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Internal plasticization of polyimides with alkyl 3,5-diaminobenzoate compounds

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An investigation was carried out to improve polyimide processability via internal plasticization. This approach entailed the synthesis of a series of diamines in which the length of the alkyl group in alkyl 3,5-diaminobenzoates was varied from one to eighteen carbons. The polyimides obtained from several of these diamines were found to have increased solubility, a lower glass transition temperature and improved processability. Copolyimides were synthesized from 4,4′-oxydianiline, n-octadecyl 3,5-diaminobenzoate and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride. It was found that incorporating only 10% of the plasticizing diamine improved processability sufficiently enough to allow moulding of the neat resin. This was in marked contrast to the parent polymer which was an insoluble and infusible polyimide.

(Keywords: internal plasticization; polyimides; processability)

INTRODUCTION

Aromatic polyimides are condensation polymers that are normally synthesized from tetracarboxylic dianhydrides and aromatic diamines. The imide heterocyclic unit imparts rigidity to the polymer backbone and also affords strong intermolecular interactions. The polymers exhibit outstanding mechanical and electrical properties, exceptional thermal and thermooxidative stability, and excellent solvent resistance. These properties make them highly desirable for high-performance applications where they often replace heavier and bulkier metal and glass components[1]. Their use in some applications, however, is prevented due to their processing requirements. Their high glass transition temperatures (T_gs) make melt processing very difficult, while their insolubilities prevent solution processing. Most conventional processing techniques involve the fabrication of poly(amic acid) (PAA) precursors followed by chemical or thermal imidization. Problems can arise because the PAAs are thermally and hydrolytically unstable. The water by-product from imidization can also form voids in bulk materials.

Thus, considerable research has been carried out aimed at developing polymers that are processable in their imide form[2–4]. Earlier polyimide research concentrated on modifying the dianhydride or diamine moiety to either increase solubility[5] or to reduce the polymer's T_g[6]. The approach varied from phenylating the dianhydride for improved solubility[7], to changing backbone catenation in order to lower the T_g[8]. The goal of this present research was to improve polyimide processability via internal plasticization.

Plasticization normally involves the incorporation of a low-molecular-weight plasticizer which improves polymer flow and processability. In internal plasticization, the plasticizer is chemically attached to or incorporated in the polymer backbone. The first objective of this research was to develop a synthetic scheme that would allow the introduction of plasticizing groups along the polyimide backbone. The approach involved the synthesis of various long-chain alkyl 3,5-diaminobenzoates. This diamine structure was selected for several reasons. The amine groups were placed in the 3- and 5-positions in order to obtain *meta*-catenation in the polymer backbone. Such catenation is known to increase solubility and reduce the T_g[9]. The amine groups were also located at a sufficient distance from the plasticizing group so that their reaction with dianhydrides would not be sterically hindered. It was postulated that the introduction of long alkyl chains along the polyimide backbone would increase the polymer's free volume, thus resulting in a reduction in the T_g. The pendant side chains were also expected to disrupt intermolecular interactions and allow the backbone more freedom for flow during processing. The pendant side chains were to be varied in order to study the effects of side-chain length, bulkiness, and stability on the polyimide solubility, thermal stability, T_g, and processability. The amount of plasticizing diamine required in a model polyimide system to improve processability without substantially reducing the polymer's properties was also to be determined.

EXPERIMENTAL

Instrumentation

Melting points were measured using a Meltemp capillary melting point apparatus and are uncorrected.

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Infra-red (i.r.) spectra were recorded on a Nicolet 5SXC FT-Infrared spectrometer using KBr pellets or NaCl plates. Proton nuclear magnetic resonance (^{1}H n.m.r) spectra were measured on a 200 MHz Varian Gemini-200 spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Viscosity measurements were made on *m*-cresol solutions using a Cannon-Ubbedholde No. 200 viscometer. Flow times were recorded for polymer concentrations of 0.50, 0.33, and 0.25 g dl^{-1} at 30°C ± 0.1°C. Differential scanning calorimetry (d.s.c.) measurements were made using a heating rate of 10°C min^{-1} on a Du Pont Model 1090 Thermal Analyzer equipped with a differential scanning calorimetry cell. Thermogravimetric analysis (t.g.a.) was carried out in nitrogen and air with a Du Pont Model 951 thermogravimetric analyzer, using a heating rate of 10°C min^{-1}. Double-torsion and modulus experiments were performed on an Instron (Model TM) Universal Testing machine. Double torsion tests were run with a crosshead speed of 0.5 cm min^{-1}. Wide-angle X-ray diffraction patterns were obtained by Dr Anqui Zhang (University of Akron) with a Rigaku X-ray generator equipped with a Cu Kα beam source.

Reagents

All materials were purchased from the Aldrich Chemical Company and used as received unless stated otherwise. The high boiling solvents, such as *m*-cresol, *N*-methyl-2-pyrrolidinone (NMP), *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were distilled under reduced pressure prior to use. The diamines, 4,4′-oxydianiline (ODA) and 1,3-diaminobenzene (*m*-PDA) were sublimed to afford white materials, with a m.p. of 190 and 64°C, respectively. The dianhydrides, 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) (m.p. 224–226°C) and pyromellitic dianhydride (PMDA) (m.p. 285°C), were purchased from the Chriskev Company, Inc., and dried at 150°C under reduced pressure prior to use.

General procedures for the preparation of alkyl 3,5-dinitrobenzoates

Method A. To a one-necked, round bottom flask, equipped with a Dean–Stark trap, a condenser, and a magnetic stirring bar, were added 0.10 mol of 3,5-dinitrobenzoic acid, 0.5 mmol of *p*-toluenesulfonic acid monohydrate and a 3 molar excess of the appropriate alcohol. The solution was heating at reflux for 24–48 h while water was collected in the Dean–Stark trap. The excess alcohol was removed by distillation, and the remaining material was poured into ice–water. The precipitate that formed was collected by filtration and recrystallized from ethyl acetate.

Method B. To a stirred solution of 0.06 mol of 3,5-dinitrobenzoic acid dissolved in 200 ml of pyridine was added 0.12 mol of *p*-toluenesulfonyl chloride. The solution was cooled in an ice-water bath before 0.06 mol of the appropriate alcohol was added. The solution was kept cool for 1 h and then poured into ice–water. The solid esters were collected by filtration, washed with excess water, and recrystallized from ethyl acetate.

*Methyl 3,5-dinitrobenzoate (**1**): Method A.* The white solid was obtained in 87% yield: m.p. 100–103°C (literature[10] m.p. 108°C); i.r. (NaCl) 1544 and 1342 (NO_2), 3076 (aromatic), 1730 cm^{-1} (C=O); ^{1}H n.m.r. ($CDCl_3$) 9.2 (d, 3H, aromatic), 4.0 ppm (s, 3H, methyl).

*n-Butyl 3,5-dinitrobenzoate (**2**): Method A.* The white solid was obtained in 71% yield: m.p. 56–58°C (literature[10] m.p. 63°C); i.r. (NaCl) 3108 (aromatic), 2961 and 2917 (aliphatic), 1729 (C=O), 1543 and 1344 cm^{-1} (NO_2); ^{1}H n.m.r. ($CDCl_3$) 9.1 (d, 3H, aromatic), 4.4 (t, 2H, $-CH_2O-$), 1.8, 1.5, and 1.0 ppm (m, 7H, aliphatic).

*n-Octyl 3,5-dinitrobenzoate (**3**): Method B.* Fluffy white material was obtained in 76% yield: m.p. 57–59°C (literature[10] m.p. 61–62°C); i.r. (NaCl) 3092 (aromatic), 2958 and 2854 (aliphatic), 1728 (C=O), 1543 and 1344 cm^{-1} (NO_2); ^{1}H n.m.r. ($CDCl_3$) 9.2 (d, 3H, aromatic), 4.4 (t, 2H, $-CH_2O-$), 1.8, 1.3, and 0.8 ppm (m, 15H, aliphatic).

*n-Dodecyl 3,5-dinitrobenzoate (**4**): Method B.* After several recrystallizations from ethyl acetate, the dinitro compound was collected in 77% yield: m.p. 57–59°C (literature[11] m.p. 59–60°C); i.r. (NaCl) 3100 (aromatic), 2849 and 2917 (aliphatic), 1728 (C=O), 1542 and 1349 cm^{-1} (NO_2); ^{1}H n.m.r. ($CDCl_3$) 9.2 (d, 3H, aromatic), 4.4 (t, 2H, $-CH_2O-$), 1.8, 1.3, and 0.8 ppm (m, 23H, aliphatic).

*n-Octadecyl 3,5-dinitrobenzoate (**5**): Method B.* Several recrystallizations from ethyl acetate were needed to remove the pyridine. Fluffy white material was obtained in 87% yield: m.p. 71–72°C (literature[10] m.p. 72–73°C); i.r. (NaCl) 3100 (aromatic), 2917 and 2849 (aliphatic), 1730 (C=O), 1543 and 1348 cm^{-1} (NO_2); ^{1}H n.m.r. ($CDCl_3$) 9.2 (d, 3H, aromatic), 4.4 (t, 2H, $-CH_2O-$), 1.8, 1.4, and 0.8 ppm (m, 37H, aliphatic).

General procedures for the preparation of alkyl 3,5-diaminobenzoates

Method A. The dinitro compound (10.0 g) and 0.01 g of a 5% Pd/C catalyst were added to 250 ml of methylene chloride and placed in a Parr hydrogenation apapratus. After several hours under 50 psi hydrogen pressure, the solution was filtered through Celite. The solution was then concentrated or cooled to 0°C to allow crystallization to occur. The yields of the diamines were quantitative.

Method B. A mixture of 100.0 g of the dinitro compound, 750 ml of absolute ethanol and 1.0 g of a 5% Pd/C catalyst was heated to reflux. A six molar excess of hydrazine monohydrate was added dropwise to the refluxing solution. The hot solution was filtered through Celite and allowed to cool. The diamine that crystallized was collected by filtration in quantitative yield.

*Methyl 3,5-diaminobenzoate (**6**): Method B.* White crystals were obtained that turned tan in colour during drying: m.p. 129–131°C (literature[12] m.p. 133–135°C); i.r. (KBr) 3387 and 3312 (NH_2), 3214 (aromatic), 1707 cm^{-1} (C=O); ^{1}H n.m.r. (DMSO-d_6) 6.4 (s, 2H, aromatic), 6.0 (s, 1H, aromatic), 5.0 (s, 4H, NH_2), and 3.7 ppm (s, 3H, methyl).

n-Butyl 3,5-diaminobenzoate (7): Method A. After removal of the hydrogenation solvent, the material was distilled to afford a yellow oil: b.p. 180–184°C (250 mmHg) (literature[13] b.p. 255°C); i.r. (NaCl) 3447 and 3367 (NH_2), 2959 (aliphatic), 1702 cm^{-1} (C=O); ^1H n.m.r. ($CDCl_3$) 6.8 (d, 2H, aromatic), 6.2 (s, 1H, aromatic), 4.2 (t, 2H, $-CH_2O-$), 3.6 (b, 4H, NH_2), and 1.7, 1.4, and 1.0 ppm (m, 7H, aliphatic).

n-Octyl 3,5-diaminobenzoate (8): Method B. Colourless diamine crystals were obtained from ethanol: m.p. 32–33.5°C; i.r. (NaCl) 3443 and 3365 (NH_2), 2925 and 2855 (aliphatic), 1700 cm^{-1} (C=O); ^1H n.m.r. ($CDCl_3$) 6.7 (s, 2H, aromatic), 6.0 (s, 1H, aromatic), 4.2 (t, 2H, $-CH_2O-$), 3.7 (b, 4H, NH_2), 1.7, 1.3, and 0.8 ppm (b, 15H, aliphatic). Analysis: calcd for $C_{15}H_{24}N_2O_2$ C 68.15, H 9.15; found C 68.24, H 9.49.

n-Dodecyl 3,5-diaminobenzoate (9): Method B. Sublimation provided a white powder: m.p. 68–70°C; i.r. (NaCl) 3413 and 3320 (NH_2), 2916 and 2850 (aliphatic), 1711 cm^{-1} (C=O); ^1H n.m.r. ($CDCl_3$) 6.7 (s, 2H, aromatic), 6.1 (s, 1H, aromatic), 4.2 (t, 2H, $-CH_2O-$), 3.6 (b, 4H, NH_2), 1.7, 1.3 and 0.8 ppm (m, 23H, aliphatic). Analysis: calcd for $C_{19}H_{32}N_2O_2$ C 71.21, H 10.06; found C 71.38, H 10.06.

n-Octadecyl 3,5-diaminobenzoate (10): Method B. Recrystallization from ethanol afforded white fluffy material: m.p. 81–82°C; i.r. (NaCl) 3412 and 3321 (NH_2), 2917 and 2849 (aliphatic), 1750 cm^{-1} (C=O); ^1H n.m.r. ($CDCl_3$) 6.7 (s, 2H, aromatic), 6.2 (s, 1H, aromatic), 4.2 (t, 2H, $-CH_2O-$), 3.7 (b, 4H, NH_2), 1.7, 1.3, and 0.7 ppm (m, 35H, aliphatic). Analysis: calcd for $C_{25}H_{44}N_2O_2$ C 74.21, H 10.96; found C 74.26, H 10.86.

General polymerization procedure (two-step method)

To a stirred solution of 5.48 mmol of diamine in NMP (15 wt% solids content) was added 5.48 mmol of dianhydride. The solution was stirred for 12 h at room temperature under a nitrogen atmosphere to generate the PAA. An aliquot was removed for viscosity measurements before a 2.2 molar excess of a 1:1 (wt/wt) acetic anhydride and pyridine mixture was added for chemical imidization. After an additional 12 h, the solution was added dropwise to vigorously stirred 95% ethanol. The polyimide that precipitated was collected by filtration, extracted with methanol, and then dried at 150°C under reduced pressure for 12 h. A second drying was carried out at 250°C under reduced pressure for 2 h.

General polymerization procedure (one-step method)

The diamine (0.05 mol) was added to a stirred solution of 0.05 mol of dianhydride in distilled *m*-cresol (15 wt% solids content) containing several drops of isoquinoline. The solution was stirred for 3 h at room temperature under a nitrogen atmosphere and then heated to 200°C. Nitrogen was rapidly purged through the reaction mixture to aid in the removal of the water of imidization. Any *m*-cresol that was lost through distillation was replaced with fresh solvent. When the solution's viscosity appeared to stop increasing (3–5 h), the solution was slowly poured into vigorously stirred 95% ethanol. The polyimide that precipitated was collected by filtration, chopped in a blender, extracted with methanol, and dried at 150°C under reduced pressure for 12 h. Additional drying was carried out at 250°C under reduced pressure for 2 h.

General copolymerization procedure (two diamines with one dianhydride)

The appropriate amount of plasticizing diamine was added to a stirred solution of dianhydride in *m*-cresol containing isoquinoline, under a nitrogen atmosphere. The solution was stirred at room temperature for 3 h and then heated at 200°C for 3 h. After cooling to room temperature, the second diamine was added and the heating cycle was repeated. The total solids concentration of the solution was 15 wt%. During the entire polymerization, the removal of the water of imidization was aided by a strong nitrogen purge. Any *m*-cresol that was lost through distillation was replaced with fresh solvent. The copolymide was isolated, washed and dried in a similar way to the homopolyimide.

General procedures for preparation and testing of neat resin samples

Compression moulding. A 10.2 cm × 5.1 cm mould that was filled with 8.0 g of polyimide powder was placed in an hydraulic press and heated to the desired moulding temperature at a heating rate of 3.5°C min^{-1}. At the processing temperature, which was usually 50 to 100°C above the polyimide's T_g, 7 MPa of pressure were applied. Both the pressure and temperature were maintained for 20 min before the mould was allowed to cool to ambient temperature. The pressure was then slowly removed once the temperature had fallen below the polymer's T_g.

Fracture energy (G_{IC}) and fracture toughness (K_{IC}) measurements[14]. Rectangular neat resin samples were machined to uniform thickness and size. A groove was milled the entire length of the sample to guide the propagating crack. The sample was pre-cracked with a razor blade. Load (P) was applied by a crosshead ram and was stopped once the fracture was complete. The critical load at fracture (P_f) was obtained from a strip chart load–displacement curve. The tear path thickness (t_n) was measured with a travelling microscope. Fracture toughness values were determined using plane strain conditions, where $k = (3/1 - \mu)$ and μ (the Poisson ratio) is assumed to be 0.35, as follows:

$$K_{1C} = P_f W_m (k/Wt^3 t_n)^{0.5} \quad (1)$$

where W is the specimen width, t is the specimen thickness, t_n is the tear path thickness, and W_m is the length of the torsion beam moment arm.

Fracture energy was calculated from the fracture toughness and Young's modulus (E) as follows:

$$G_{1C} = K_{1C}^2/E \quad (2)$$

Young's modulus measurements. One of the arms from a double torsion specimen was placed in a three-point bend apparatus. The load was applied in 1 kg increments up to a total of 6 kg. After 5 min, the deflection was measured with a cathometer. The load (P) values were plotted *versus* deflection and the initial slope (m)

of the line was used in the following equation to calculate the Young's modulus:

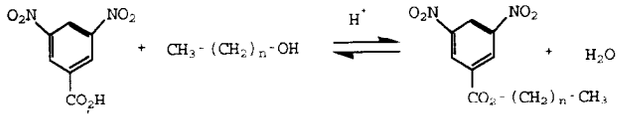
$$E = S^3 m / 4Wt^3 \quad (3)$$

where S is the support span, t is the specimen thickness, and W is the specimen width.

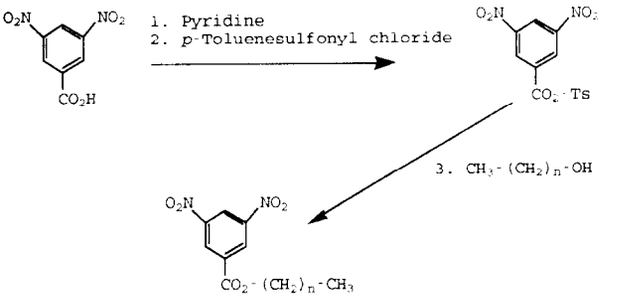
RESULTS AND DISCUSSION

Monomer synthesis

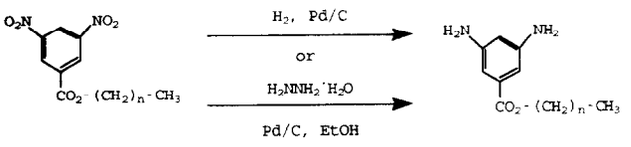
The monomer intermediates were prepared via an esterification reaction. 3,5-Dinitrobenzoic acid was esterified with methanol and 1-butanol in the presence of *p*-toluenesulfonic acid monohydrate to produce methyl 3,5-dinitrobenzoate (**1**) and n-butyl 3,5-dinitrobenzoate (**2**) in 87 and 71% yields, respectively. The water by-product was removed from the reaction mixture by the formation of an azeotrope.



The dinitro compounds with side chains of eight carbons or longer were synthesized via a second reaction pathway. In this procedure, pyridine and tosyl chloride were used to form a mixed anhydride, which was then converted to the ester by reaction with the alcohol. The reaction yields were 76% for n-octyl 3,5-dinitrobenzoate (**3**), 77% for n-dodecyl 3,5-dinitrobenzoate (**4**), and 87% for n-octadecyl 3,5-dinitrobenzoate (**5**).



The dinitro compounds were then hydrogenated under 50 psi hydrogen pressure over a 5% Pd/C catalyst in a Parr hydrogenation apparatus, or reduced with hydrazine monohydrate in refluxing ethanol containing a 5% Pd/C catalyst. The diamines were purified either by recrystallization from ethanol, sublimation or by vacuum distillation.

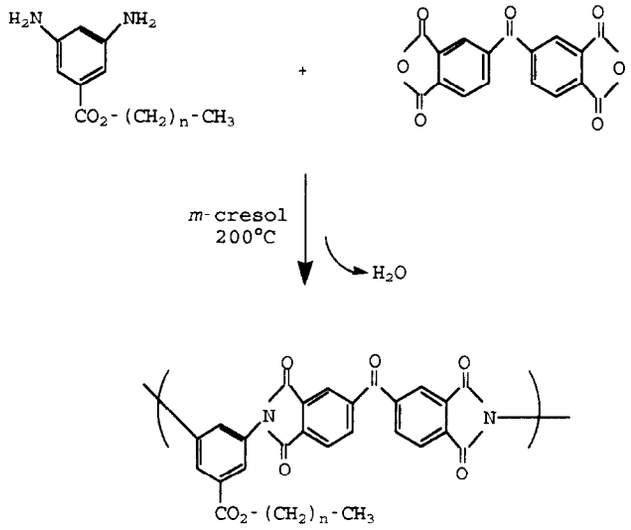


Polymerization using the two-step method

Initially, the diamines and BTDA were polymerized using a two-step polymerization procedure. Thus, the diamine and the dianhydride were mixed in the polar aprotic solvent, NMP, under nitrogen. The PAA that formed at ambient temperature was then chemically imidized by treatment with acetic anhydride and pyridine. However, this procedure was generally unsuccessful. In the case of the polymerizations of diamines **6** and **9**, the polymerization mixtures set to gel-like states within minutes after the addition of the chemical dehydrating agents. Gelation evidently occurred due to the insolubility of the polymers in the NMP. The PAA prepared from **10** had an intrinsic viscosity of only 0.03 dl g^{-1}. It is postulated that this diamine's low reactivity was due to the large size of the pendant group which could sterically hinder the approach of the dianhydride.

Polymerization using the one-step method

A one-step polymerization procedure has been used for monomers with low reactivities that form soluble polyimides[7]. In this procedure the polymerization is carried out at elevated temperature in a refluxing solvent. Under these conditions chain extension and imidization occur simultaneously.



Thus, each diamine was added to a solution of BTDA in *m*-cresol (15 wt% solids content) containing isoquinoline. After the solution was stirred for 3 h at room temperature, it was heated for 3–5 h at 200°C to form the polyimide. The product was isolated by precipitation in ethanol, dried under reduced pressure at 120°C for 12 h and then at 250°C for 1 h.

In order to help determine the effect of the pendent alkyl-ester groups on the polyimides' properties, a model polyimide was synthesized from *m*-PDA and BTDA (**11**). This polyimide was insoluble and precipitated only minutes after the polymerization was started. The highest inherent viscosity reached was 0.18 dl g^{-1} (methanesulfonic acid, 0.5 dl g^{-1}, 30°C) (*Table 1*).

The solution of polyimide **12**, which was prepared with **6** and BTDA, set to a gel-like state within minutes after reflux had begun. The gel-like solid could not be redissolved even with dilution and heating. The inherent viscosity of the polymer obtained was 0.3 dl g^{-1} in methanesulfonic acid.

Polyimide **13**, which was prepared from **7** and BTDA, stayed in solution when the total solids content was 8 wt% or less. The polymer precipitated at higher solids concentrations. The highest viscosity obtained was 0.6 dl g^{-1}.

Polyimides **14**, **15** and **16** were obtained from the polymerization of BTDA with **8**, **9** and **10**, respectively. All three of these polyimides remained in solution throughout the polymerization. They were isolated as

Table 1 Polymerization results[a]

Polyimide	$[\eta]$[b]	T_g (°C)[c]	T_m (°C)[d]	T.g.a. results[e] (°C)
11	0.18[f]	–[g,h]	–	–
12	0.3[f]	–	–	426/400
13	0.6	225	290	406/385
14	1.4	180	310	393/373
15	1.3	182	318	377/340
16	1.0	180	334	395/350
17	0.12[f]	–[i]	–	551/540
18	1.7	270	–	436/470
19	2.0	218	–	410/450
20	1.1	191	–	386/400

[a] Dianhydride used was BTDA
[b] Intrinsic viscosity in dl g^{-1} determined in *m*-cresol at 30 ± 0.1°C
[c] Mid-point of change in slope on d.s.c. thermogram obtained with a heating rate of 10°C min^{-1} in nitrogen
[d] Minimum point of melting endotherm on d.s.c. thermogram obtained with a heating rate of 10°C min^{-1} in nitrogen
[e] Temperature at which a 5% weight loss occurred with a heating rate of 10°C min^{-1} in the designated atmosphere
[f] The polymer precipitated; inherent viscosity in dl g^{-1} was determined in methanesulfonic acid with concentrations of 0.5 g dl^{-1} at 30 ± 0.1°C
[g] No value could be detected from the d.s.c. thermogram
[h] Literature T_g = 300°C (ref. 15)
[i] Literature T_g = 290°C (ref. 16)

yellow fibres upon precipitation in ethanol. The i.r. spectra of the polyimides have characteristic imide absorbances at 1784 and 1732 cm^{-1} (coupled carbonyls), and 1092 and 716 cm^{-1} (cyclic structures). The long aliphatic side-chain absorbances appear at 2924 and 2852 cm^{-1}.

The polymerization results indicate that a pendant methyl ester group is not large enough to sterically hinder intermolecular interactions sufficiently to improve solubility. An ester side-chain length of four carbons improves the solubility of a BTDA-based polyimide to a limited extent. Longer ester side chains, i.e. longer than eight carbons, are very effective in increasing solubility and permitting the attainment of high-molecular-weight products.

In order to see if similar results could be obtained with a more rigid dianhydride, pyromellitic dianhydride (PMDA), was polymerized with **10** under the one-step conditions. Although solid concentrations as low as 8.5 wt% were employed, the product always precipitated out.

Thermal analysis of homopolyimides

The polyimide powders were analysed by using both d.s.c. and t.g.a. (*Table 1*). The polymer's T_gs were determined from the d.s.c. thermograms of samples that had been heated to 320°C and rapidly quenched prior to the run. The d.s.c. thermograms of low-molecular-weight samples of **11** and **12**, did not show any discernible baseline shifts. Polymer **11** had been previously reported to be insoluble, with a T_g of 300°C[15].

The d.s.c. thermogram of **13** showed a strong baseline shift centred at 225°C. This is 75°C below the T_g reported for **11**. Thus, pendant butoxycarbonyl groups provide a significant plasticizing effect. Surprisingly, the polymer's thermogram also contained an apparent melting endotherm at 290°C. The development of crystallinity was not expected because of the pendant groups and the *m*-catenation in the backbone. In fact, initially it was believed that the endotherm could be due to thermal decomposition of the pendant ester group. This hypothesis, however, was ruled out after the polymer's t.g.a. results were obtained. No weight loss occurred until the temperature was significantly higher than that of the endotherm. If decomposition were associated with the endotherm, it is highly likely that some weight loss would occur at the endotherm temperature. The wide-angle X-ray diffraction pattern of **13** confirmed the presence of crystallinity; the amount of crystallinity was estimated to be less than 10%.

The octyl ester side chains on polyimide **14** provided a strong plasticization effect. The baseline shift on the d.s.c. thermogram of **14** was centred at 180°C, i.e. 120°C lower than that of the control **11**. The additional carbon atoms in the pendant ester groups of **15** and **16** did not result in any further reduction in T_g. The T_gs of these polymers were 182 and 180°C, respectively.

The similarity in the T_gs of polyimides **14**, **15** and **16** was unexpected. In fact, it was initially suspected that molecular-weight effects might be playing a role. Thus, a short study was carried out to determine if the T_g values were being influenced by the differences in the polymers' molecular weights. Several batches of polyimide **16** were prepared. The viscosity values ranged from 0.7 to 1.3 dl g^{-1}, while the T_g values were all approximately 180°C. This indicates that the molecular weight does not significantly influence the T_g of **16** over this molecular-weight range.

Wide-angle X-ray scans showed a decreased amount of crystallinity as the side-chain length increased. Homopolyimides **14** and **15** exhibited less than 10% crystallinity, while **16** contained less than 5% crystallinity. The polymers' d.s.c. thermograms showed that their melting points increased as their side-chain lengths increased.

The polymers were subjected to t.g.a. in both air and nitrogen with a heating rate of 10°C min^{-1}. The polyimides showed a two-step weight loss profile (*Figure 1*). It appeared that they first lost their pendant ester groups and then underwent main-chain degradation. The temperature at which their 5% weight losses occurred ranged from 370 to 426°C in nitrogen and from 340 to 400°C in air.

Preparation of copolyimides

To determine the ability of the diamine plasticizers to affect the processability of a polyimide system, a model study was carried out. A control polyimide, **17**, which was known to be difficult to process in the imide form, was prepared from 4,4′-oxydianiline (ODA), and BTDA form. In fact, the polymer precipitated while it was being prepared in *m*-cresol soon after the solution had reached 200°C. The highest-molecular-weight sample obtained had an inherent viscosity of only 0.12 dl g^{-1} (methanesulfonic acid at 30°C ± 0.01) (*Table 1*).

Various amounts of ODA were then replaced with the diamine plasticizer **10** in a series of copolymerizations (*Table 1*). The copolyimides were synthesized in order to determine the effect of different amounts of the plasticizing diamine on processability. Five per cent of plasticizer was not sufficient to keep a copolymer in solution. The polymerization solution containing the copolymer prepared from a 95:5 molar ratio of ODA to **10** set to an insoluble gel-like state. Copolymers containing

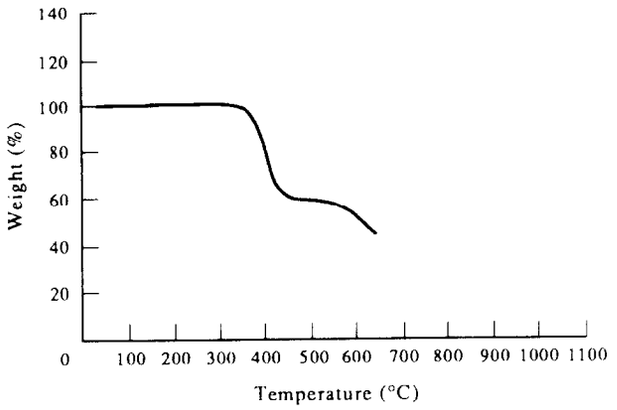


Figure 1 T.g.a. profile of polyimide **16** obtained with a heating rate of 10°C min^{-1} in nitrogen

10 (**18**), 25 (**19**), and 50 mol% (**20**) of **10** remained in solution throughout the polymerization. The copolymers' viscosities ranged from 1.0 to 2.0 dl g^{-1} (*m*-cresol at 30°C ± 0.1). The results with copolymide **18** were quite encouraging. Only 10 mol% of the plasticizing diamine was needed to keep the copolymer in solution.

Thermal analysis of copolyimides

Although the d.s.c. thermogram of the control polymer **17** did not contain any noticeable baseline shifts, the polymer was previously reported to have a T_g of 290°C[16]. The T_gs of the copolymers, which could be detected with d.s.c., decreased as their n-octadecyl 3,5-diaminobenzoate content increased (*Table 1*). The T_gs of **18**, **19**, and **20** were 270, 218, and 191°C, respectively. Evidently, their free volume increased as their plasticizing diamine content increased.

There was a dramatic reduction in thermal stability upon the introduction of the alkyl ester groups on to the polyimide backbone. The control polymer **17** underwent a 5% weight loss at 551°C in nitrogen when subjected to t.g.a. The corresponding weight loss for the copolymers ranged from 386 to 436°C. The copolymers underwent 5% weight losses between 350 and 510°C in air.

Polyimide properties

Solubility tests were performed on the homopolyimides and copolyimides. Each polymer (3 wt%) was immersed in a variety of common organic solvents and heated below the refluxing temperature for 12 h (*Table 2*). Polyimides **11**, **12**, and **17** were completely insoluble in all of the solvents that were used. Polymers **13**, **14**, and **18** were soluble in *m*-cresol and partially soluble in NMP. The remaining polymers and copolymers, **15**, **16**, **19**, and **20**, were completely soluble in *m*-cresol and partially soluble or swellable in NMP, tetrachloroethane (TCE), and methylene chloride (CH_2Cl_2). Thus, the only good solvent for the polymers was *m*-cresol. An effort was therefore made to cast films from *m*-cresol solutions. However, only opaque films, containing large voids and residual solvent, were obtained.

An attempt was made to compression-mould the polyimides. The polymer powders were placed in an aluminium mould and heated to 50–100°C above their T_gs where 7 MPa of pressure was applied. After the temperature and pressure were maintained for 20 min, the mould was slowly cooled to ambient temperature. The neat resin samples were then inspected to determine if sufficient flow had occurred to afford a homogeneous specimen. D.s.c. analysis was also repeated to insure that the T_g values had not changed. An increase in T_g was taken to mean that crosslinking had occurred during processing.

Table 2 Polyimide solubility[a]

	Solvent[b,c]						
Polymer	C	N	T	M	F	A	S
11	i	i	i	i	i	i	i
12	i	i	i	i	i	i	i
13	s	p	i	i	i	i	i
14	s	p	i	i	i	i	i
15	s	p	p	p	i	i	i
16	s	p	p	p	i	i	i
17	i	i	i	i	i	i	i
18	s	p	i	i	i	i	i
19	s	p	p	p	i	i	i
20	s	p	p	p	i	i	i

[a] Solutions (3 wt%) were prepared and heated below reflux for 12 h
[b] *m*-Cresol (C); *N*-methyl-2pyrrolidinone (N); 1,1,2,2-tetrachloroethane (T); methylene chloride (M); *N*,*N*-dimethylformamide (F); *N*,*N*-dimethyl acetamide (A); dimethyl sulfoxide (S)
[c] Soluble polymer (s); insoluble polymer (i); polymer that was partially soluble or swelled during heating (p)

Table 3 Mechanical properties of copolyimides

Polymer	Moulding temperature[a] (°C)	Stress intensity[b] (MN $m^{1.5}$)	Fracture energy[b] (kJ m^{-2})	Modulus[c] (GPa)
16	280	1.20	1.070	1.35
18	315	2.46	1.948	3.05
19	300	1.78	1.510	2.43
20	300	1.75	1.310	2.35

[a] Temperature of aluminium mould required to afford a homogeneous sample using a pressure of 7 MPa
[b] Obtained from a machined compression-moulded sample tested in a double-torsion experiment using a pre-crack technique
[c] Obtained from a three-point bend experiment on samples tested as above

Polymers **11**, **12**, and **17** did not undergo flow at the highest available processing temperature of 330°C. Although polyimides **13**, **14**, and **15** underwent considerable flow, the d.s.c. thermograms indicated that crosslinking had also occurred. The homo- and copolyimides of n-octadecyl 3,5-diaminobenzoate (**16**, **18**–**20**) were well consolidated after processing between 280 and 315°C. The T_gs of these polymers did not increase during processing.

The effect of the pendant ester groups on the mechanical properties of the polymers was determined next. Samples were machined to size, and their fracture toughness (K_{1C}) and fracture energy (G_{1C}) determined in an Instron Universal Testing machine using a double torsion set-up. Three-point bend experiments were used for flexural modulus measurements. The data obtained from the mechanical tests are shown in *Table 3*. The fracture energy is closely related to the fracture toughness. Both sets of parameters decreased as the amount of plasticizing component in the polymer increased. Although the factors influencing a material's properties are quite complex, it is likely that the more plasticizer in

the system, then the greater the interruption of the intermolecular interactions and the lower the energy needed to fracture the material. The modulus also decreased as the diamine plasticizer content increased, which was expected since stiffness is known to decrease with plasticization.

CONCLUSIONS

A series of alkyl 3,5-diaminobenzoates was obtained from the esterification of 3,5-dinitrobenzoic acid with various alcohols, followed by reduction to the respective diamines. The alkyl groups consisted of linear, saturated, hydrocarbon chains of one to eighteen carbons. The diamines were polymerized with BTDA using a one-step procedure in refluxing *m*-cresol. All the diamines that contained linear alkyl side chains, except for methyl 3,5-diaminobenzoate, produced soluble polyimides. The side chains were effective in lowering the T_gs of polyimides. The polyimides containing pendant ester groups with more than eight carbons in their alkyl chains had T_g values which were 120°C lower than a control polyimide without pendant groups. The polymers' T_gs decreased as the length of the pendant esters' alkyl chains increased to eight carbons. Further increases in the length of the alkyl chain did not result in any further reductions in T_g. Surprisingly, the polymers were semicrystalline. Although their T_m values increased as the length of the esters' alkyl chains increased, their degree of crystallinity also decreased.

A series of copolyimides was synthesized from BTDA and various amounts of the plasticizing diamine, n-octadecyl 3,5-diaminobenzoate, and ODA. The incorporation of only 10 mol% of the plasticizer was sufficient to keep the polymer in solution in the *m*-cresol solvent that was used. The T_gs of this series decreased with increasing amounts of incorporated plasticizer. The copolyimides were melt-processable. Moulded samples were subjected to mechanical testing. The polymers flexural moduli decreased as their plasticizing diamine contents increased.

The incorporation of the pendant alkyl esters along the polymers' backbones, however, caused a reduction in thermal stability. The polymers underwent a two-step weight loss when subjected to t.g.a. The first weight loss was equivalent to the amount of pendant ester groups present in the system.

Overall, internal plasticization through the incorporation of alkyl 3,5-diaminobenzoates was shown to be successful. The pendant side chains did influence polyimide properties as desired by aiding solubility and reducing the T_g. It would now be interesting to incorporate these diamines into additional polyimide systems and to more fully evaluate their effects on melt processing and material properties.

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