade IDPA, based on starting isophthaloyldichloride, was 69%. The structure of the resulting IDPA-1,3-BABB polyimide is given in Figure 3. By utilizing an unusually high molecular weight diamine and dianhydride, we have diluted some of the imide linkage in the backbone to generate polyimides containing increased numbers of phenyl, ether and ketone groups. This dilution may help explain the unexpected semicrystallinity of this polyimide.

Figure 4 records a DSC experiment performed on the 300°C air-imidized film. The 350°C endotherm (melting) and its preceeding crystallization peak (a) were unexpected. A rerun (b) after quenching gave essentially an amorphous polyimide with a T_g of 213°C. The torsional braid analysis spectrum (TBA) gave a sharp T_g damping peak at 214°C (average of the heat-up and cool-down values) after a braid cure of 1 h each at 100°, 200° and 220°C in nitrogen.

DSC melting of the 300°C cured film could not be reintroduced (Figure 4, c) by slow cooling from the previous run to 25°C, nor could transitions other than T_g and melting after steeping in DMAc at 25°C for 24 h and air drying at 100°C for 1 h (d). Unlike the corresponding BTDA-1,3-BABB composition which could be annealed to semicrystallinity from the amorphous state (3), we were unable to reintroduce semicrystallinity in films taken by DSC through the melt, held at 350°C for 2 h and cooled. Likewise, we were unsuccessful with a 4 mol % aniline-endcapped IDPA-1,3-BABB polyimide film cured to 200°C and held

for 3 h at 325°C or 5 min. at 400°C. (Ambient cooling made under DSC glass cover, ~ 2 h).

The semicrystallinity of this same IDPA-1,3-BABB polyimide film cured in air to 300°C was confirmed by wide-angle x-ray scattering (WAXS) in Figure 5. Three large scattering peaks above the amorphous halo were seen, typical of semicrystalline phthalimide reflections.

Another DSC study was initiated in an attempt to further understand the nature of this crystallinity (Figure 6). DSC scans were run on separate polymer films staged on glass to various temperatures. Surprisingly, the first experiment (A) with this air-dried poly(amic acid) film cured 1 h at 100°C yielded five first order transitions, which were assigned as follows: 169°C (endo), DMAc loss and imidization; 180°C (exo), kinetic crystallization; 286°C (endo), kinetic or initial melting; 315°C (exo), thermodynamic crystallization; and 348°C (endo) thermodynamic or final melting. Film A was probably only slightly imidized before the DSC run; no doubt, imidization and crystallization occur during heating in the DSC pan.

In film B (cured to 125°C in air) the early imidization and solvent loss peaks have disappeared, leaving what may be a second-order transition, perhaps a DMAc-laden T_g of polymer. The first clear polyimide T_g appears after the 275°C cure (film E). After the 300°C cure (film G) the kinetic melting and thermodynamic crystallization peaks have been lost to leave only one thermodynamic melting and a T_g transition.

In answer to the question as to whether these two types of crystallinity could have arisen by interaction of the polymer with the glass surface during cure, we cast IDPA-1,3-BABB films on Kapton H® film and cured these to 200°C in air. DSC of the resulting composite films were identical to those in Figure 6C, indicating that the nature of the glass surface had no effect in developing

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crystallinity. (The T_g of Kapton is known to be very high and outside the boundary of this experiment).

The 125°C curing temperature appears to be a transition point between amorphous and semicrystalline polymer (Figure 6, B). Film A, which had been cured at 100°C for 1 h in air, was soluble in DMAc at 25°C, creasable and transparent. All films taken to cure temperatures (B) or higher (films B-H) were insoluble in refluxing DMAc after 0.5 h, creasable, translucent and displayed some evidence of T_g by DSC. They had almost no curing or DMAc loss peaks below approximately 250°C and were semicrystalline by WAXS.

Figure 7 displays additional DSC data taken after early cure stages. The initial run (A), 10 h at 50°C (vacuum), gave multiple transitions around 166°C, perhaps due to break-up of poly(amic acid) - DMAc complexes as has been reported for those of NMP (7,8). Studies in this laboratory have shown that no imidization occurs below 50°C, hence this thermal treatment apparently only removes DMAc. Scan A also displays a sharp exotherm at 181°C. With increasing severity of cure (B-D), this peak sharpens and grows in area, and the baseline flattens. We interpret this exotherm at 194°C to represent the initial or kinetic crystallization exotherm. Dynamic TGA of film D shows a 11.6% plateau weight loss. The theoretical water of imidization is 3.88%. Thus, after 24 h at 50°C (vacuum) followed by 72 h at 100°C (air), film D still contains a significant amount of solvent.

It appears that this initial exotherm, increasing from 181° to 194°C, represents the (initial) kinetic crystallization of some polymer species still containing DMAc molecules. The second order transition at 143°C may be the T_g of a low molecular weight, solvent-containing form of the polymer.

Figure 8 presents the macromolecular WAXS diffraction intensities of a series of poly(amic acids) thermally staged at various conditions. Crystallinity of

about 5.5% first appeared after heating the film for 24 h at 50°C (vacuum) followed by 1 h at 125°C (air) (C). According to the Hermans-Weidinger method (12), the maximum crystallinity (Figure 8, graph F) was calculated to be 25 ± 3.5% after the 275°C cure.

All films cured for 1 h at 125°C or higher became translucent, indicative of their semicrystallinity; those treated below this temperature were clear and light yellow in color. Direct observation of spherulites by polarized light microscopy was made in only two thin films, one cured to 250°C and another cured to 275°C in air (Figure 9). These thin IDPA-1,3-BABB polyimide films showed a moderate number of spherulites 6-8 ± 0.5 μm in diameter, having their characteristic Maltese cross patterns. For reasons unknown we observed no spherulites in any of the other translucent thin films.

Further qualitative analysis of this series of thermally staged films (Figure 10) by TMA (not taken to break) showed three softening regions. The first (160°C) stretching may be due to the Tg of the solvent-laden poly(amic acid) or polyimide or due to stretching accompanying rapid DMAc loss. TGA results, discussed subsequently, showed that after thermal treatment for 24 h at 50°C (vacuum) followed by 72 h at 100°C (air) this film displayed a plateau weight loss of 11.6%. (The theoretical water of imidization is 3.88%). Meaningful interpretation in this region appears impossible because of the complexity of events.

The second softening phenomenon in Figure 10 (278-287°C) correlated well with kinetic melting temperatures obtained by DSC. Values from the third softening phenomenon correlated with the thermodynamic melting temperatures (357° and 359°C) from DSC. Thus, TMA seems useful as a qualitative tool for measuring these transitions. Further analysis (Figure 11) of the 160°C softening film from Figure 10 taken to break showed softening

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temperatures of 157°C, 295°C and 391°C. The film contracted in the TMA clamp before breaking at point x.

In an attempt to try to understand further details about the nature of the crystallinity in these polyimide films, several additional experiments were performed. Figure 12 shows the effect of steeping an air-dried poly(amic acid) film in methylene chloride for three days at 25°C. The resulting film was dried 24 h at 50°C (vacuum) followed by 1 h at 125°C (air). As can be seen, the DSC of the steeped and dried film (a) showed an imidization endotherm at 211°C; however, no thermal transitions due to crystallization or melting were seen, nor could they be induced in the DSC pan. The TGA of a similarly treated methylene chloride steeped film (dried 1 h at 100°C in air) displayed a 6.6% plateau weight loss (theoretical water of imidization, 3.88%).

The identically cured unsteeped film (Figure 12, d) lost approximately 9.4% volatiles at the TGA plateau; it had a solvent depressed T_g of 175°C and showed both kinetic and thermodynamic melting. It is apparent that steeping in methylene chloride before imidization removes essentially all of the DMAc, the absence of which prevents crystallization during imidization. Thus, it appears that the kinetic crystallization is a solvent induced crystallization aided by DMAc.

Further WAXS evidence of the solvent induced crystallization hypothesis is given in Figure 13. Whereas two unextracted poly(amic acid) films cured and annealed to 250° and 300°C were crystalline by WAXS, identical methylene chloride extracted films which were then cured showed only a broad amorphous halo.

Brekner and Feger have concluded that during imidization, decomplexation of NMP from a PMDA-aniline diamic acid model occurs (7). "After full decomplexation hydrogen bonds still exist and hinder imidization." Only at temperatures high enough to break the hydrogen bonds can the highly

reactive free groups react "to form imide or anhydride." Our results appear to confirm theirs. We observed an imidization endotherm in the methylene chloride steeped and dried film at 211°C (Figure 12); the DMAc-containing (unsteeped) film displayed only a trace of a transition in the same region (Figure 6). Thus, the unsteeped poly(amic acid) appeared to have undergone substantial imidization much earlier (169°C) based on DSC after the 100°C, 1 h (air) cure.

Likewise, a similar annealing study is shown in Figure 14. Two air-dried poly(amic acid) films were steeped in methylene chloride for 24 h at 25°C and heated to 100°C (air) for 1 h. One film was then annealed at 265°C (vac.) for 7 h (2/3 between T_g and kinetic melting point) and the other at 295°C (vac.) for 7 h (2/3 between T_g and thermodynamic melting point). Both were slowly cooled (overnight) to 25°C to try to induce crystallinity. DSC experiments (Study 1 and 2) revealed no crystallization or melting transitions and a T_g of 212°C.

Furthermore, when the polymerization was conducted in tetrahydrofuran (THF) (Figure 15) the DSC scans revealed a polyimide that was amorphous. Yet, when this same THF solution was diluted 1:1 with DMAc and a similar film was prepared (Figure 15), DSC revealed both kinetic and thermodynamic crystallinity. Thus, it appears that DMAc (or perhaps other similar amide solvents) are necessary to induce crystallinity in this polyimide.

The dynamic TGA results (previously discussed) of films cured under various conditions are given in Figure 16. Weight-loss plateaus have been compared with cure conditions. Thus, a poly(amic acid) film vacuum dried 10 h at 50°C still contained approximately 17% DMAc (20.8%-3.88%). That same film dried to 125°C in air retained 5.5% DMAc (9.4%-3.9%), whereas one steeped in methylene chloride 24 h at 25°C and then dried in air 1 h at 100°C contained only 2.7% DMAc.

Table 1 presents the tensile film properties of two films, the first cured to 275°C and the second cured to 325°C. These temperatures were chosen since they indicate approximate temperatures of maximum crystallinity by DSC. Values of average yield strength, tensile strength, tangent modulus and percent elongation were however, essentially the same after each set of air imidization conditions, both measured at 25°C and at 200°C. The nature of the two crystalline phases does not appear to significantly affect the relative tensile properties of the films.

CONCLUSIONS

A new semicrystalline polyimide designated IDPA-1,3-BABB has been prepared and found to proceed through a kinetic and a thermodynamic crystalline form during cure. The initial kinetic crystallization (exo) was observed at 194°C by DSC and appeared to involve solvent (DMAc) induced crystallization. We also observed a kinetic melting transition at 285°C (endo), a thermodynamic crystallization at 320°C (exo) and a final thermodynamic melting (endo) at 350°C. Removal of most of the DMAc from the poly(amic acid) film before cure using methylene chloride extraction impeded crystallization, resulting in a fully cured polyimide that was thick, porous and amorphous.

All films cured from DMAc at or above 125°C were translucent and semicrystalline as determined by WAXS and DSC. After a cure temperature of 300°C or more the kinetic transitions disappeared, leaving a semicrystalline form (thermodynamic) having a Tg of 213°C and a melting point of approximately 350°C. Polarized transmission light microscopy revealed spherulites 6-8 ± 0.5 μm in diameter present in only those films cured to 250°C and 275°C, although all films cured to 125°C or above were translucent and

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semicrystalline as determined by WAXS. X-ray diffraction studies on film pieces using the method of Hermans and Weidinger indicate the polyimide had a maximum crystallinity of 25 ± 3.5%.

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81%

Anhydrous AlCl₃ in excess o-xylene

IDPA

1. HNO₃/185°C, 2h
2. Ac₂O, toluene, Δ

1. 93%
2. 91%
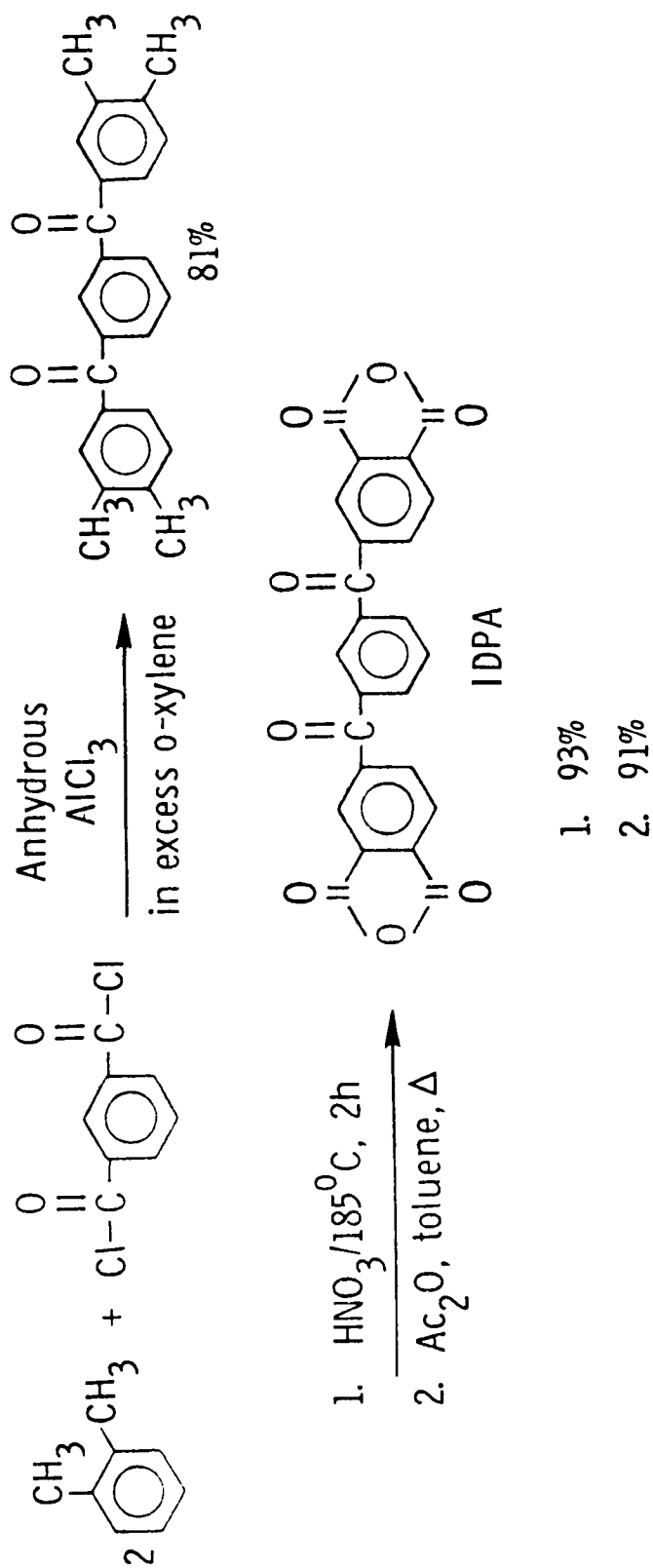
J. R. Pratt, D. A. Blackwell, T. L. St. Clair, and N. L. Allphin,

Polymer Preprints, 29 (1), 128 (1988) (Toronto).

Figure 1. Preparation of the IDPA Monomer.

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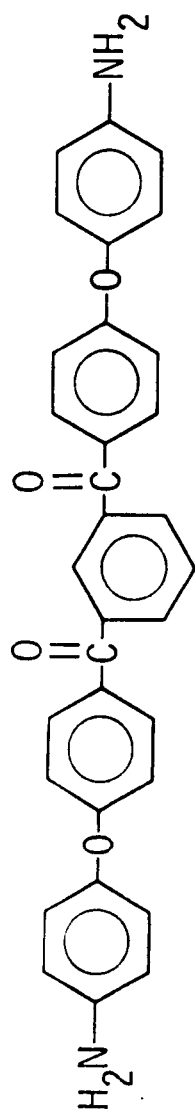
P. M. Hergenrother, N. T. Wakelyn & S. J. Havens,

J. Poly. Sci: Part A: Polymer Chemistry, 25, 1093(1987).

Figure 2. 1,3-BIS(4-AMINOPHENOXY-4'-BENZOYL) BENZENE
(1,3-BABB) SYNTHESIS.
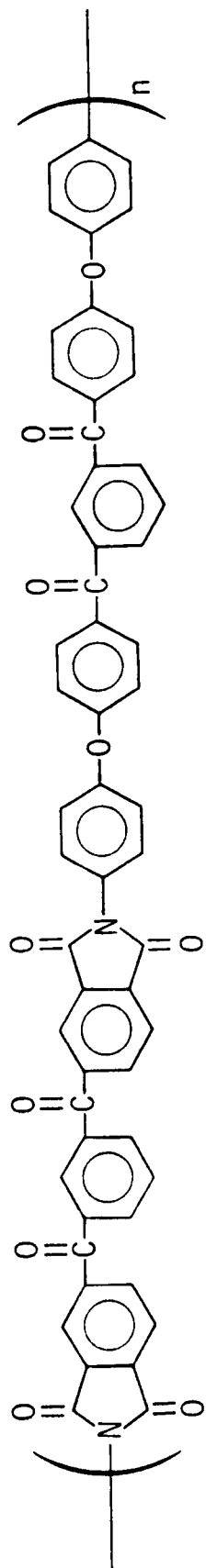
Figure 3. Structure of 4,4'-Isophthaloyldiphthalic Anhydride-
1,3-Bis (4-aminophenoxy-4'-benzoyl) benzene
(IDPA-1,3-BABB) polyimide

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Exo ← Heat flow → Endo

Temperature, °C

0 50 100 150 200 250 300 350 400 450 500 550 600

Tg = 213°C

a
b
c
d

3.9 mg sample

a. RT→350°C, 20°C/min: fast cool, range 0.5

b. RT→400°C, 20°C/min: slow cool ~2h, range 0.5

c. 80°C→500°C, 100°C/min, range 1.0

7.8 mg sample

d. RT→500°C, 20°C/min, range 0.5

Sensitivity: (mcal/sec)/in
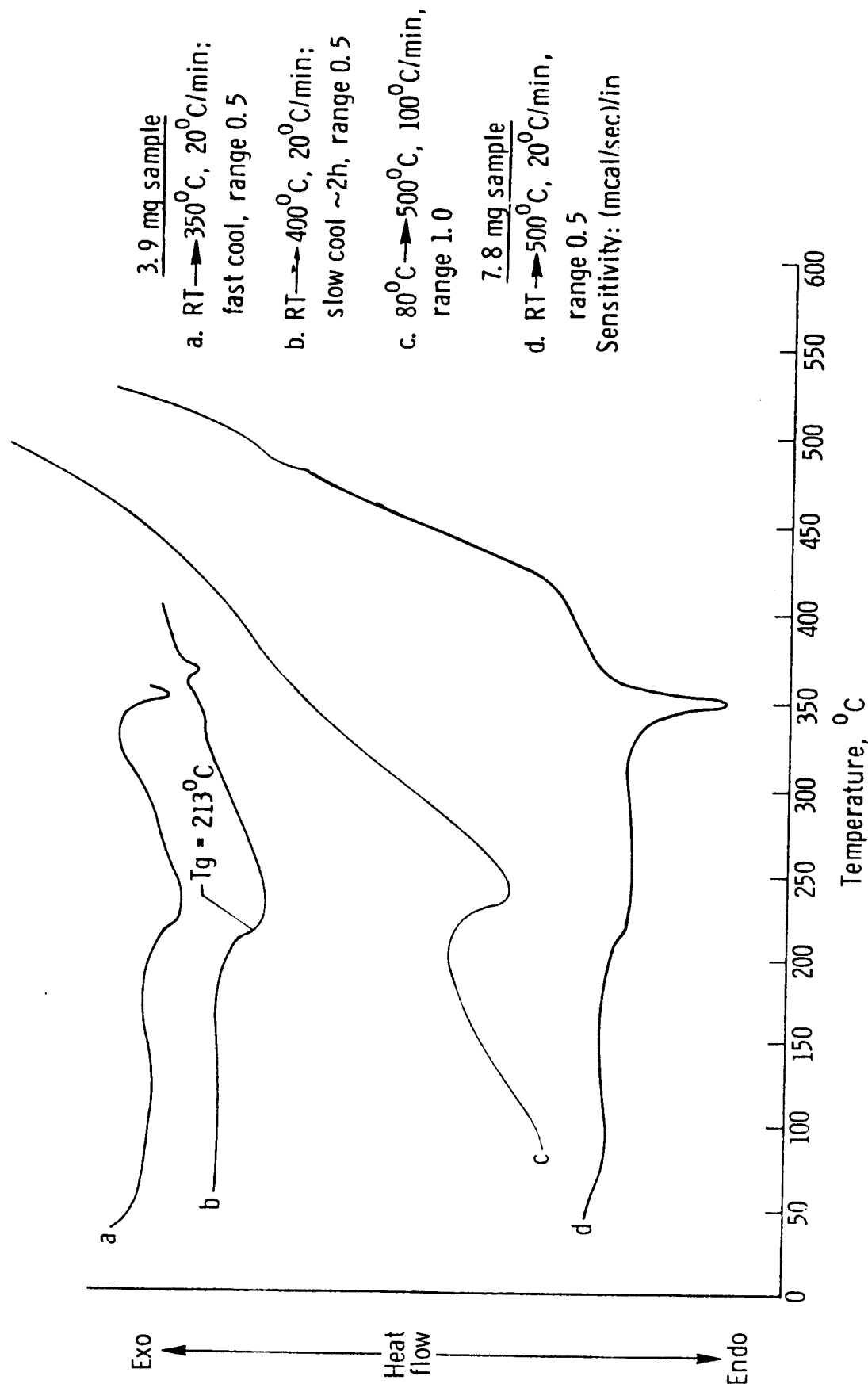
Figure 4. Original DSC experiment (a-c) of IDPA-1,3-BABB film cured 1 hour each 100°C, 200°C, 300°C in air. DSC scan (d) of identical film after steeping in DMAc at 25°C, 24 h then air dried 1 hr at 100°C.

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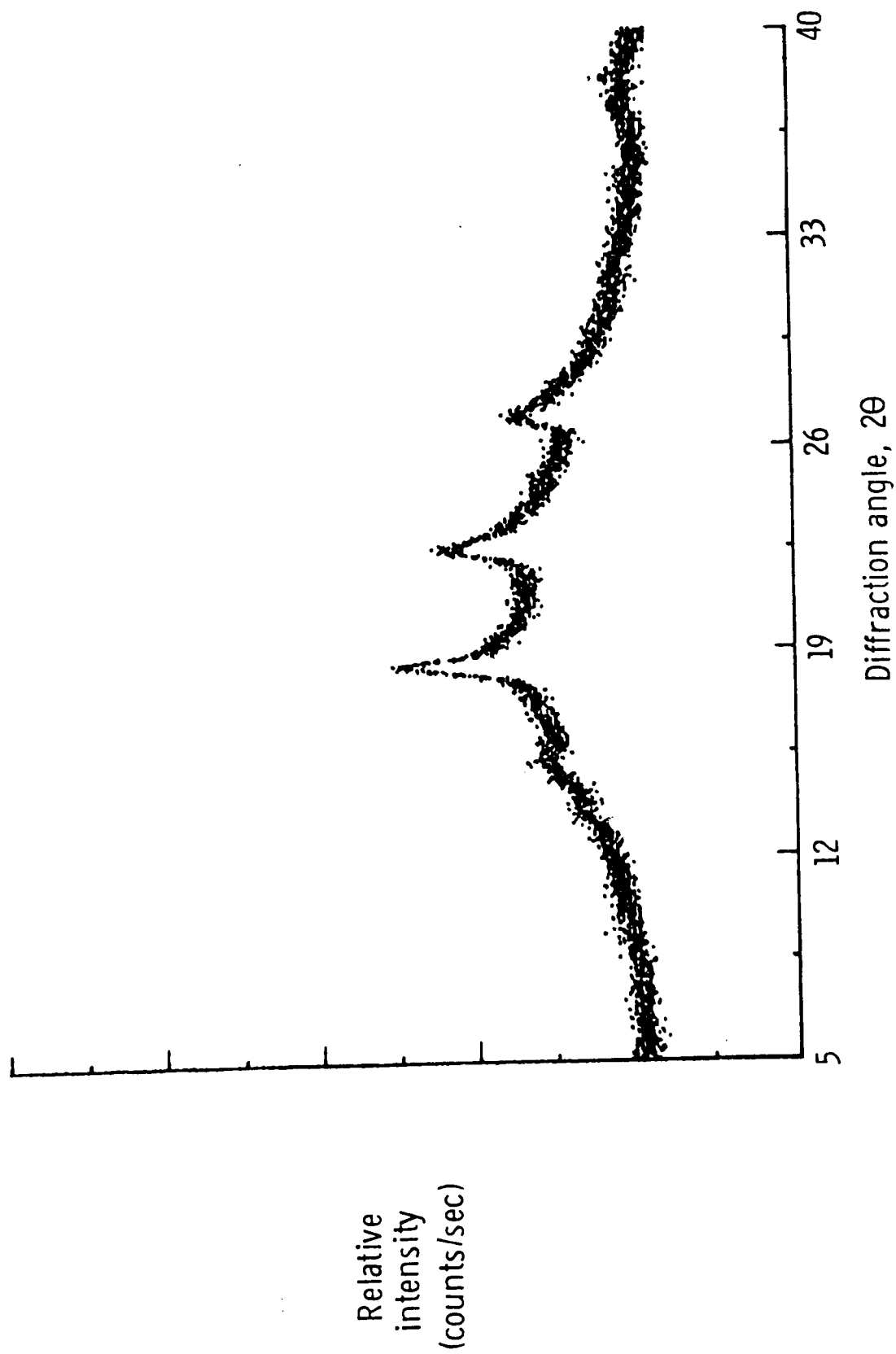
Figure 5. X-ray diffractogram (WAXS) of original IDPA-1,3-BABB film cured to 300°C in air.
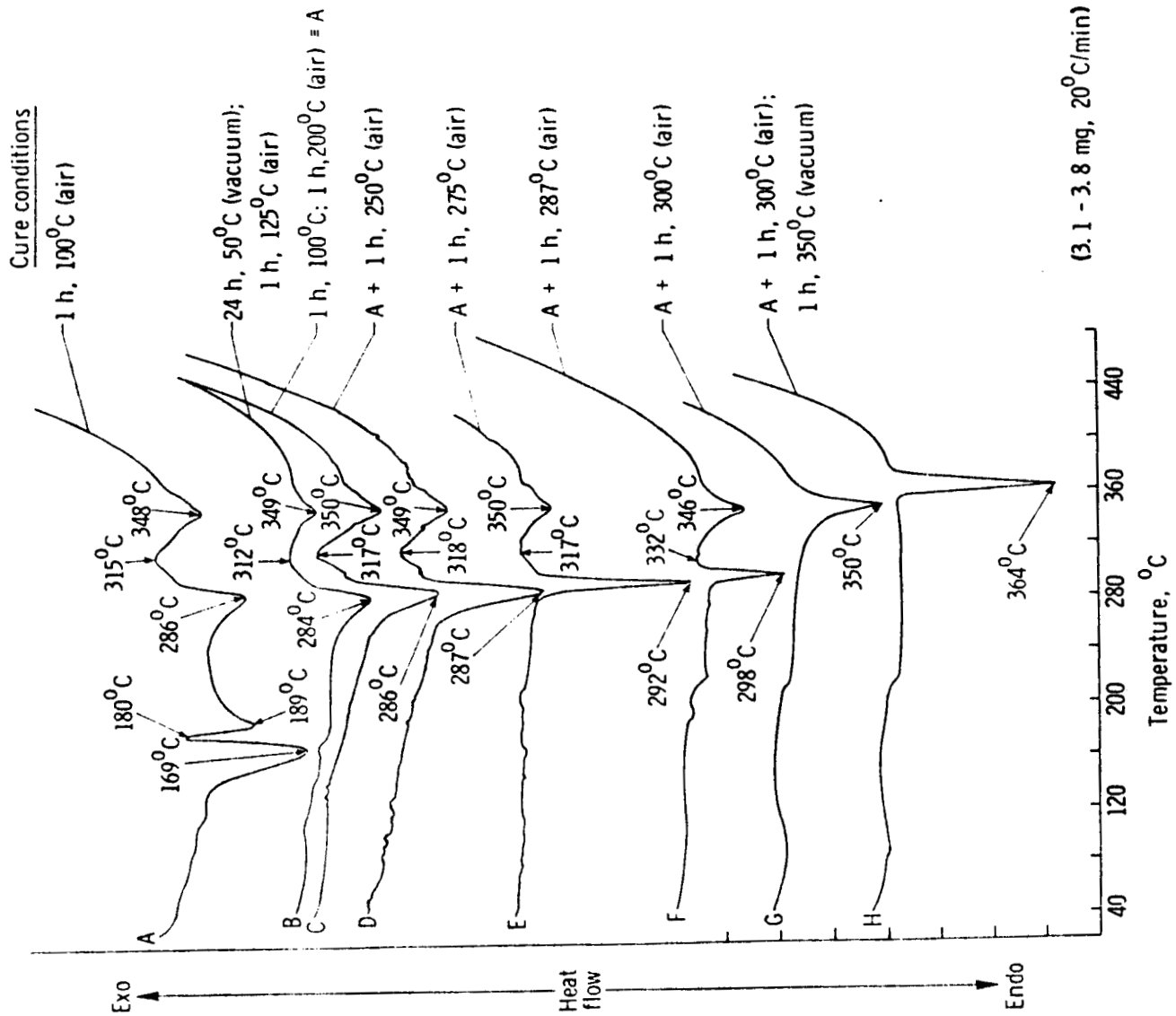
Figure 6. DSC transitions of IDPA-1,3-BABB films as cured.

21
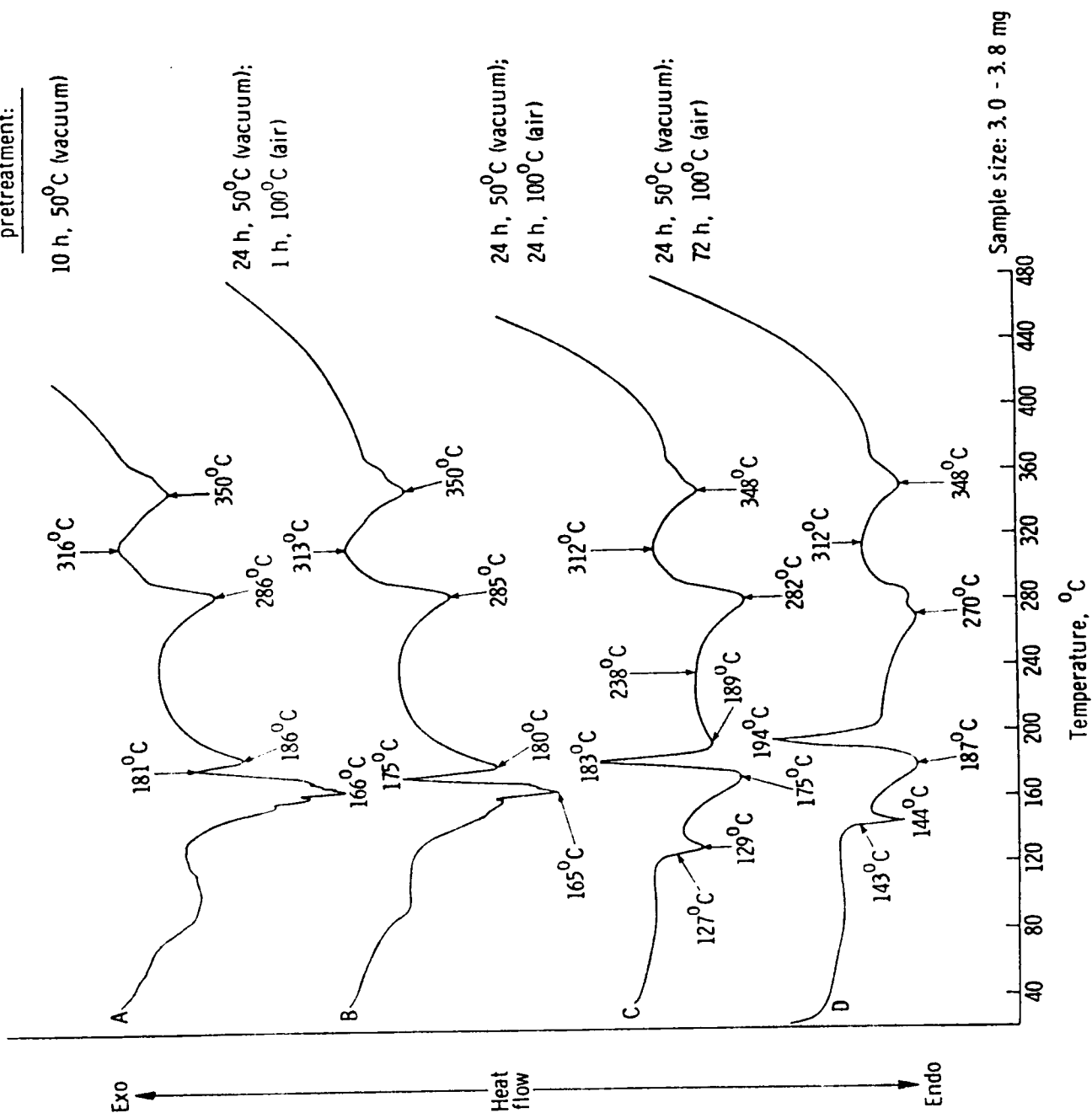
Figure 7. DSC transitions of IDPA-1,3-BABB films during initial cure stages

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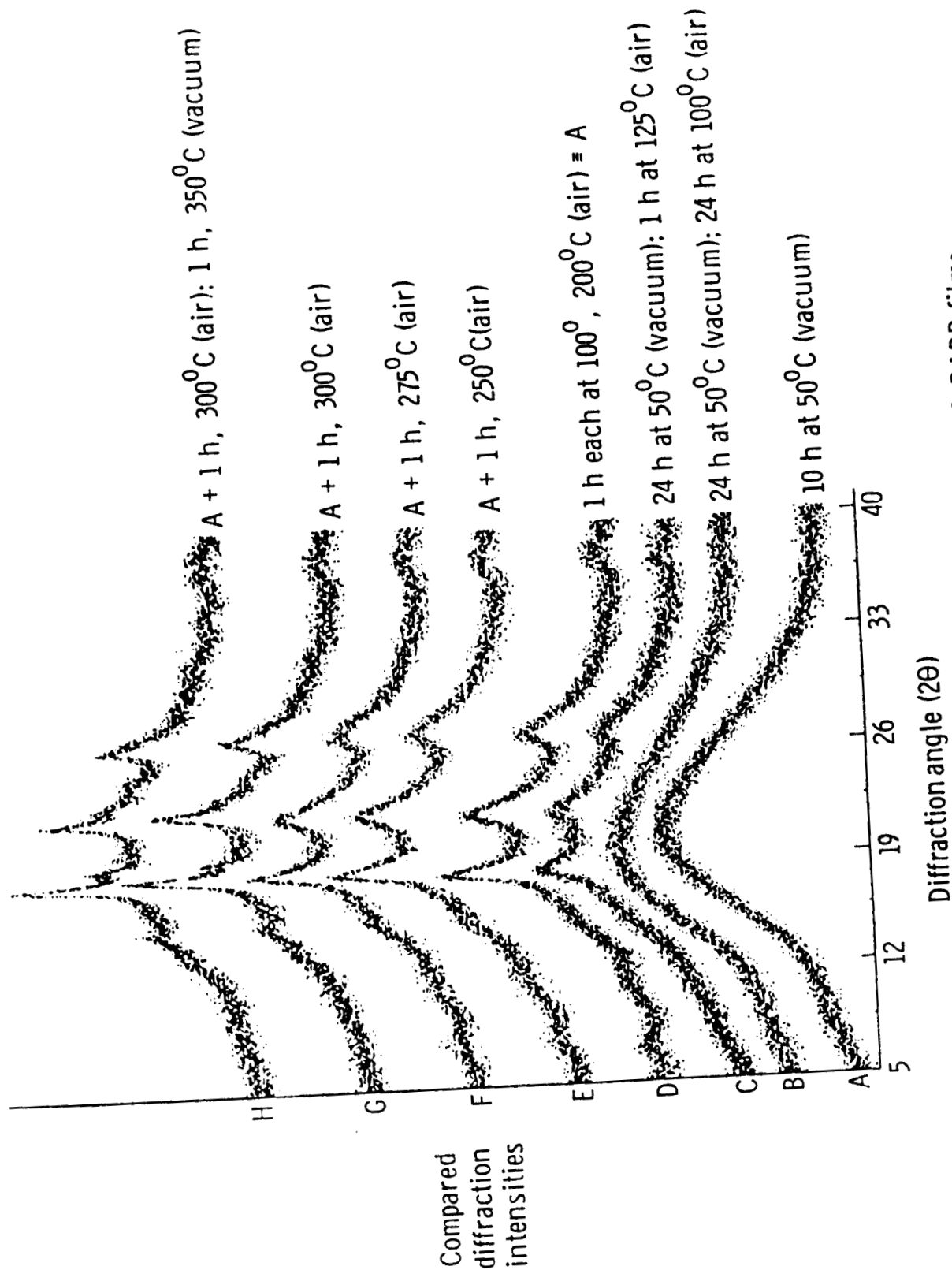
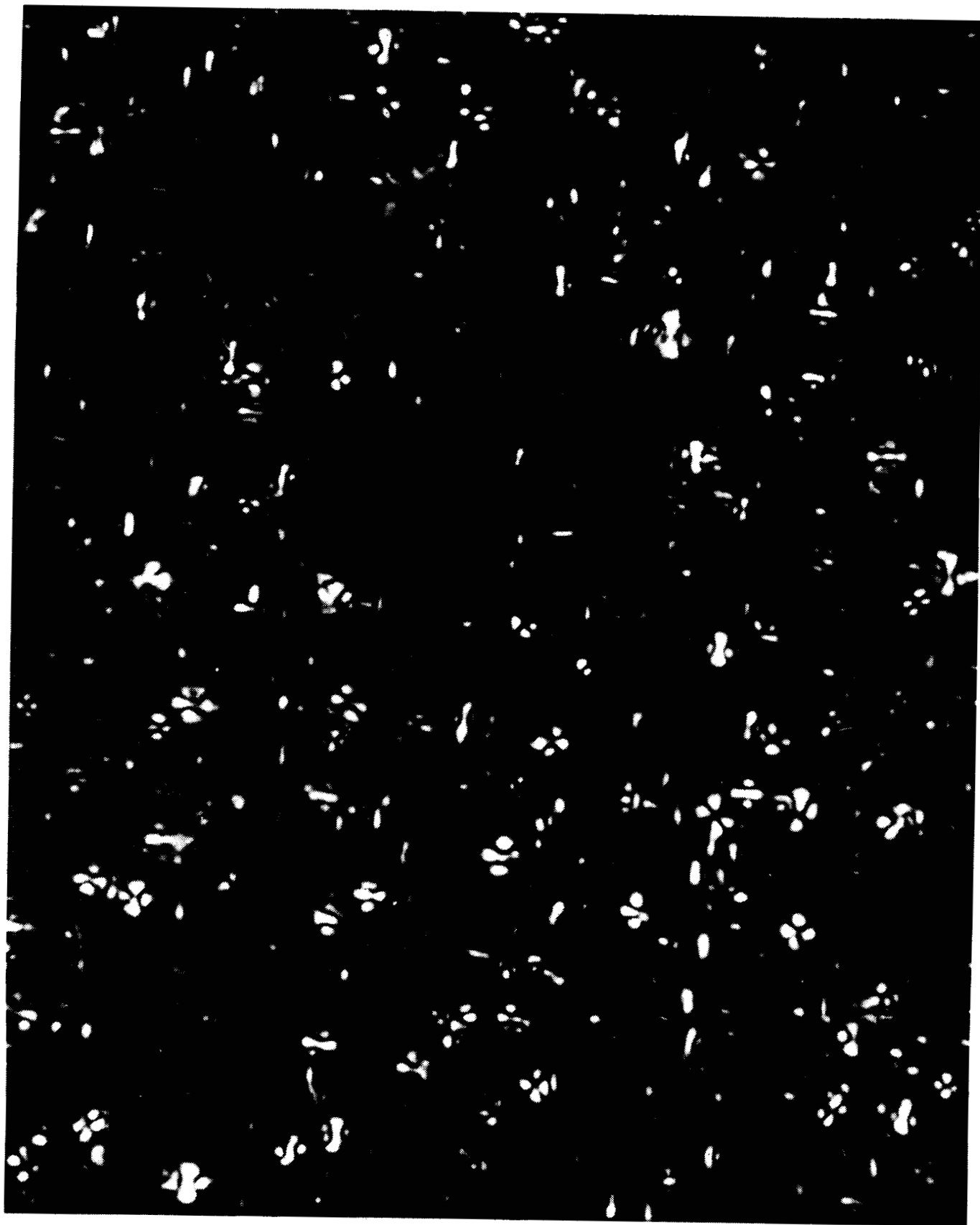Figure 8 . WAXS vs cure conditions of IDPA-1,3-BABB films

H — A + 1 h, 300°C (air): 1 h, 350°C (vacuum)

G — A + 1 h, 300°C (air)

F — A + 1 h, 275°C (air)

— A + 1 h, 250°C(air)

E — 1 h each at 100°, 200°C (air) ≡ A

D — 24 h at 50°C (vacuum): 1 h at 125°C (air)

C — 24 h at 50°C (vacuum): 24 h at 100°C (air)

B — 10 h at 50°C (vacuum)

Compared
diffraction
intensities

Diffraction angle (2θ)

5   12   19   26   33   40

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Figure 9. Polarized light micrograph (220 x) of IDPA-1,3-BABB polyimide cured to 275°C in air.

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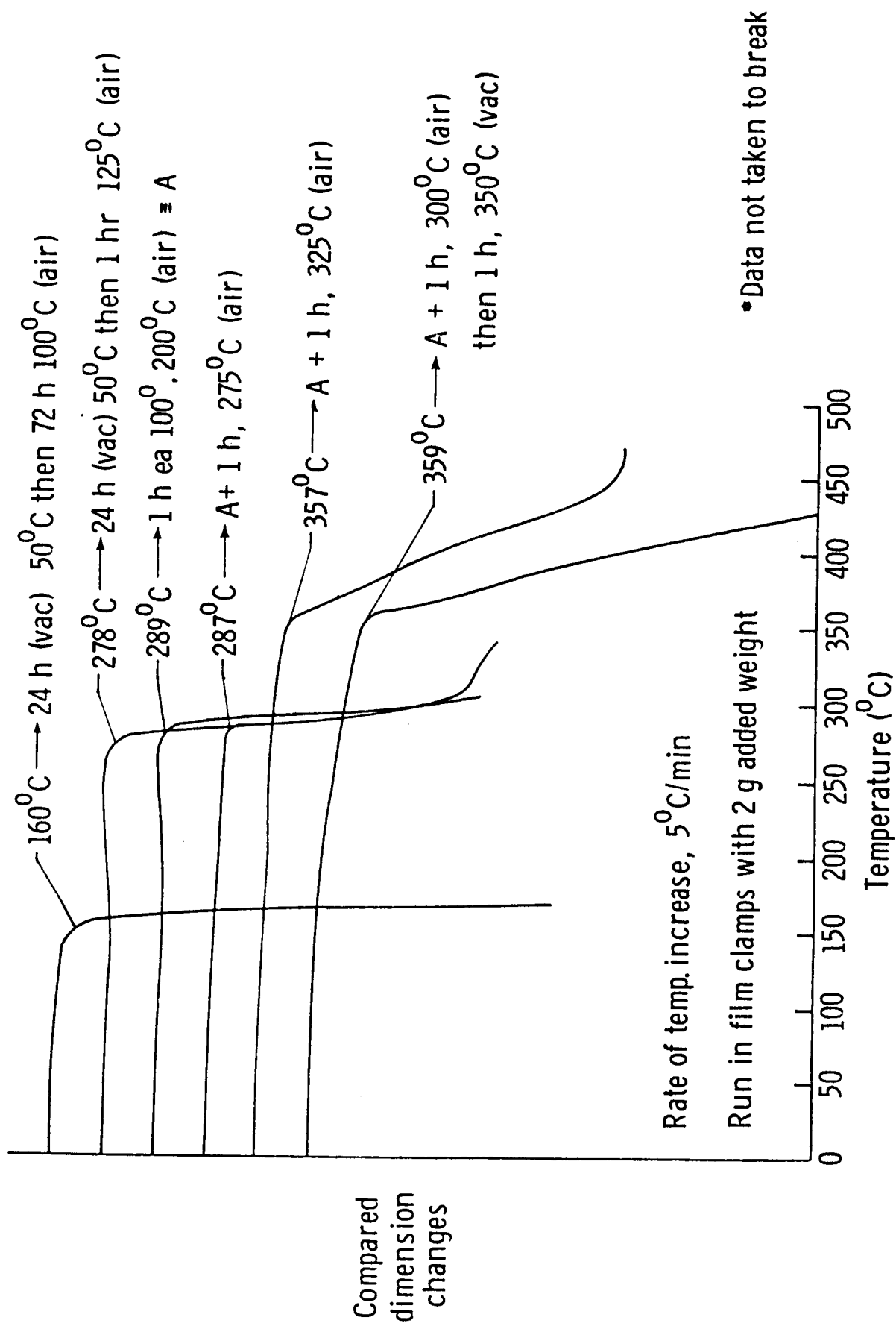
Figure 10. Thermomechanical analysis (TMA) of IDPA-1,3-BABB films *
vs extent of cure. (Thermal history of films included.)

Initial length, 1.600 mm

Initial thickness, 0.0450 mm

clamps, 0.0g added weight

Elongation:
1055 μm
66.0%

157°C

295°C

391°C

X

Cured 24 h, 50°C (vac); 72 h, 100°C (air)

X, elongation to break:

5°C/min

Dimension change (μm)

0   -400   -800   -1200   -1600   -2000

Temperature (°C)

0   100   200   300   400   500
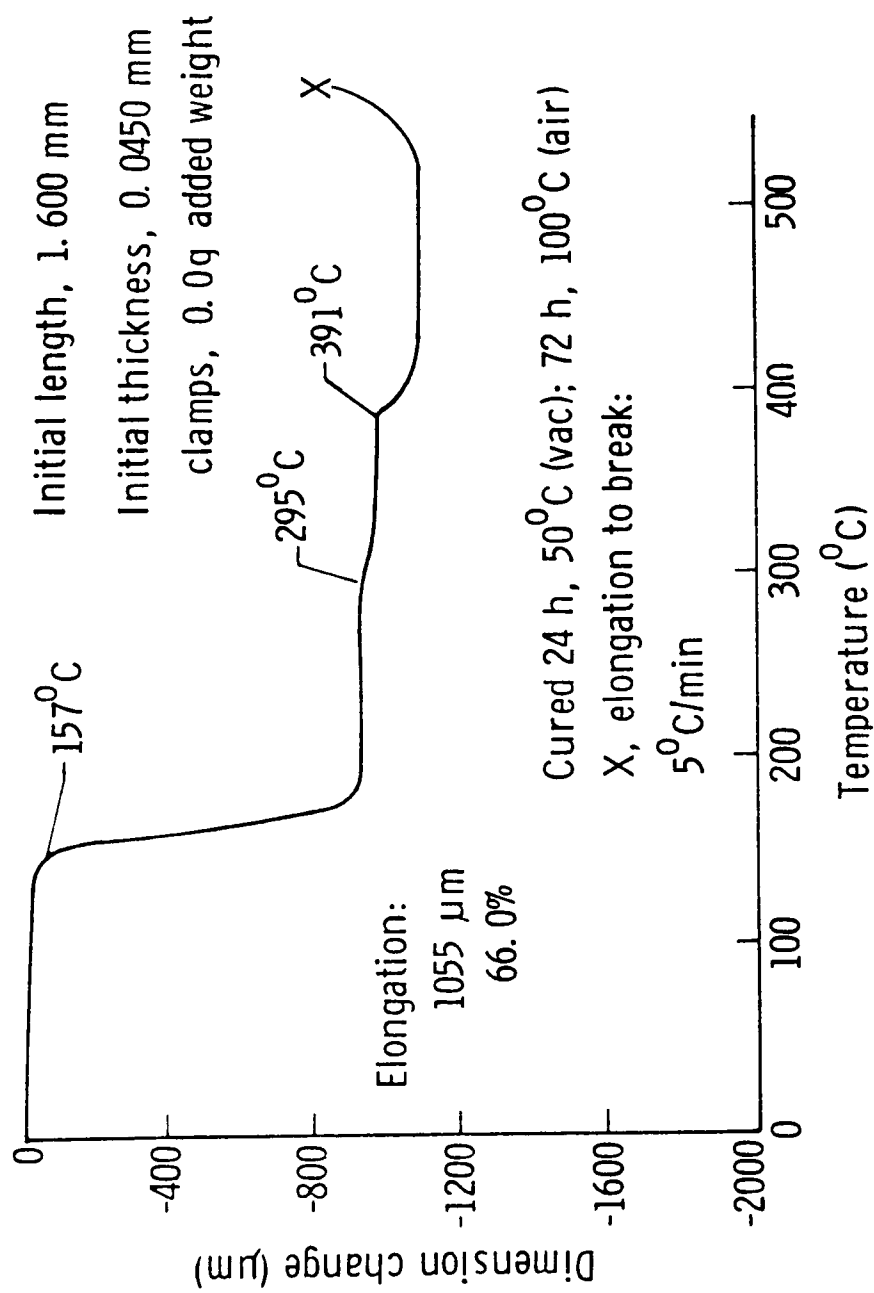
Figure 11. TMA of the IDPA-1,3-BABB poly(amic acid) film during imidization

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Figure 12. Effect of methylene chloride extraction on DSC transitions of IDPA-1,3-BABB films.
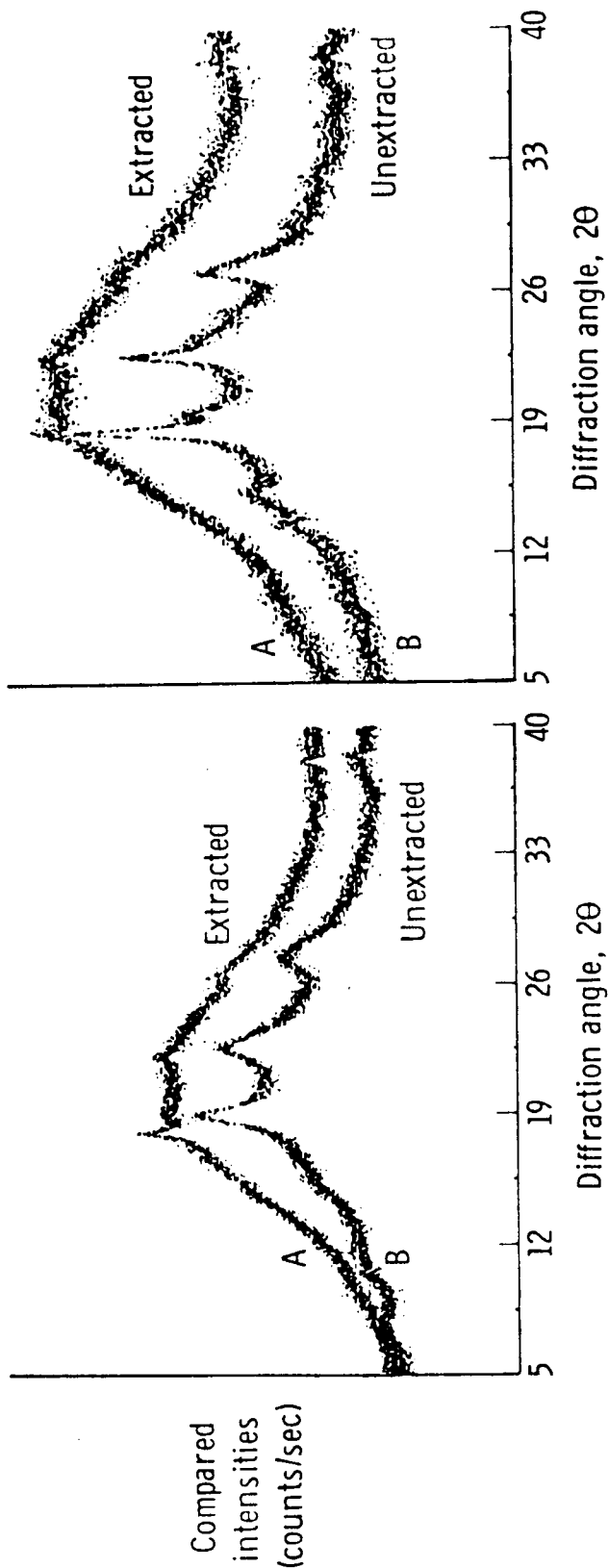
Figure 13. WAXS of methylene chloride extracted and unextracted, imidized and annealed poly(amic acid) films. Annealing was performed for 6 h at temperatures 2/3 between Tg and Tm.

A. 24 h methylene chloride; 1 h, 100^0, 6 h, 265^0C

B. 1 h each 100^0, 200^0; 6 h, 250^0C

A. 24 h methylene chloride; 1 h, 100^0; 6 h, 300^0C

B. 1 h each 100^0, 200^0; 6 h, 300^0C

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Polymer history

1. Air dried poly(amic acid) film
2. Steeped in CH_2Cl_2 24 h at 25°C
3. Heated 1 h 100°C in air

Study 1: Annealed film on glass,
7 h at 265°C (vac)

a

b

c

Study 2: Annealed film on glass,
7 h at 295°C (vac)

a

b

c

DSC experiment:

a. RT →350°C, quench on Al
b. RT →400°C, slow cool ~ 2h
c. RT →550°C
Scan rate:20°C/min

Tg, 212°C

Exo

Heat flow

Endo

Temperature, °C

0 50 100 150 200 250 300 350 400 450 500 550
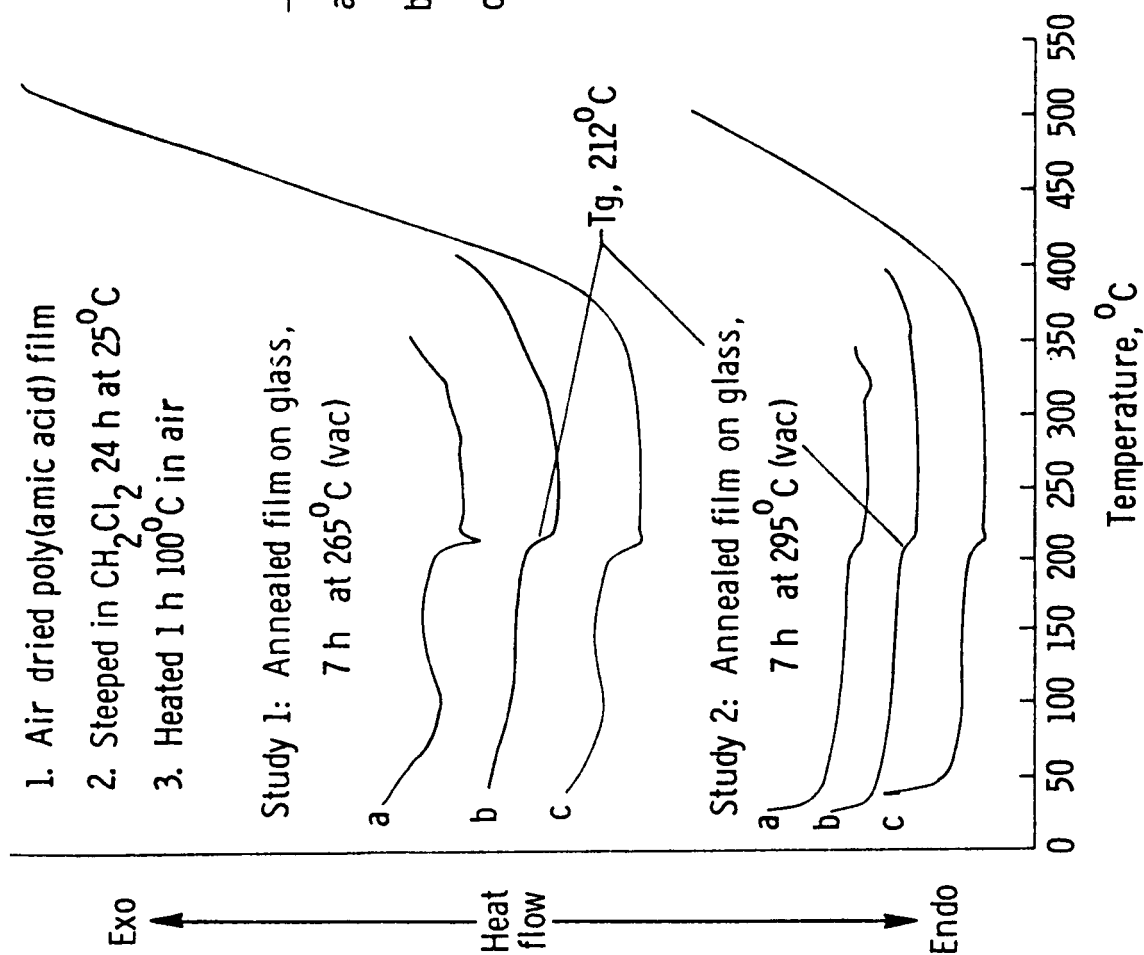
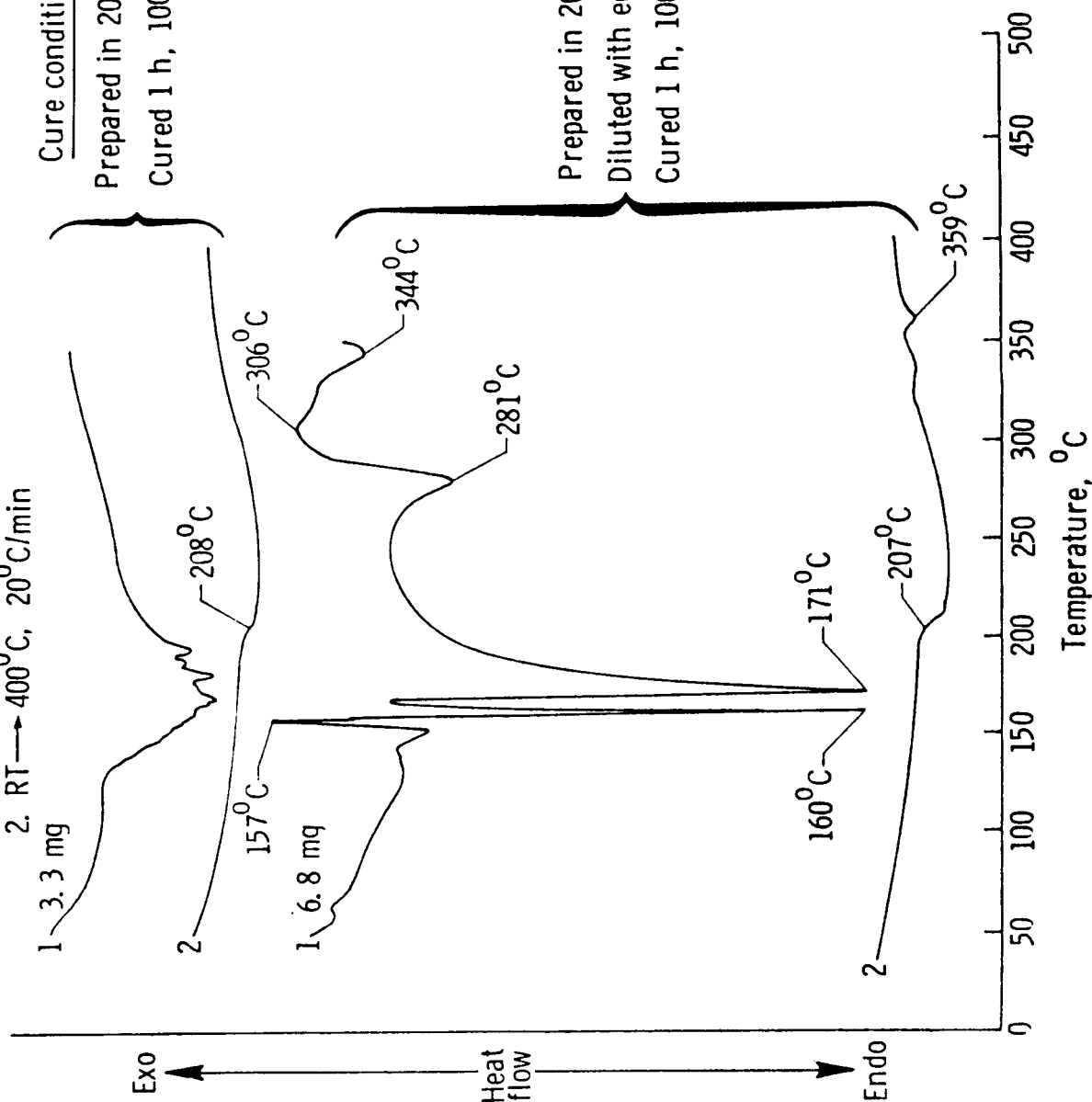Figure 14. Annealing study of the IDPA-1,3-BABB Polyimide

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Figure 15.   Effect of imidization solvent on DSC crystallization.
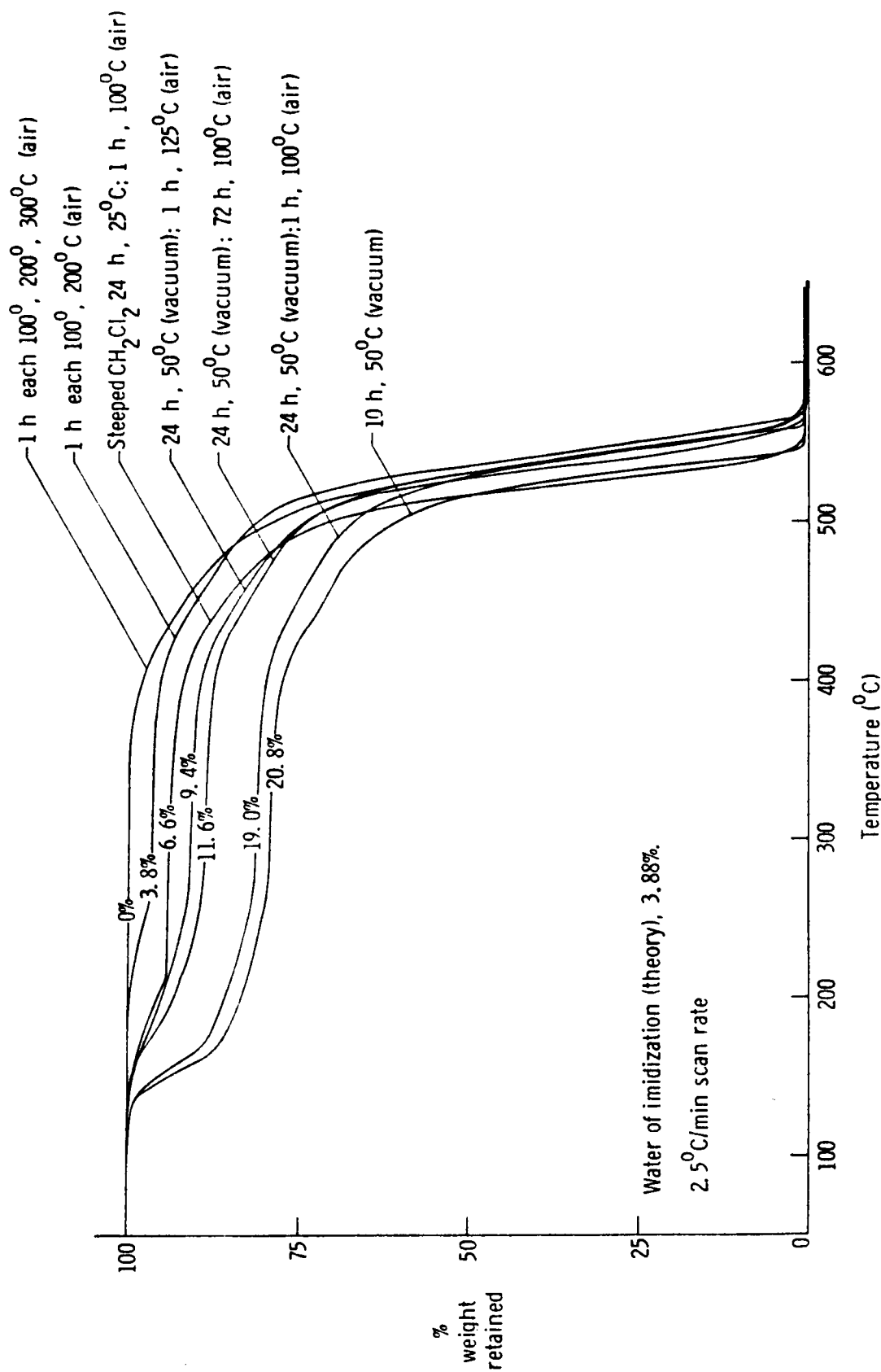
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Figure 16. TGA of IDPA-1,3-BABB films vs extent of cure. (% value listed is the weight loss at the plateau.)

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Air imidization conditions	Stress temperature (^{o}C)	Average yield strength[•] (psi)	Average tensile strength[•] (psi)	Average tangent modulus[•] ($\times 10^{6}$ psi)	Average % elongation[•]
1 h each 100°,200°,275°C	25	12,200[+] (11,600-13,300)	16,700[+] (14,900-18,400)	0.590[+] (0.533-0.694)	3.7[+] (3.3-4.7)
"	200	6,210 (6,000-6440)	7,980 (7,500-8560)	0.402 (0.370-0.461)	7.5 (3.0-14)
1 h each 100°,200°,325°C	25	12,300[+] (11,600-13,100)	17,400[+] (16,500-18,300)	0.539[+] (0.519-0.554)	4.1[+] (3.7-4.4)
"	200	6,290 (5,560-6,890)	7,030 (6,630-7,650)	0.408 (0.344-0.466)	12. (9.8-17)

Nominal 2 mil films

• Values in parenthesis represent range.

+ Average of 4 values

Table 1. Film tensile properties of the IDPA-1,3-BABB polyimide cured to 275° and 325°C in air. (Average of five values for each specimen unless otherwise noted)

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15. Supplementary Notes

Use of trade names of manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration. J. Richard Pratt and Margaret K. Gerber, Planning Research Corporation, Hampton, Virginia. Terry L. St. Clair, Langley Research Center, Hampton, Virginia. Carol R. Gautreaux, Analytical Services and Materials, Inc., Hampton, Virginia.

16. Abstract

A new polyimide derived from 4,4'-isophthaloyldiphthalic anhydride (IDPA) and 1,3-bis(4-aminophenoxy-4'-benzoyl)benzene (1,3-BABB) having semicrystalline behavior has been prepared and characterized by differential scanning calorimetry (DSC) and wide angle x-ray scattering (WAXS). Thus, a poly(amic acid) film cured

in air for one hour each at 100° and 200°C displayed an endotherm at 286°C, followed by a crystallization exotherm at 317°C and a second melting transition at 350°C. The 286°C melting point appeared to result from earlier solvent-induced crystallization. Films cast from DMAc, air dried and soaked in methylene chloride could not be induced into semicrystallinity.

The fully cured polyimide had a Tg of 216°C. Films heated to temperatures as high as 100°C for one hour in air were transparent and light yellow in color. Those films heated to or above 125°C were translucent. Polarized light microscopy revealed the presence of spherulites 6-8 μm in diameter in a sample cured to 275°C in air.

Two film samples, one cured to 275° and the other 325°C, were evaluated for tensile and ultimate strength, modulus and percent elongation at 25° and 200°C. These values remained essentially constant at each test temperature.

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