Polyimide Structure–Property Relationships. III. Polyimides from Multi-Ring Diamines

VERNON L. BELL, L. KILZER, E. M. HETT, and GEORGE M. STOKES,
*Langley Research Center, National Aeronautics and Space Administration,
Hampton, Virginia 23665*

Synopsis

The effects of increasing the distance between, and varying the isomeric positions of, the amine groups on the glass transition temperatures of aromatic polyimides were studied in order to investigate routes to improve processability. A number of isomers of three- and four-ring benzenoid diamine systems were polymerized with 3,3',4,4'-benzophenone tetracarboxylic acid dianhydride to poly(amic acids), which were converted to polyimides. The use of methylene and carbonyl groups to connect the benzene rings of the diamines, and in one case the dianhydride, afforded a comparison of the thermomechanical properties of the polyimides to those prepared from diphenylmethane- and benzophenone-diamines, respectively. Generally, the dilution of the imide content by the insertion of benzylene and benzoylene segments into the diamines significantly reduced the glass transition temperatures, with the benzylene group being more effective in that respect than the benzoylene. However, there was evidence that the position isomerism (*ortho, meta, para*) of the amine groups was more influential in affecting the glass transition temperatures of aromatic polyimides than was the dilution of the imide content.

INRODUCTION

The past decade of research on aromatic polyimides has been exemplified by attempts to improve the processing characteristics of these relatively intractible polymers. The excellent thermal, thermooxidative, and chemical stability of the wholly aromatic polyimides is generally attributed to the structural features of the polymers, including the inert nature of the imide and aromatic groups. The initial method of overcoming the intractibility of the polyimides utilized the polyamide-acid stage, which could be fabricated into certain end-use forms by virtue of its good solubility in certain aprotic solvents. Subsequent cyclodehydration of the polyamide-acid resulted in the polyimide form of the end-use article. While this process has been employed successfully for thin films, the problems associated with the necessary removal of volatiles (solvent and water of cyclodehydration) makes this technique unsatisfactory for other polyimide products such as thick laminated composites and compression molded materials.

Although improvements in processability were realized by using aromatic imide oligomers terminated with olefinic groupings which could cure or propagate by addition reactions,[1] the aliphatic character of the unsaturated end groups compromised significantly the thermooxidative stability of the aromatic polyimides. Early workers in the field soon recognized that aromatic polyimides prepared from dianhydrides having two phthalic anhydride moieties joined by connecting groups, most notably 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA), softened at lower temperatures than did polyimides made

from pyromellitic dianhydride. Also, the use of diamines having two anilino functions joined by the same types of connecting groups also gave polyimides with lower softening points than did those made by unicyclic *m*- and *p*-phenylene diamines. Further improvement in the solubility and thermoplasticity of aromatic polyimides was also demonstrated for those structures using *meta* and *ortho* amino groups,[2,3] with respect to their locations on the aromatic rings of the bisdianilino-type monomers. More recently, the incorporation of acetylenic groups at both ends of oligomeric polyimide segments made possible a curing technique through which three acetylene groups *theoretically* reacted simultaneously to a trisubstituted benzene group, thus preserving an intended all-aromatic polyimide composition.[4]

Another approach to polyimide structural modification which has resulted in greater thermoplasticity involves extending the lengths of the diamine and dianhydride segments by inserting additional phenyl groups, together with appropriate "couplers" between those phenyl rings. This approach leads not only to a dilution of the phthalimide groups in the polymer chain (groups which are noted for their contribution to the intractibility of polyimides) but also to the introduction of flexibilizing groups coupling the aromatic portions of the polymer chains. Perhaps the earliest research which clearly showed the extent to which such an approach could change the thermomechanical nature of the polyimides was that performed by Rudakov and co-workers.[5] They prepared a series of polyimides in which the imide content was systematically decreased by the insertion of *p*-phenoxy moieties, with the result that the softening points of the polyimides were lowered markedly with increased phenoxy groups (and decreased imide content). Other researchers have exploited this approach using either a *m*-terphenyl ether diamine,[4] or dianhydrides[6] and diamines[7] with oxygen, sulfone, and perfluoroisopropyl[8] couplers between the four benzene rings of the monomers.

Interest in aromatic polyimides in our laboratory has focused on monomer units based on the benzophenone and diphenylmethane moieties, the former because of its excellent inherent thermooxidative stability[9] and apparent beneficial effect on polyimide adhesivity[10] and the latter by reason of its contribution to the thermoplasticity[2] of polymers as well as its tendency to oxidatively crosslink.[11] As a means of demonstrating the effects of diluting the imide content of polyimides by the insertion of benzoylene (carbonyl coupling groups) and benzylene (methylene coupling groups) segments, several systematically varied sets of polyimides were investigated. The variation of isomeric points of attachment of the coupling groups was combined with the imide dilution approach. Since aromatic anhydrides are rather difficult to prepare with the methylene bridge, all but one of the "extended" monomers were aromatic diamines. A single extended dianhydride, 4,4'-terephthaloylene-bis(3,4-phthalic anhydride), was used in this study.

EXPERIMENTAL

Monomers

3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride (BTDA), used for the preparation of all but one of the polyimides, was obtained from commercial sources and was purified by recrystallization from anisole, after which it was
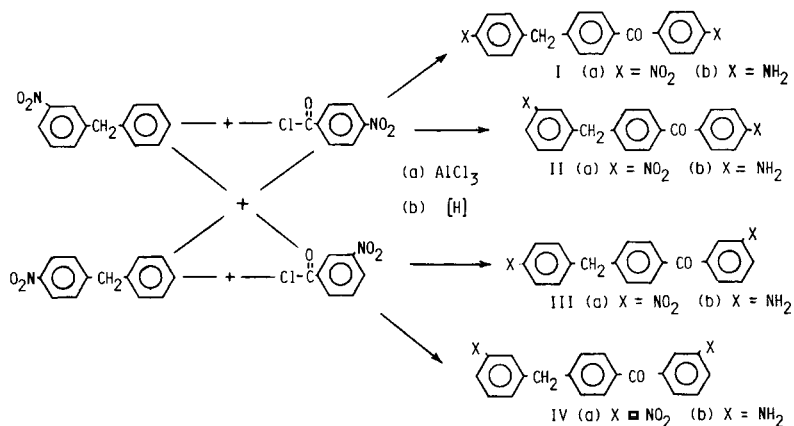
Fig. 1. Synthesis scheme for isomeric benzoyl–benzyl derivatives of benzene.

sublimed *in vacuo*, as reported previously.[12] 4,4'-terephthaloylene-bis(3,4-phthalic anhydride) was prepared by a previously reported procedure.[13] The reaction schemes for the preparation of the diamine monomers are shown in Figures 1–3.

1-(p-Aminobenzoyl)-4-(p-aminobenzyl)benzene (Ib): The catalytic hydrogenation of 4.3 g (0.0119 mol) of 1-(*p*-nitrobenzoyl)-4-(*p*-nitrobenzyl)benzene[14] (Ia) was accomplished in 300 mL of benzene in a Paar shaker, using 0.5 g of 5% platinum-on-carbon catalyst and 0.6 g of anhydrous magnesium sulfate. A nearly quantitative yield of Ib(Fig. 1) was obtained, mp 151.5–152°C.

ANAL. Calcd for $C_{20}H_{18}N_2O$: C, 79.5%; H, 6.0%; N, 9.3%; O, 5.3%. Found: C, 79.6%; H, 6.2%; N, 9.3%; O, 5.0%.

1-(p-Aminobenzoyl)-4-(m-aminobenzyl)benzene (IIb): *m*-Nitrodiphenylmethane (bp 135°C/0.35 mm) was prepared in 79% yield by the Friedel–Crafts alkylation of benzene with *m*-nitrobenzyl chloride using aluminum chloride catalyst. The reaction of *p*-nitrobenzoyl chloride (19.5 g) with 15.0 g of *m*-nitrodiphenylmethane and 14.5 g of aluminum chloride in 300 mL of refluxing
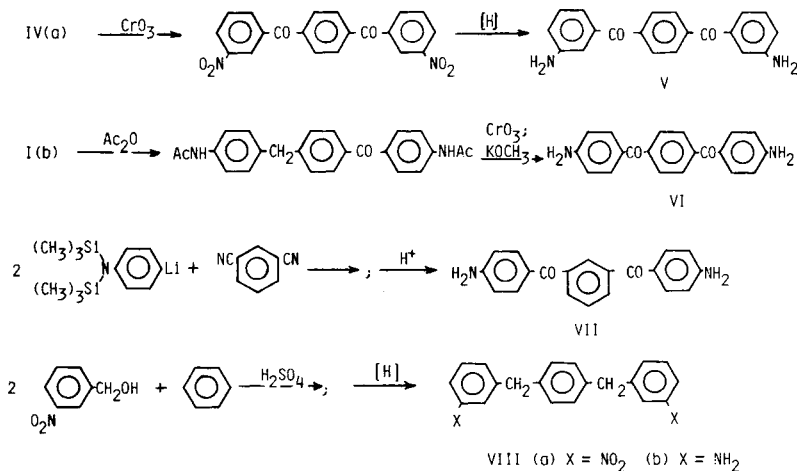

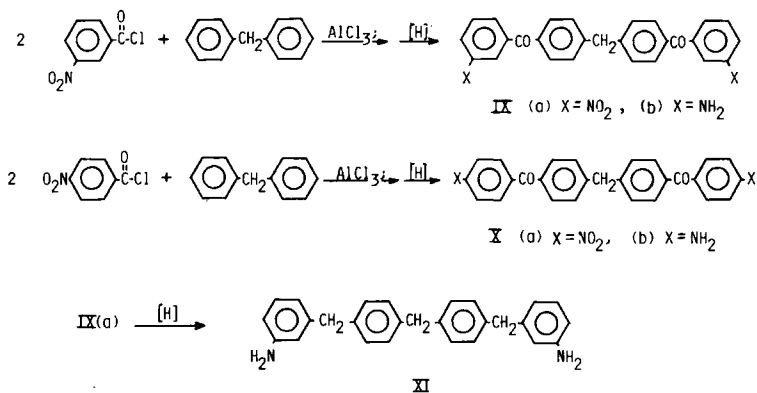Fig. 2. Synthesis of three isomeric bis(aminobenzoyl)benzenes and 1,4-bis(aminobenzyl)benzene.

Fig. 3. Synthesis of three bis(aminobenzoyl) and bis(aminobenzyl) derivatives of diphenyl-methane.

carbon disulfide for 30 h gave a 22% yield of 1-(p-nitrobenzoyl)-4-(m-nitro-benzyl)benzene as tan crystals, mp 110–112°C.

ANAL. Calcd for $C_{20}H_{14}N_2O_5$: C, 66.3%; H, 3.9%; N, 7.8%. Found: C, 66.7%; H, 4.1%; N, 7.5%.

Catalytic hydrogenation of 1.5 g of the dinitro compound in 200 mL of benzene with 0.3 g of 5% platinum-on-carbon catalyst and 1 g of magnesium sulfate drying agent gave 1.0 g (80%) of yellow crystals of diamine (IIb), mp 125–126°C.

ANAL. Calcd for $C_{20}H_{18}N_2O$: C, 79.5%; H, 6.0%; N, 9.3%; O, 5.3%. Found: C, 79.3%; H, 6.2%; N, 9.1%; O, 5.8%.

1-(m-Aminobenzoyl)-4-(p-aminobenzyl)benzene (IIIb): The reaction of 21.1 grams of m-nitrobenzoyl chloride with 24.2 g of p-nitrodiphenylmethane, using 17.0 g of aluminum chloride, in 300 mL of refluxing carbon disulfide for 16 h gave a yield of 17.1 g (42%) of tan crystals of 1-(m-nitrobenzoyl-4-(p-nitrobenzyl)benzene after recrystallization from acetic acid, mp 150–152°C.

ANAL. Calcd for $C_{20}H_{14}N_2O_5$: C, 66.3%; H, 3.9%; N, 7.8%; O, 22.1%. Found: C, 66.3%; H, 4.1%; N, 7.7%; O, 22.4%.

The catalytic hydrogenation of the dinitro compound (16.9 g) was conducted in a Paar shaker in 400 mL of benzene using 2 g of 5% platinum-on-carbon catalyst and 2 g of magnesium sulfate to absorb the water of reduction. A yield of 96% of diamine (IIIb) as yellow crystals resulted, mp 95–96°C.

ANAL. Calcd for $C_{20}H_{18}N_2O$: C, 79.5%; H, 6.0%; N, 9.3%; O, 5.3%. Found: C, 80.3%; H, 6.2%; N, 8.9%; O, 5.7%.

1-(m-Aminobenzoyl)-4-(m-aminobenzyl)benzene (IVb): The overall procedure for preparation of this diamine was similar to that used to prepare diamine I. m-Nitrodiphenylmethane (26.7 g) was acylated with 23.2 g of m-nitrobenzoyl chloride by refluxing with 17.5 g of aluminum chloride for 6 h in 200 mL. of carbon disulfide. After precipitating the product by pouring the reaction mixture onto ice, it was recrystallized from acetic acid to give a 41% yield of light tan crystals of 1-(m-nitrobenzoyl)-4-(m-nitrobenzyl)benzene, mp 144°C.

ANAL. Calcd for $C_{20}H_{14}N_2O_5$: C. 66.3%; H, 3.9%; N, 7.8%. Found: C, 67.0%; H, 3.9%; N, 7.7%.

The catalytic hydrogenatioin of the dinitro compound (29 g) was performed in 1500 mL of benzene with 2 g of 5% platinum-on-carbon catalyst, using 3 g of magnesium sulfate to absorb the water of reduction. A yield of 21.9 g (88% yield) of diamine IVb was obtained in the form of yellow crystals from benzene, mp 126–126.5°C.

ANAL. Calcd for $C_{20}H_{18}N_2O$: C, 79.5%; H, 6.0%; N, 9.3%. Found: C, 79.5%; H, 5.8%; N, 9.0%.

1,4-Bis(m-*aminobenzoyl*)*benzene* (*V*).   Dinitro compound IVa (3.62 g) was oxidized with 2 g of chromic anhydride in 100 mL of refluxing glacial acetic acid for 3 h.   The crude solid which precipitated was washed with fresh acetic acid, giving 3.6 g (96%) of white powder, mp 262°C.

ANAL. Calcd for $C_{20}H_{12}N_2O_6$: C, 63.8%; H, 3.2%; N, 7.4%; O, 25.5%. Found: C, 64.0%; H, 3.4%; N, 7.5%; O, 25.4%.

The above dinitro compound was hydrogenated with 5% platinum-on-carbon catalyst in benzene to give a 90% yield of 1,4-bis(*m*-aminobenzoyl)benzene (V, Fig. 2) as a pale yellow powder, mp 197–198.5°C.

ANAL. Calcd for $C_{20}H_{16}N_2O_2$: C, 75.9%; H, 5.1%; N, 8.9%; O, 10.1%. Found: C, 75.7%; H, 5.2%; N, 8.6%; O, 10.3%.

1,4-Bis(p-*aminobenzoyl*)*benzene* (*VI*):   The starting material for the synthesis of VI was Ib, 16.0 g of which was acetylated by refluxing in a solution of 12 mL of acetic anhydride and 150 mL of glacial acetic acid. The solid product which precipitated when the reaction solution was cooled was collected by filtration and recrystallized from fresh acetic acid, yielding 17.5 g (86%) of light tan crystals, mp 228–230°C, of 1-(*p*-acetaminobenzoyl)-4-(*p*-acetaminobenzyl)benzene. Oxidation of the methylene group was accomplished by reacting 16.7 g of the acetamino derivative with 24.7 g of chromic anhydride in 900 mL of refluxing glacial acetic acid for 6 h. A 55% yield (9.5 g) of 1,4-bis(*p*-acetaminobenzoyl)benzene was obtained, mp 315–316°C. Hydrolysis was carried out with Claisen's alkali[15] to give a 90% yield of 1,4-bis(*p*-aminobenzoyl)benzene (VI) as golden-colored crystals from acetone, mp 288°C (lit[14]: 293–294°C).

1,3-Bis(p-*aminobenzoyl*)*benzene* (*VII*):   The preparation of diamine VII has been reported previously[16] and it was kindly supplied by those investigators.

1,3-Bis(m-*aminobenzyl*)*benzene* (*VIIIb*):   The reaction of *m*-nitrobenzyl alcohol with benzene in 80% aqueous sulfuric acid was used to prepare 1,3-bis(*m*-nitrobenzyl)benzene (VIIIa). Although several variations in the reaction conditions were tried, the yields were always low because of the accompanying formation of mono- and poly(nitrobenzyl)benzene products. Laborious fractional crystallization was often required to separate the desired VIIIa from tri(*m*-nitrobenzyl)benzene (mp 130–133°C) and tetra(*m*-nitrobenzyl)benzene (mp 208–215°C). The most convenient method is described as follows.

m-Nitrobenzyl alcohol (33.7 g, 0.22 mol) was added in portions to a solution of 7.8 g (0.10 mol) of benzene in 125 mL of ice-cooled 80% sulfuric acid, stirred with a magnetic stirring bar in a 250-mL Erlenmeyer flask. After the addition was complete, the reaction mixture was stirred for 1 h, after which a ball of solid product had precipitated from solution. The mother liquor (which contained much unreacted *m*-nitrobenzyl alcohol, benzene, and *m*-nitrodiphenylmethane) was decanted. The solid product was added to ice water and allowed to stand, after which the solid was collected by filtration and washed until acid free. This product was dried and then recrystallized from ethyl acetate to give 4.2 g (12%) of 1,4-bis(*m*-nitrobenzyl)benzene, mp 164–167°C.

ANAL. Calcd for $C_{20}H_{16}N_2O_4$: C, 68.9%; H, 4.6%; N, 8.0%; O, 18.4%. Found: C, 68.4%; H, 4.4%; N, 7.9%; O, 18.1%.

Catalytic hydrogenation of VIIIa (2.7 g), conducted in 300 mL of benzene with 0.2 g of 5% platinum-on-carbon catalyst and 1 g of magnesium sulfate, gave a quantitative yield of 1,4-bis(*m*-aminobenzyl)benzene as colorless crystals, mp 141–142°C.

ANAL. Calcd for $C_{20}H_{20}N_2$: C, 83.3%; H, 7.0%; N, 9.7%. Found: C, 83.9%; H, 6.7%; N, 9.8%.

4,4'-Bis(m-*aminobenzoyl*)*diphenylmethane (IXb):*   The necessary dinitro precursor to IXb (Fig. 3) was obtained via the Friedel–Crafts reaction of *m*-nitrobenzoyl chloride with diphenylmethane.   A mixture of 37.1 g (0.20 mol) of *m*-nitrobenzoyl chloride, 16.8 g (0.10 mol) of diphenylmethane and 27 g (0.22 mol) of aluminum chloride in 400 mL of carbon disulfide was stirred at room temperature for 48 h.   The reaction mixture was then poured onto ice and the resulting gummy product was extracted with methanol to remove *m*-nitrobenzoyldiphenylmethane, the monosubstituted reaction product.   The remaining solid was recrystallized several times from glacial acetic acid to give 12.5 g (27%) of 4,4'-bis(*m*-nitrobenzoyl)diphenylmethane (IXa) as an off-white solid, mp 151–152°C.

ANAL. Calcd for $C_{27}H_{18}N_2O_6$: C, 69.5%; H, 3.9%; N, 6.0%; O, 20.6%. Found: C, 70.0%; H, 3.9%; N, 5.5%; O, 20.8%.

Hydrogenation of 7.05 g (0.015 mol) of IXa in 285 mL of tetrahydrofuran with 1.4 g of 5% Pt-on-C catalyst resulted in 88% yield of 4,4'-bis(*m*-aminobenzoyl)-diphenylmethane (IXb) as light yellow crystals from isopropanol, mp 191–193°C.

ANAL. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.8%; H, 5.5%; N, 6.9%; O, 7.9%. Found: C, 79.4%; H, 5.7%; N, 6.8%; O, 7.6%.

4,4'-Bis(p-*aminobenzoyl*)*diphenylmethane (Xb):*   A solution of 16.8 g (0.10 mol) of diphenylmethane and 37.1 g (0.20 mol) of *p*-nitrobenzoyl chloride in 200 ml of carbon disulfide, together with 27.0 g (0.2 mol) of aluminum chloride, was refluxed for 5 h and then poured over ice.   The crude product, after evaporation of carbon disulfide, was washed with ethanol to remove the monosubstituted diphenylmethane.   Recrystallization of the residual solid gave 6.7 g (14% yield) of tan flakes of 4,4'-bis(*p*-nitrobenzoyl)diphenylmethane (Xa), mp 190–191°C.

ANAL. Calcd for $C_{27}H_{18}N_2O_6$: C, 69.5%; H, 3.9%; N, 6.0%; O, 20.6%. Found: C, 69.6%; H, 3.8%; N, 6.0%; O, 21.3%.

The dinitro compound (2.33 g, 0.005 mol) was hydrogenated in 175 mL of benzene and 50 mL of tetrahydrofuran with 0.25 g of 5% Pt-on-C catalyst in the presence of 0.5 g of magnesium sulfate.   A 75% yield of 4,4'-bis(*p*-aminobenzoyl)diphenylmethane (Xb) was obtained, mp 200°C.

ANAL. Calcd for $C_{27}H_{22}N_2O_2$: C, 79.8%; H, 5.5%; N, 6.9%; O, 7.9%. Found: C, 79.6%; H, 5.6%; N, 6.7%; O, 8.2%.

4,4'-Bis(m-*aminobenzyl*)*diphenylmethane (XI):*   The catalytic hydrogenation of IXa was kindly performed by Dr. Terry Onopchenko, Gulf Research and Development Co., using Raney nickel catalyst for 1 h at 180°C and 600–800 psig hydrogen, in tetrahydrofuran.   A near quantitative yield of 4,4'-bis(*m*-aminobenzyl)diphenylmethane (XI), mp 108–115°C, was obtained.

ANAL. Calcd for $C_{27}H_{26}N_2$: C, 85.7%; H, 6.9%; N, 7.4%. Found: C, 85.8%; H, 7.3%; N, 7.2%.

Polymers

The poly(amic acid) precursors to the polyimides were prepared by the customary solution polymerization methods in *N,N*-dimethylacetamide (DMAc) solvent.   The polymerizations (summarized in Tables I–III) were generally carried out in dry serum bottles equipped with stoppers and magnetic stirring bars.   The diamine was dissolved in DMAc which had been vacuum-distilled at about 100°C/80 mm from calcium hydride and stored under nitrogen.   Granular dianhydride was added at one time in quantities equimolar to the di-

amines. Polymerization solutions were generally stirred at least overnight (16–24 h), after which inherent viscosities at 0.5% concentration in DMAc at 35°C were determined. No attempt to optimize the molecular weight was made, except when viscosities were low. The polymer solutions, normally prepared at concentrations of 15% solids, were then stored at −20°C until required for use.

Preparation of Films

Films were prepared from the polymers by spreading the poly(amic acid) solutions, usually at 15% solids concentration, onto glass plates with 15-mil doctor knives. Dry films obtained in this manner were nominally 1 mil thick. The use of 3-mil doctor blades resulted in 0.2-mil dry films suitable for infrared analysis. The films for thermomechanical analysis and thermogravimetric analysis were dried in air overnight at room temperature in a laminar flow station. The films were then dried further and cyclodehydrated to the polyimide form either in a forced air oven at 100, 200, and 300°C for 1 h at each temperature, or in either a nitrogen oven or a vacuum oven, when oxidizable methylene groups were present.

Thermomechanical Analysis (TMA)

The technique for thermomechanical analysis of the films with the use of an E. I. DuPont Model 940 Thermomechanical Analyzer has previously been described.[17]

Torisonal Braid Analysis (TBA)

Torsional braid analyses were performed according to a reported procedure.[18] The glass braids were impregnated with 5% solutions of the poly(amic acids) in DMAc. The braids were dried either in air or in nitrogen for 1 h at each of three temperatures, 100, 200, and 300°C, and cooled before the spectra were determined.
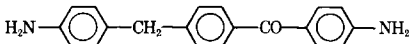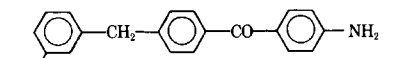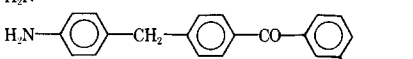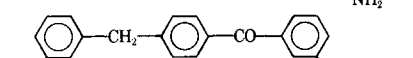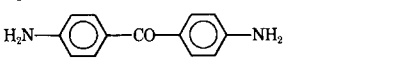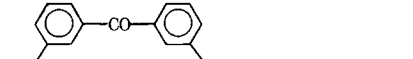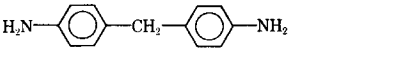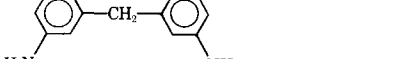
RESULTS AND DISCUSSION

A spectrum of thermal transitions covering a broad range of temperatures can be used to reflect polymer property changes resulting from structural modifications. While torsional braid analysis (TBA) has been shown[18] to be an effective technique for measuring not only the high temperature transitions (T_m and T_g) but also for detecting the subtle changes in low temperature transitions (e.g., T_β), the glass transition temperature was considered to be the single thermal transition most suitable for reflecting potential changes in processability of polyimides resulting from polymer structure changes. The determination of T_g was accomplished by means of thermomechanical analysis (TMA) of high molecular weight thin films, with TBA used for comparison of polymers with molecular weights too low to provide self-supporting films.

Three-Ring Keto-Methylene Diamines

The series of polyimides prepared from 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and the four isomeric aminobenzoylaminobenzylbenzenes (I–IV) proved easy to prepare in reasonable molecular weights. Table I gives the viscosities of the four poly(amic acids), and also the glass transition temperatures of the four polyimide films. In addition, T_g's for BTDA polyimides made from four base diamines, both the m,m'- and p,p'-isomers of diaminobenzophenone (DABP) and diaminodiphenylmethane (MDA), have been listed for comparative purposes, since diamines I–IV can be considered to be either benzylogs or benzoylogs of them. As was the case with polymers from DABP and MDA isomers,[2] the polyimides from BTDA and diamines I–IV showed the same trends in T_g. That is, the polyimide from the m,m'-diamine isomer (IV) had the lowest T_g while that from the p,p'-diamine (I) had the highest T_g, and the mixed m,p'-diamine-derived polyimides had T_g's intermediate between the two extremes. The T_g values given in Table I were all obtained by thermomechanical analysis (TMA) on nominal 1-mil films which had been dried and thermally imidized *in vacuo* at 300°C in order to minimize any oxidative crosslinking of the methylene groups. The glass transition temperatures obtained on some of the polymer films which had been imidized in an air environment tended to be higher than those in Table I, but they were erratic values, with no clear discernible trends.

TABLE I
Properties of Polymers from BTDA[a] and Various Isomeric Diamines

Diamine		η_{inh}[b]	T_g[c]
H₂N—⟨◯⟩—CH₂—⟨◯⟩—CO—⟨◯⟩—NH₂	(I)	0.57	264°C
⟨◯⟩—CH₂—⟨◯⟩—CO—⟨◯⟩—NH₂ (H₂N)	(II)	0.64	254°C
H₂N—⟨◯⟩—CH₂—⟨◯⟩—CO—⟨◯⟩ (NH₂)	(III)	0.65	254°C
⟨◯⟩—CH₂—⟨◯⟩—CO—⟨◯⟩ (H₂N)(NH₂)	(IV)	0.89	236°C
H₂N—⟨◯⟩—CO—⟨◯⟩—NH₂		—	295°C
⟨◯⟩—CO—⟨◯⟩ (H₂N)(NH₂)		—	264°C[d]
H₂N—⟨◯⟩—CH₂—⟨◯⟩—NH₂		—	290°C[d]
⟨◯⟩—CH₂—⟨◯⟩ (H₂N)(NH₂)		—	234°C[d]

[a] 3,3',4,4'-Benzophenone tetracarboxylic acid dianhydride.
[b] Viscosity of polyamic acid, 0.5% in dimethylacetamide, 35°C.
[c] By thermomechanical analysis of 1-mil polyimide film.
[d] Reference 2.

Figure 4 illustrates the general effects of inserting either p-benzylene or p-benzoylene segments into polyimides made from BTDA and isomeric diamino-diphenylmethanes (MDA) and isomeric diaminobenzophenones (DABP). While the insertion of p-benzylene segments into all of the BTDA—DABP polyimides (left-hand side of Fig. 4) markedly lowered the T_g's, the same was true for the effect of inserting p-benzoylene groups into BTDA—p,p'-MDA (top right of Fig. 4), but little or no decrease in T_g resulted when a p-benzoylene unit was inserted into those BTDA—MDA polymers already having one *meta* amine in the MDA structure (middle and lower right, Fig. 4).

Three-Ring Diketo Diamines

Table II shows the properties of polyimides synthesized from several isomeric three-ring aromatic diketo diamines. In contrast to the ready polymerizability of diamines I–IV, those in Table II gave somewhat lower viscosities for the poly(amic acids), with the exception of VII, in which the *meta*-arrangement of the central benzene ring differed from the *para*-linked central benzene ring in V and VI. Extensive monomer purification efforts failed to result in higher viscosities for BTDA-V and BTDA-VI, or for the polyamic-acid from VI and 4,4'-terephthaloylene-bis(3,4-phthalic anhydride). Again, the polyimide with the amine groups oriented *meta* (BTDA-V) had a significantly lower glass transition temperature (240°C) than the one with the amines in a *para*-arrangement (BTDA-VI, T_g = 286°C). Since most of the polymers in this series were too low in molecular weight to produce flexible films, their glass transition temperatures were obtained *via* torsional braid analysis (TBA).

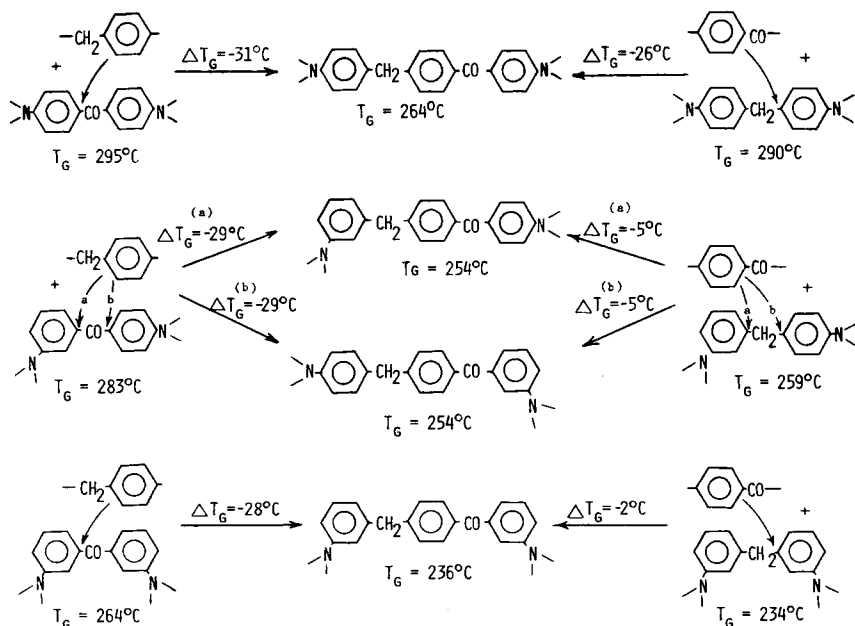The extent to which the dilution of the imide content of polyimides by the

Fig. 4. Decrease in glass transition temperature by insertion of benzylene and benzoylene segments into BTDA polyimides from benzophenone and diphenylmethane diamines.

TABLE II
Properties of Polymers from Several Keto-Diamines with BTDA[a] and a Diketo Dianhydride

Diamine		η_{inh}[b]	T_g[c]
H_2N—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—NH_2	(VI)	0.34	286°C
⟨C₆H₄⟩—CO—⟨C₆H₄⟩—CO—⟨C₆H₄⟩ (m,m′, H_2N, NH_2)	(V)	0.43	240°C
H_2N—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—NH_2 (meta center)	(VII)	0.78	276°C
H_2N—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—NH_2 (VI) + diketo dianhydride structure	(VI)	0.39	260°C
H_2N—⟨C₆H₄⟩—CO—⟨C₆H₄⟩—NH_2		—	295°C[d]
⟨C₆H₄⟩—CO—⟨C₆H₄⟩ (H_2N, NH_2)		—	264°C[d]

[a] 3,3′,4,4′-Benzophenone tetracarboxylic acid anhydride.
[b] Viscosity of polyamic acid, 0.5% in dimethylacetamide, 35°C.
[c] By torsional braid analysis (TBA).
[d] Reference 2.

addition of p-benzoylene units to BTDA—DABP polymers affected the glass transition temperatures is illustrated in Fig. 5. The insertion of the p-benzoylene unit into BTDA—p,p'-DABP [eq. (1)] lowered the T_g slightly ($-9°$C), but the effect was much greater when the same grouping was inserted into BTDA—m,m'-DABP [eq. (3)] (from $T_g = 264°$C to $T_g = 240°$C for BTDA-V). This may suggest that the orientation of the amino groups is more influential on T_g of polyimides than is the dilution of the imide content. However, the insertion of a $meta$-benzoylene unit into the BTDA—p,p'-DABP polyimide [eq. (2)] seemed to cause an even greater decrease in T_g than did the $para$ unit, with a T_g of 276°C ($\Delta T_g = -19°$C) resulting from BTDA-VII so the orientation of the diluting group (benzoylene) also influences the T_g. And, finally, when a p-benzoylene segment was inserted into both the dianhydride (BTDA) and the diamine (p,p'-DABP) [eq. (4)], the decrease in T_g which resulted ($-35°$C) was much greater than when the same unit was inserted into only the diamine ($-9°$C).

Multi-Ring Methylene Diamines and Four-Ring Diketo-methylene Diamines

Two aromatic diamines with only methylene groups separating the benzene moieties were used to prepare polyimides with BTDA (Table III). The polyimide with the three-ringed diamine (VIII) had the lowest T_g in this study: 205°C as determined by torsional braid analysis. Surprisingly, that polymer from the
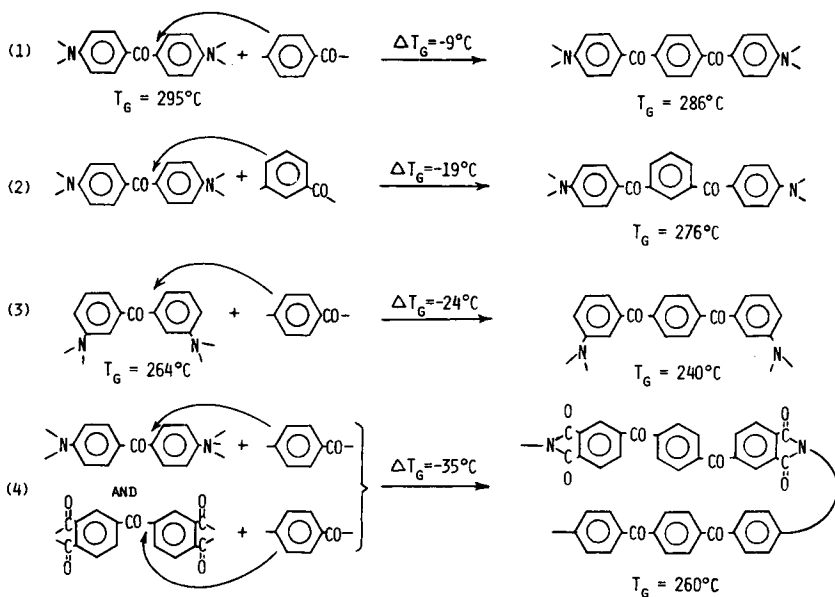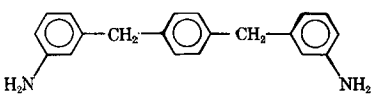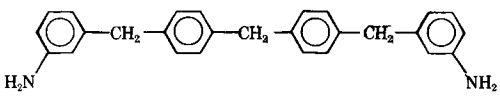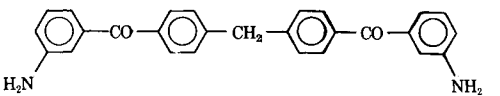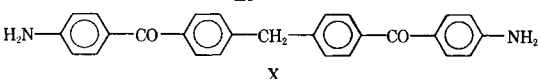
Fig. 5. Decrease in glass transition temperature by inserting benzoylene segments into polyimides from BTDA and diaminobenzophenones.

p-benzylog, bis(m-aminobenzyl)diphenylmethane (IX), had a T_g somewhat higher, at 217°C. The last two diamines studied in this investigation were four-ringed diamines, each with two carbonyl groups and one methylene group separating the benzenoid portions from each other. As Table III and Figure 6 show, the effects on glass transition temperature were mixed. In the case of the

TABLE III
Properties of Polymers from Three- and Four-Ringed Methylene and Keto-Methylene Diamines with BTDA[a]

Diamine	η_{inh}[b]	T_g[c]
VIII	0.75	205°C
XI	0.35	217°C
IX	0.80	228, 232°C
X	0.29	256°C

[a] 3,3′,4,4′-Benzophenone tetracarboxylic acid dianhydride.
[b] Viscosity of polyamic acid, 0.5% in dimethylacetamide, 35°C.
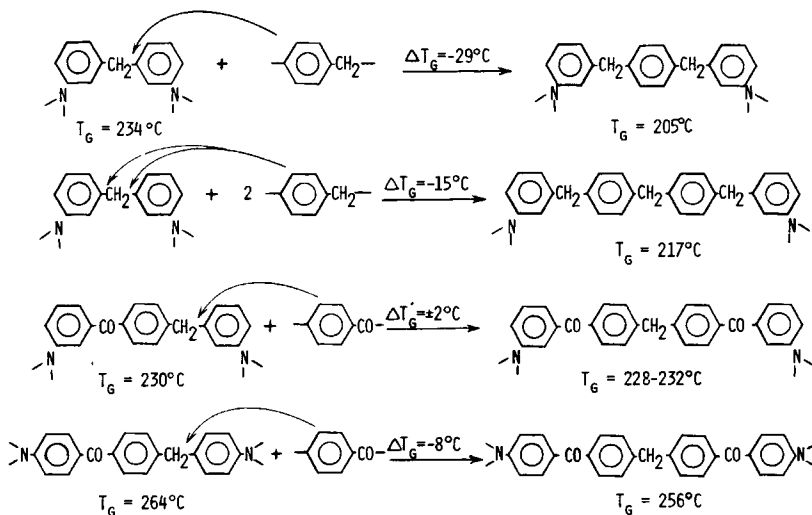[c] By torsional braid analysis.

Fig. 6. Decrease in glass transition temperature by insertion of benzylene and benzoylene segments into various BTDA polyimides.

diamine with the amino groups oriented *para* (X), the insertion of a *p*-benzoylene unit into the polyimide from diamine I decreased the T_g of the polyimide BTDA-X slightly ($-8°C$), but the same segment inserted into the polyimide containing the diamine with the *meta*-oriented amine groups (IV) resulted in virtually no change in T_g ($\pm 2°C$). Perhaps these findings support the position, mentioned previously, that the arrangement of the amine groups in *meta*-configurations plays a bigger part in reducing the glass transition temperatures of polyimides derived from three- and four-ringed diamines than does the dilution of the imide content of polymers from *para*-oriented diamines with *p*-benzylene and *p*-benzoylene segments.

CONCLUSIONS

An investigation of the combined effects of *meta* vs *para* orientation of the amine groups of aromatic diamines and the dilution of the imide content on the thermomechanical properties of diphenylmethane- and benzophenone-derived polyimides was conducted to study possible ways to improve polyimide processability. The results showed that a polyimide with a glass transition temperature of only 205°C could be obtained by polymerizing with BTDA a diamine with three benzene rings separated with two methylene groups, and having two *meta*-oriented amine groups terminal to the three-ring system. There were indications that the use of *p*-benzylene segments was more effective than *p*-benzoylene segments in reducing the T_g's, and perhaps the *m*-benzoylene unit was somewhat more effective than the use of the *p*-benzoylene unit in lowering the T_g. However, there was strong evidence that the change of the terminal amine groups from the *para*- to the *meta*-configuration was more instrumental than any other single modification in decreasing the glass transition temperature of aromatic polyimides.

References

1. H. R. Lubowitz, U.S. Pat. 3,528,950 (1970).

2. V. L. Bell, B. L. Stump, and H. Gager, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2275 (1976).

3. T. L. St. Clair, A. K. St. Clair, and E. N. Smith, paper presented at American Chemical Society Meeting, San Francisco, Calif., August 1976; *Polym. Preprints*, **17**(2), 359 (1976).

4. A. L. Landis, N. Bilow, R. H. Boschan, R. E. Lawrence, and T. J. Aponyi, papers presented at American Chemical Society Meeting, Atlantic City, N.J., September 13, 1974; *Polym. Preprints*, **15**(2), 533,537 (1974).

5. A. P. Rudakov, M. I. Bessanov, Sh. Tuichiev, M. M. Koton, F. S. Florinskii, B. M. Ginzburg, and S. Ya. Frenkel, *Vysokomol. Soyed.* **A12** (3), 641 (1970); *Polym. Sci. USSR (Engl. Trans.)*, **12**, 720 (1970).

6. H. R. Lubowitz, U.S. Pat. 3,699,075 (1972).

7. G. L. Brode, J. H. Kawakami, G. T. Kwiatkowski, and A. W. Bedwin, *J. Polym. Sci., Polym. Chem. Ed.*, **12**(3), 575 (1974).

8. R. J. Jones, M. K. O'Rell, and J. M. Hom, U.S. Pat. 4,111,906 (1978); R. J. Jones and M. K. O'Rell, U.S. Pat. 4,196,277 (1980); R. J. Jones, M. K. O'Rell, and J. M. Horn, U.S. Pat. 4,203,922 (1980).

9. V. L. Bell, paper presented to Division of Organic Coatings and Plastics Chemistry, American Chemical Society Meeting, Dallas, Texas, April 9, 1973; *Preprints*, **33**, 201 (1973).

10. D. J. Progar, V. L. Bell, and T. L. St. Clair, U.S. Pat. 4,065,345 (1977).

11. R. A. Jewell and G. F. Sykes, paper presented to Division of Organic Coatings and Plastics Chemistry, American Chemical Society Meeting, San Francisco, Calif., August 31, 1976; *Preprints*, **36**(2), 258 (1976).

12. V. L. Bell, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 225 (1976).

13. G. S. Mironov, M. I. Farberov, G. N. Timoshenko, and V. A. Kazanskaya, *Zh. Org. Khim.*, **6**(7), 1453 (1970).

14. H. Kühnis and H. Diesback, *Helv. Chim. Acta*, **41**, 894 (1958).

15. L. Claisen, *Ann.*, **418**, 96 (1919).

16. J. R. Pratt, W. D. Massey, F. H. Pinkerton, and S. F. Thames, *J. Org. Chem.*, **40**, 1090 (1975).

17. H. D. Burks, *J. Appl. Polym. Sci.*, **18**, 627 (1974).

18. J. K. Gillham and H. C. Gillham, *Polym.-Eng. Sci.*, **13**, 447 (1973).