Synthesis and characterization of aromatic polyisoimides derived from PMDA and *para*-diamines. An approach to *in situ* generated rigid-rod molecular composites

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A new concept for the processing and fabrication of rigid-rod molecular composites aiming at the elimination or minimization of phase separation is proposed. This approach calls for a coil-like aromatic polyisoimide which is soluble and compatible with an amorphous matrix polymer or thermosettable oligomer and can undergo facile transformation to the corresponding rigid-rod polyimide in solid composite state, thus imparting the inherently high strength/high modulus properties to the final form. To this end, various synthetic routes were explored to obtain *para*-diamines which could afford high molecular weight and aprotic-solvent-soluble polyisoimides upon polymerization with pyromellitic dianhydride (PMDA). Four such polyisoimides were prepared, with their inherent viscosities ranging from 0.25 to 1.89 dl g^{-1} in dimethylacetamide at 30°C. Facile thermally induced isoimide–imide conversion was demonstrated by solid-state (film) Fourier transform infrared spectroscopy. A preliminary evaluation of the compatibility of the polyisoimide/matrix resin was made. In one instance, a film prepared from the polyisoimide derived from PMDA and 3,3′,5,5′-tetramethylbenzidine (TMB) showed no visually detectable phase separation.

(Keywords: polyisoimides; rigid-rod polyimides; *in situ*-generated rigid-rod molecular composites; isoimide–imide conversion; diaryloxy benzidine monomers; 3,3′,5,5′-tetramethylbenzidine; 2-aryloxy-1,4-phenylenediamines)

INTRODUCTION

Extensive studies in our laboratory[1,2] have been focused on the development of aromatic heterocyclic ordered polymers whose all-*para* backbone geometry defines their rigid-rod structures. The rod-like character of this class of polymers, PBX[3], as exemplified by polybenzothiazoles (PBZT), polybenzoxazoles (PBO) and polybenzimidazoles (PBI), provides a vehicle for molecular ordering in a relatively dilute solution. Such solution anisotropy has furnished a mechanism to attain extremely high modulus/high strength fibres and oriented films. Since rigid-rod macromolecules in small bundles are molecular analogues of macroscopic fibres used in the conventional reinforced composites, the dispersion of a rigid-rod polymer at the molecular level in a suitable ductile matrix results in the formation of a new material referred to as a rigid-rod molecular composite (RRMC). These materials exhibit significant improvements in mechanical properties as well as good thermal and chemical stability compared with conventional fibre/whisker reinforced composites[4–6]. There are, however, limitations in the application of PBX polymers in molecular composites. For example, they are only soluble in strong organic acids such as methanesulphonic acid and mineral acids like polyphosphoric acid. The latitude in the choice of matrix materials is thus restricted with respect to their solubility and stability in these acidic solvents.

Strictly, to achieve a true molecular composite, there must be no phase separation on the van der Waals scale. Unfortunately, the current state-of-the-art approaches, which entail the blending of a rigid-rod polymer and a flexible coil polymer[7] and/or thermosettable oligomers[8] in a strongly acidic solvent, have resulted in varying degrees of phase separation at either the coagulation stage or during the process of consolidation. This is primarily due to the fact that thermodynamics disfavour the mixing of the inherently dissimilar coil-like matrix molecules and rod-like reinforcing molecules. The strong proclivity of the rod-like molecules to aggregate in solution is manifested in the existence of a characteristic critical concentration which is a function of the axial ratio of the rods, the contour length of the coils and their compositions[9]. In solid state, it has been shown that facile phase separation of the rigid rods could be effected thermally, especially approaching the melting temperature regime of the matrix[7].

We wish to propose a new concept for the processing and fabrication of molecular composite materials with the objective of circumventing or minimizing the extent of phase separation in RRMC. In this approach, the key element is the thermally induced isomerization of a coil-like precursor to the respective rigid rod within the matrix. Presumably, since the isomerization process is taking place after the coil-like precursor and the matrix polymers/oligomers have been uniformly mixed, there is a high probability that the aggregation of the rigid rods may be prevented. The success of this '*in situ* rod' approach is dependent upon, at the minimum, the following factors: first, the molecular weight of the rigid-rod precursor must be sufficiently high and must

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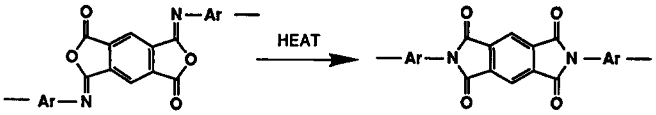
not be adversely affected by the isomerization reaction; second, the efficiency of the isomerization process must be high enough to generate the necessary aspect ratio for reinforcement; and, third, the rigid-rod precursor and the matrix materials must be compatible and soluble in a common solvent to form a stable homogeneous solution.

PBX polymers are not applicable for obvious reasons and aromatic polyimides were selected based on the following considerations. First, polymers derived from pyromellitic dianhydride (PMDA) and aromatic *para*-diamines will provide the rigid-rod structures. Second, the thermal isomerization of an isoimide function to an imide group is a well known process and an important factor in the processing and fabrication of commercial thermoset systems, such as acetylene-terminated IP-600 resins[10,11]. Therefore, the crucial first step of this approach is to identify the requisite aromatic polyisoimides (also known as polyiminolactones). In this investigation, four different candidate polyisoimides were synthesized and evaluated for solubility, molecular weight and matrix compatibility.



EXPERIMENTAL

Preparation of 3-phenoxy nitrobenzene (1a)

Phenol (18.0 g, 0.19 mol) and KOH pellets (8.2 g, 0.15 mol) were placed in a three-necked, 250 ml round-bottomed flask equipped with a mechanical stirrer, a reflux condensor and an adaptor fitted with a thermometer. The mixture was heated until an internal temperature of 135°C was reached, at which time a dark liquid formed. Then the phenoxide solution was allowed to cool down to ≈100°C, and about half the amount of a mixture of copper bronze (0.20 g) and *m*-iodonitrobenzene (25.0 g, 0.10 mol) was delivered through the mouth, which was originally fitted with the adaptor/thermometer. The reaction mixture was vigorously stirred and at the same time rapidly heated to ≈160°C, at which temperature a quantitative amount of fine KI particles started to precipitate. Heat was removed and the reaction mixture was allowed to cool to ≈110°C. Then the other half of the mixture of copper bronze and *m*-iodonitrobenzene was added. Heat was applied again until the temperature of 160°C was reached and maintained for another 30–40 min. Subsequently, the reaction mixture was allowed to cool to ≈110°C and then poured into NaOH (10.0 g)/300 ml ice/H_2O. The dark mixture was filtered to remove insolubles. The filtrate was extracted with benzene (5 x 100 ml). The dark extract was dried over $MgSO_4$ and filtered through a cake of Celite. The filtrate was stripped on a rotary evaporator and the liquid residue was transferred to a small flask. Vacuum distillation led to the isolation of about 14.0 g of bright yellow, viscous liquid. B.p.: 138–140°C/0.2 Torr*. Yield: 65%. Analysis – calc. for $C_{12}H_9O_3N$: C, 66.70; H, 4.22; N, 6.50; O, 22.30%; found: C, 66.69; H, 4.25; N, 6.58; O, 22.36%. I.r. (KBr): $\nu(NO_2)$ at 1528, 1357 cm^{-1}; ν(Ar–O–Ar) at 1240 cm^{-1}.

Preparation of 3-(3-phenoxyphenoxy) nitrobenzene (1b)

3-(3-Phenoxyphenoxy)nitrobenzene was prepared similarly from potassium hydroxide pellets (5.6 g, 100 mmol), *m*-phenoxyphenol (Eastman Kodak Chemical Co., 28.0 g, 150 mmol) copper bronze (0.1 g) and *m*-iodonitrobenzene (18.7 g, 75 mmol). 16.0 g of yellow viscous liquid was isolated after vacuum distillation of the crude product at 199–201°C/0.2 Torr. It solidified upon standing at room temperature. Analysis – calc. for $C_{18}H_{13}NO_4$: C, 70.35; H, 4.26; N, 4.56; O, 20.83%; found: C, 69.89; H, 4.32; N, 4.10; O, 21.42%. I.r.: $\nu(NO_2)$ at 1530, 1350 cm^{-1}; ν(Ar–O–Ar) at 1222 cm^{-1}.

Preparation of 3-azoxy phenoxybenzene (2a)

To the solution of KOH (9.1 g, 0.16 mol) in 145 ml absolute ethanol was added 3-phenoxy nitrobenzene (1a). The resultant yellow homogeneous solution was refluxed for 2 h. About 50 ml of the solvent was removed from the dark reaction mixture by rotary evaporation. Then 350 ml of distilled water was added and the reaction mixture was chilled in a refrigerator overnight. The dark brown precipitate was collected by filtration, washed with water and petroleum-ether, and air-dried. The crude product was then dissolved in 100 ml of benzene and the dark red solution was treated with anhydrous $MgSO_4$. After removal of the drying agent by filtration, the benzene solution was stripped to afford a semi-solid. About 20 ml of methanol and 30 ml of petroleum-ether was added. Rust brown microcrystalline solid formed during the rotary evaporation of the mixture. It was collected by filtration, washed with petroleum ether and vacuum-dried at room temperature for 24 h. Yield: 5.0 g (56%). Analysis – calc. for $C_{24}H_{13}O_3N_2$: C, 75.38; H, 4.74; N, 7.33; O, 12.55%; found: C, 75.25; H, 4.99; N, 7.16; O, 12.50%. I.r. (KBr): ν(azoxy) at 1252 cm^{-1}; ν(Ar–O–Ar) at 1218 cm^{-1}.

Preparation of 3,3′-bis(3-phenoxyphenoxy) azobenzene (2b)

A three-necked, 250 ml round-bottomed flask was equipped with a magnetic stir bar, an addition funnel and a nitrogen adaptor. Under dry nitrogen, the flask was charged with sodium borohydride (18.4 g, 0.487 mol) dissolved in 100 ml of dry dimethyl sulphoxide (DMSO). A solution of 3-(3-phenoxyphenoxy)nitrobenzene (1b) (25.0 g, 0.081 mol) in 100 ml of dry DMSO was added to the $NaBH_4$ solution while stirring over 0.5 h. The addition was accomplished at room temperature and an exotherm was noted. The milky yellow reaction mixture turned red–brown after about 15 min. Next, 500 ml of methylene chloride was added to the reaction mixture. The resulting solution was subsequently washed with three 200 ml portions of 10% hydrochloric acid and one 300 ml portion of distilled water. The bright, yellow–orange solution was dried over anhydrous $MgSO_4$. Finally, solvent was removed completely via a rotary evaporator and a dark orange oil remained, which was further dried under vacuum at 50°C. Yield: 22.7 g (98%). Analysis – calc. for $C_{18}H_{13}N_2O_4$: C, 78.52; H, 4.77; N, 5.09; O, 11.23%; found: C, 77.91; H, 4.71; N, 5.01; O, 11.79%.

Preparation of 2,2′-diphenoxybenzidine dihydrochloride (3a)

$SnCl_2 . H_2O$ (23.6 g, 0.105 mol) was dissolved in 75 ml of concentrated HCl in a 500 ml round-bottomed flask.

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* 1 torr ≈ 133 Pa

To the resultant colourless solution was added portionwise a slurry of 3-azoxy phenoxybenzene (5.0 g, 0.013 mol) in 100 ml Et_2O. Immediately, black colour developed in the reaction mixture, which was continuously stirred at room temperature for ≈4 d. During this period, the colour changed from black to dark brown and finally to light brown. After Et_2O had been evaporated off on a warm hot plate in a hood, the resulting dark viscous material was extracted with hot 20% $EtOH/H_2O$ (5 × 60 ml) and filtered through a layer of Celite. White precipitate formed when the filtrate was treated with NH_4OH at 0°C. The crude product was collected, washed with copious amounts of water and air-dried for 48 h. 4.1 g of gray solid was obtained. Its mass spectrum showed a strong molecular ion peak at $m/e = 368$ (rel. abundance = 100%) and i.r. spectrum indicated the presence of NH_2 groups: 3350, 3372, 3435 and 3463 cm^{-1}.

3.0 g of the crude diamine was dissolved in ≈380 ml of 2.5 N HCl at 80°C. The hot solution was filtered through Celite. The filtrate was chilled in an ice bath and 50 ml of concentrated HCl was added slowly. White fine crystals slowly appeared. The product was collected, washed with anhydrous Et_2O and dried *in vacuo* at ≈55°C for 24 h. Yield: 0.88 g. Analysis – calc. for monohydrate $C_{24}H_{22}N_2Cl_2 . H_2O$: C, 62.75; H, 5.26; N, 6.10; Cl, 15.43%; found: C, 62.91; H, 4.96; N, 5.90; Cl, 14.99%.

Preparation of 2,2'-(3-phenoxyphenoxy) benzidine dihydrochloride (3b)

To a three-necked, 1000 ml round-bottomed flask, equipped with a mechanical stirrer and an addition funnel, a solution of stannous chloride (26.85 g, 0.142 mol) in 250 ml of concentrated hydrochloric acid was added. A solution of 3,3'-bis(3-phenoxyphenoxy) azobenzene (2b) (10.0 g, 18.16 mmol) in 150 ml of methylene chloride was prepared and added dropwise over 1 h to the stannous chloride/concentrated HCl solution. A light pink precipitate formed as the addition proceeded. The mixture was stirred overnight and then transferred to a one-necked, 500 ml round-bottomed flask and methylene chloride removed under reduced pressure with low heat, causing a precipitate (the salt of newly formed diamine) to form. The precipitate was collected by filtration and washed on a fritted glass funnel with concentrated HCl (3 × 100 ml) and dried under vacuum at 40°C overnight. The crude salt was stirred with 200 ml of 1 N ethanolic KOH to produce the free diamine. The basic aqueous mixture was extracted with three portions of methylene chloride to produce (after drying under vacuum) 9.0 g of a light brown oil. The oil was chromatographed on a quartz column filled with activated silica gel (600 g). The second band (product) was eluted with n-hexane/ethyl acetate (9:1) to yield 3.11 g (31%) of off-white viscous oil. The oil was dissolved in 100 ml of a 1:1 mixture of concentrated HCl and ethanol. Concentrated HCl was added until the solution was slightly cloudy. It was then heated until clear and allowed slowly to cool. A white precipitate formed, was collected and dried to afford 2.98 g (30%) of white solid. Analysis – calc. for $C_{36}H_{30}N_2O_4Cl_2$: C, 69.12; H, 4.80; N, 4.48; Cl, 11.33%; found: C, 70.16; H, 5.05; N, 4.93; Cl, 10.60%. Spectroscopic data for the free diamine are as follows: mass spectrum showed a strong molecular ion at $m/e = 552$ (relative abundance = 100%); i.r. showed $\nu(NH_2)$ at 3460 and 3380 cm^{-1}; and ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm): 6.40–7.49 (complex multiplets, aromatic protons, 24H); 3.69 ppm (singlet, NH_2, 4H).

Preparation of model compounds (isomers) (4a) and (4b)

1-Phenoxyaniline (Aldrich Chemical Co., 1.0000 g, 5.399 mmol) and pyromellitic dianhydride (PMDA) (0.5888 g, 2.699 mmol) were stirred in 14.29 g of freshly distilled dimethylacetamide (DMAC) at room temperature and under N_2 atmosphere. After ≈2 h, a white precipitate formed. The reaction mixture was stirred for another 12 h. Then the white solid was collected by filtration, washed with three portions of isopropanol and dried under vacuum at 50°C for 24 h. Yield of (4a) and (4b) was 1.49 g (94%). Analysis – calc. for $C_{34}H_{24}N_2O_8$: C, 69.38; H, 4.11; N, 4.76%; found: C, 69.44; H, 4.61; N, 4.78%.

Preparation of 3,3'-dichlorobenzidine (5)

150.0 g (0.46 mol) of 3,3'-dichlorobenzidine dihydrochloride (Sigma Chemical Co.) was dissolved in 80% H_2O/ethanol at 50°C under a nitrogen atmosphere. After the solution had been at 50°C for 30 min, it was filtered under N_2. To the cooled solution, 138 g (1.0 mol) of anhydrous potassium carbonate was added in small portions with stirring. After the addition was completed, stirring was continued for an additional 45 min. The precipitate was collected by filtration under N_2 and washed with water, after which the free amine was dried in a vacuum oven at 40°C for 48 h. Yield: 82 g (70%).

Preparation of 3,3'-dichloro-4,4'-dinitrobiphenyl (6)

To a four-necked, 5 l round-bottomed flask, equipped with a mechanical stirrer, an addition funnel, a thermometer, a reflux condensor and an ice bath, were added 1500 ml of methylene chloride and 90 ml of 90% hydrogen peroxide. 386 ml of trifluoroacetic anhydride was added dropwise from the addition funnel over a period of 2 h, while maintaining the reaction temperature below 10°C. Subsequently, 69.0 g (0.273 mol) of 3,3'-dichlorobenzidine (5) was added in small portions (≈5 g each), while keeping the temperature of the reaction mixture at 10°C. The reaction mixture was stirred for another 1 h in an ice bath. The yellow precipitate was collected by suction-filtration and washed with water. The filtrate was concentrated to about one quarter of its original volume and additional product precipitated, which was filtered, washed with water and combined with the first crop. The crude product was air-dried for 24 h and then recrystallized twice from acetone/water (2:1 by volume). Yield: 61.0 g (72%). M.p.: 221–222°C. I.r. (KBr): $\nu(NO_2)$ at 1520, 1325 cm^{-1}. Analysis – calc. for $C_6H_6N_2O_4Cl_2$: C, 46.03; H, 1.93; N, 8.95; Cl, 22.65%; found: C, 45.91; H, 1.96; N, 9.01; Cl, 22.73%.

General procedure for preparation of 3,3'-diaryloxy-4,4'-dinitrobiphenyls

To a 50 ml, three-necked, round-bottomed flask, equipped with a magnetic stir bar and nitrogen inlet/outlet, was added 30 ml of dry DMSO. While stirring under nitrogen, phenol or 3-phenoxyphenol (36.0 mmol) and potassium methoxide (38.0 mmol) were added. The mixture was stirred at 40°C for 1 h, after which generation of the phenoxide salt was judged complete. A 250 ml, three-necked, round-bottomed flask was equipped with gas inlet/outlet, addition funnel, and magnetic stir bar and charged with 3,3′-dichloro-4,4′-dinitrobiphenyl (6) (11.0 mmol) dissolved in 40 ml of dry DMSO (heating to 60°C was required to form a clear-orange solution). The potassium phenoxide was transferred (under N_2) to the addition funnel and added to the above solution over 1 h. The solution turned much darker and the reaction temperature was maintained at 60°C for an additional $2\frac{1}{2}$ h. The reaction mixture was poured into 700 ml of 1 N sodium hydroxide and stirred. A precipitate formed (orange) and was collected by suction filtration, washed (on the filter) with 200 ml of distilled water, dissolved in 200 ml of methylene chloride, dried (magnesium sulphate), and filtered. The filtrate was concentrated (rotary evaporator) and crystallized on standing. The crude solid was recrystallized from ethyl acetate/hexanes (1:5 by volume).

3,3′-Di-3-phenoxy-4,4′-dinitrobiphenyl (*7a*). Light-orange solid, yield: 70.5%. M.p.: 158–159°C. I.r. (KBr): $\nu(NO_2)$ at 1520 and 1325 cm^{-1}; ν(Ar–O–Ar) at 1210 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm): 7.95–8.15 (d, aromatic, 2H); 6.9–7.5 (m, aromatic protons, 14H). Analysis – calc. for $C_{24}H_{16}N_2O_6$: C, 67.28; H, 3.77; N, 6.54%; found, C, 67.74%; H, 3.89; N, 6.71%.

3,3′-Di-3-phenoxyphenoxy-4,4′-dinitrobiphenyl (*7b*). Light-yellow needles, yield: 54%. M.p.: 118.5–119.5°C. I.r. (KBr): $\nu(NO_2)$ at 1510 and 1335 cm^{-1}; ν(Ar–O–Ar) at 1230 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm): 7.92–8.21 (d, aromatic protons, 2H), 6.60–7.45 (m, aromatic protons, 22H). Analysis – calc. for $C_{36}H_{24}N_2O_8$: C, 70.57; H, 3.95; N, 4.57%; found: C, 70.38; H, 4.05; N, 4.70%.

General procedure for preparation of 3,3′-diaryloxy benzidine

In a 500 ml Paar hydrogenator flask, equipped with mechanical agitator and high-pressure hydrogen inlet, were added the diaryloxy dinitrobiphenyl (7.94 mmol), 10% palladium on charcoal (0.3 g), magnesium sulphate (2.5 g) and 100 ml of degassed ethyl acetate. The flask was pressurized to 50 psig and agitated for 18 h. The resulting clear, colourless solution was pressure-filtered with nitrogen through diatomaceous filter aid, which had been previously washed with dry ethyl acetate, to remove the catalyst and magnesium sulphate. The clear filtrate was reduced to half the original volume (rotary evaporator) and 75 ml of hexane added. Upon cooling, large off-white crystals formed and were collected by nitrogen pressure filtration to yield 2.72 g of crude crystalline product. The crude crystals were recrystallized from heptane/methylene chloride (10/1).

3,3′-Di-phenoxybenzidine (*8a*). Off-white crystalline solid, yield: 78.02%. M.p.: 126.0–126.6°C. I.r. (KBr): $\nu(NH_2)$ at 3595 and 3498 cm^{-1}; ν(Ar–O–Ar) at 1210 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm): 6.68–7.50 (m, aromatic protons, 16H); 3.70 (s, NH_2, 4H). Analysis – calc. for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60%; found: C, 78.41; H, 5.64; N, 7.69%.

3,3′-Di-3-phenoxyphenoxy-benzidine (*8b*). Light-pink plates, yield: 75.9%. M.p.: 136–137°C. I.r. (KBr): $\nu(NH_2)$ at 3570 and 3380 cm^{-1}; ν(Ar–O–Ar) at 1215 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm): 6.42–7.51 (m, aromatic protons, 24H); 3.69 (s, NH_2, 4H). Analysis – calc. for $C_{36}H_{28}N_2O_4$: C, 78.24; H, 5.11; N, 5.07%; found: C, 78.25; H, 5.33; N, 5.23%.

Preparation of 2-bromo-4-nitroaniline (*9*)

100 g (0.724 mol) of *p*-nitroaniline was slowly added to 1550 ml of glacial acetic acid at 40°C. After cooling the solution to 20°C, 37.4 ml (116.65 g, 0.730 mol) of bromine was added dropwise over 1 h, after which the solution was stirred for an additional 45 min at 20°C. The precipitate which formed during the reaction was collected by suction filtration and stirred with 2500 ml of 10% aqueous sodium bisulphite for 16 h, collected again by suction filtration and washed with 2500 ml of water. The solid was air-dried for 24 h. The crude material (139 g) was recrystallized twice from 65% methanol to yield 103 g (65.5%) of a yellow crystalline solid which melted at 101–102°C. I.r. (KBr): $\nu(NH_2)$ at 3500 and 3400 cm^{-1}; $\nu(NO_2)$ at 1500 and 1325 cm^{-1}. Analysis – calc. for $C_6H_5N_2O_2Br$: C, 33.18; H, 2.30; N, 12.90%; found: C, 33.26; H, 2.28; N, 12.92%.

General procedure for preparation of 2-aryloxy 4-nitroanilines

A solution of potassium carbonate (0.07 mol) and phenol or 3-phenoxyphenol (0.14 mol) was heated at 120°C to form the requisite phenolic nucleophile under nitrogen in a three-necked, 50 ml round-bottomed flask equipped with a reflux condensor, a magnetic stir bar and a nitrogen adapter. Next, copper–bronze (0.5 g) was added with stirring. While stirring, 2-bromo-4-nitroaniline (9) (5.0 g, 0.025 mol) was added in two equal portions and the reaction temperature raised to 135°C and maintained overnight. The dark reaction mixture, while still hot, was poured into 600 ml of 1 N aqueous potassium hydroxide and stirred for 1 h. The resulting dark-brown precipitate was collected on diatomaceous filter aid by suction filtration. The filter aid and crude product were extracted with 150 ml of methylene chloride. The CH_2Cl_2 extract was completely stripped on a rotary evaporator to afford a dark-gray solid which was subsequently chromatographed on a quartz column filled with activated silica gel (400 g). The second band was eluted with methylene chloride/hexanes (1/1) to yield the desired product, which was recrystallized from ethanol/water (4/1).

2-Phenoxy-4-nitroaniline (*10a*). Light-yellow crystalline solid, yield: 68.1%. M.p.: 116–117°C. I.r. (KBr): $\nu(NH_2)$ at 3500 and 3360 cm^{-1}; $\nu(NO_2)$ at 1490 and 1290 cm^{-1}; νAr–O–Ar) at 1225 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm) 6.71–8.15 (m, aromatic protons, 8H), 4.75 (s, NH_2, 2H). Analysis – calc. for $C_{12}H_{10}N_2O_3$: C, 62.60; H, 4.38; N, 12.17%; found: C, 62.64; H, 4.38; N, 11.78%.

2-(3-Phenoxyphenoxy)-4-nitroaniline (*10b*). Bright-yellow plate-like crystals, yield: 73.2%. M.p.: 121–122°C. I.r. (KBr): $\nu(NH_2)$ at 3500 and 3380 cm^{-1}; $\nu(NO_2)$ at 1500 and 1295 cm^{-1}; ν(Ar–O–Ar) at 1210 cm^{-1}. ^1H n.m.r. ($CDCl_3$, TMS, δ-values in ppm) 7.80–8.15 (m, aromatic protons, 2H), 6.60–7.55 (m, aromatic, 10H); 4.65 (s, NH_2, 2H). Analysis – calc. for $C_{18}H_{14}N_2O_3$: C, 67.07; H, 4.37; N, 8.69; found: C, 67.10; H, 4.49; N, 8.91%.

General procedure for preparation of 2-aryloxy 1,4-phenylenediamine dihydrochlorides

In a 500 ml Paar hydrogenator flask, equipped with mechanical agitator and high pressure hydrogen inlet, were added the 2-aryloxy-4-nitroaniline (15.2 mmol), 10% palladium on charcoal (0.3 g), and 75 ml of ethanol which had been previously saturated with hydrogen chloride gas. The flask was pressurized to 50 psi and agitated for 16 h. The resulting clear, colourless solution was pressure-filtered with nitrogen through diatomaceous filter aid, which had been previously washed with ethanol saturated with HCl, to remove the catalyst. The collected filtrate was saturated with HCl gas and 50 ml of anhydrous diethyl ether added (causing a slight cloudiness). Upon cooling overnight (0°C) a white precipitate formed, which was collected by filtration under N_2 pressure and dried under vacuum at 60°C over phosphorus pentoxide for 48 h.

2-Phenoxy-1,4-phenylenediamine dihydrochloride (11a). White solid, yield: 85.8%, decomposed above 120°C. I.r. (KBr): ν(Ar–O–Ar) at 1205 cm^{-1}. Analysis – calc. for $C_{12}H_{14}N_2Cl_2O$: C, 52.76; H, 5.17; N, 10.26; Cl, 25.96%; found: C, 49.55; H, 4.71; N, 9.35; Cl, 29.12%.

2-(3-Phenoxyphenoxy)-1,4-phenylenediamine dihydrochloride (11b). White solid, yield: 81%, decomposed above 140°C. I.r. (KBr): $\nu(NH_2)$ at 1627 cm^{-1}; ν(Ar–O–Ar) at 1215 cm^{-1}. Analysis – calc. for $C_{18}H_{18}N_2O_2Cl_2$: C, 59.19; H, 4.97; N, 7.17; Cl, 19.41%; found: C, 54.73; H, 4.50; N, 7.15; Cl, 24.16%.

POLYMER PREPARATION

Typical procedure for preparation of benzidine-based polyisoimides

A 500 ml, three-necked, round-bottomed flask was fitted with a mechanical stirrer and nitrogen adaptor. The flask was charged (under nitrogen) with tetramethylbenzidine (TMB) (3.04219 g, 12.657 mmol), pyromellitic dianhydride (2.7604 g, 12.6570 mmol) and 58.02 g of freshly distilled DMAC. After stirring at room temperature for 2 h, all of the starting materials dissolved and a significant increase in the reaction mixture viscosity was noted. The reaction mixture was stirred (at room temperature) for an additional 12 h, diluted with 246.95 g of anhydrous DMAC and 1.45 g of anhydrous lithium chloride. (In the PMDA/TMB system, LiCl is not necessary.) The mixture was stirred for 1 h, after which all lithium chloride had dissolved.

To this solution, DCC (4.933 g, 23.91 mmol) was added with stirring causing a rapid colour change (dark red). The reaction mixture was stirred at room temperature for 12 h, poured into 2400 ml of fresh isopropanol, and stirred for 2 h. A bright red–orange precipitate was collected on a coarse fritted funnel (keeping the material covered with alcohol), washed with three 200 ml portions of fresh isopropanol (again not allowing the material to dry), and finally washed with three 200 ml portions of anhydrous benzene. The final slurry of benzene and product was freeze dried at 0.1 mm Hg for 72 h. This procedure yielded 5.82 g of a bright red-orange fibrous solid.

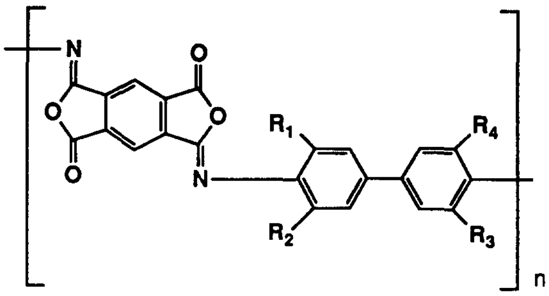
Typical procedure for preparation of 1,4-phenylenediamine-based polyisoimides

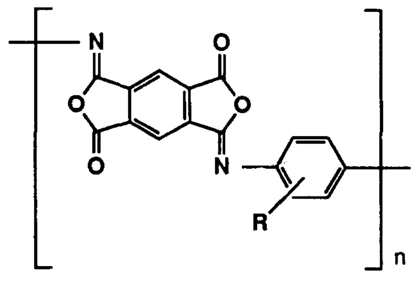
A 100 ml resin kettle was fitted with a four-necked ground-glass top, a mechanical stirrer, two nitrogen adaptors and a glass stopper. The kettle was charged with 2-(3-phenoxyphenoxy)-1,4-diaminobenzene dihydrochloride (0.6252 g, 1.712 mmol), pyromellitic dianhydride (0.3734 g, 1.712 mmol), lithium carbonate (0.1130 g, 1.883 mmol) and 9.02 g of freshly distilled DMAC. After stirring at room temperature for a few minutes, evolution of gas was noted and continued for 0.5 h. The light-yellow reaction mixture was stirred (at room temperature) for 12 h, diluted with 43.50 g of anhydrous DMAC, and stirred for an additional hour. To the solution, DCC (0.7205 g, 3.492 mmol) was added with stirring, causing a rapid colour change (dark red). The reaction mixture was stirred at room temperature for 12 h, poured into 500 ml of fresh isopropanol and stirred for 2 h. A bright red–orange precipitate was collected on a medium fritted glass funnel, dried briefly under vacuum, redissolved in 50 ml of THF and reprecipitated in 500 ml of isopropanol. The collected (suction filtration) red–orange solid weighed 0.86 g (98%) after drying at 40°C for 48 h.

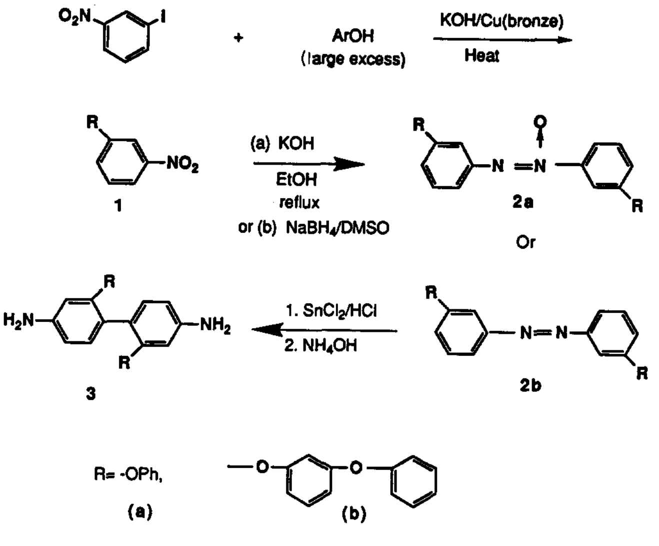
RESULTS AND DISCUSSION

As mentioned in the Introduction, the pivotal component of the '*in situ* rod molecular composites' concept rests with a flexible aromatic polyisoimide which must be relatively soluble in a aprotic solvent. Unfortunately, the aromatic polyisoimides derived from PMDA and common aromatic *para*-diamines such as *p*-phenylenediamine and 2,3,5,6-tetramethyl-1,4-phenylenediamine showed poor solubility. A possible solution to this problem was the addition of solubilizing pendent groups to the aromatic backbone. Indeed, this approach has successfully promoted the solubility of coil-like aromatic polyimides from aprotic DMAC to hydrocarbon[12] and chlorohydrocarbon solvents[13].

To test the applicability of the above backbone modification, a series of high molecular weight polyisoimides with pendent groups (which could later be converted to all-*para* rigid-rod polyimides) were synthesized. The general structures of the polyisoimides are shown below:







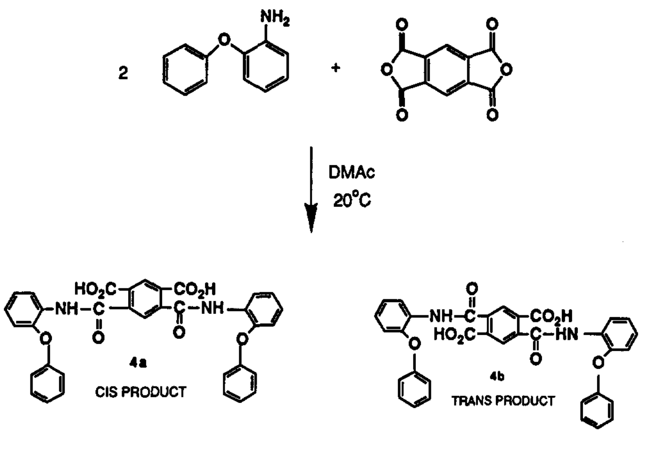
Scheme 1 Synthetic route to 2,2′-diaryloxy benzidine monomers

In addition to the above systems another polyisoimide was synthesized using the commercially available, highly pure diamine, 3,3′,5,5′-tetramethylbenzidine (TMB). This structure offered the opportunity to see what effect four pendent methyl groups per repeat unit would have on the solubility of the polymer.

Monomer synthesis

Conceptually, structural modification of polyisoimides and polyimides can be proceeded with from either of the comonomers, namely, the diamines or dianhydrides or both the monomers. The diamine rather than the anhydride was chosen primarily because of readily available starting materials. In an initial study, two 2,2′-disubstituted benzidine monomers were synthesized. It was hoped that the 2,2′-substitution would minimize any steric problems which might retard or inhibit polymerization of the co-monomers. The synthesis of these monomers was accomplished as outlined in *Scheme 1*. Ullmann ether reaction between 3-iodonitrobenzene and phenolate (or 3-phenoxyphenolate) afforded 3-phenoxy nitrobenzene (1a) (or 3-(3-phenoxyphenoxy) nitrobenzene (1b)). Treatment of (1a) with refluxing ethanolic potassium hydroxide led to the isolation of the corresponding azoxy compound (2a) in 65% yield. However, when (1b) was subjected to similar reaction conditions, only a low yield (16%) of the desired azoxy compound was obtained. But, when it was treated with sodium borohydride in dimethyl sulphoxide (DMSO)[14], an excellent yield (98%) of 3,3′-di-3-phenoxyphenoxy-azobenzene (2b) resulted. Both the azoxy and azo compounds underwent benzidine rearrangement reaction to form the respective 2,2′-diaryloxybenzidines, (3a) and (3b). As expected, (3b) was considerably more soluble in common organic solvents than (3a).

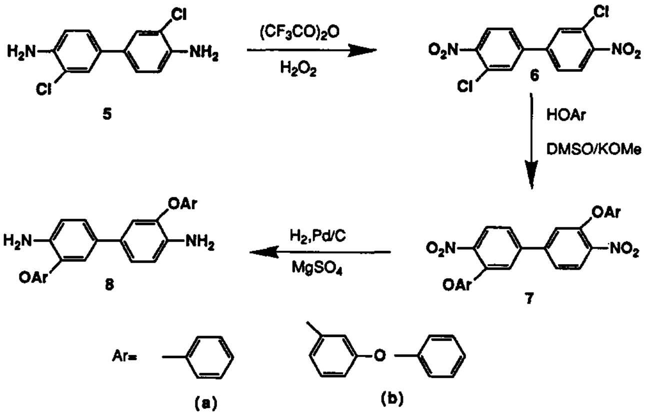
Unfortunately, several attempts to polymerize (3b) with PMDA failed to produce polymer of any significant molecular weight. This problem was most likely caused by the tenacious isomeric impurities produced during the benzidine rearrangement[15] step in the monomer synthesis. As a result, we turned to explore the possibility of polymerizing a 3,3′-disubstituted benzidine, which was selected on the basis of its synthetic chemistry to allow better control of diamine purity. However, the steric effect of the *ortho* substituents on the polymer-forming reaction needed to be addressed. Therefore, a model reaction involving PMDA and 2-phenoxyaniline was performed:



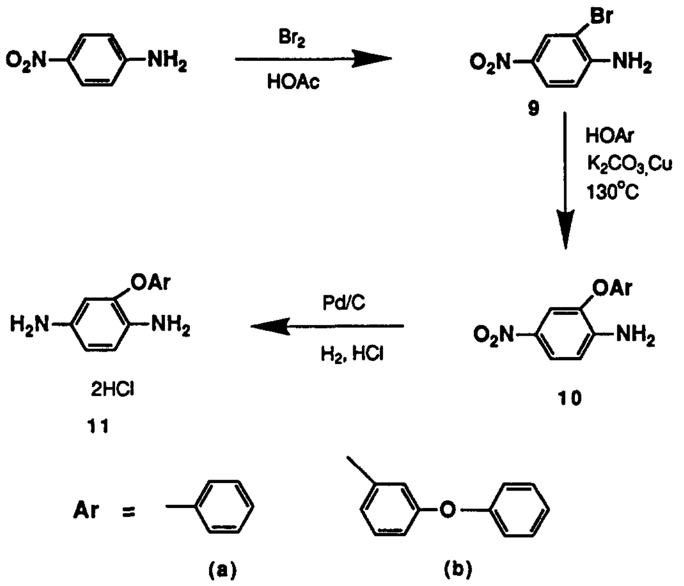
A mixture of *cis* and *trans* diamic acids, (4a) and (4b), was obtained in quantitative yield, and their identities confirmed by spectroscopic as well as elemental analysis data (the isomers were shown by high performance liquid chromatography to be present in almost equal amounts). Attempts to convert the mixture of (4a) and (4b) to bis(isoimides) by treating them with *N*,*N*′-dicyclohexyl dicarbodiimide (DCC) were unsuccessful owing to their poor solubility in dimethylacetamide (DMAC) and other aprotic solvents.

The approach used to synthesize the 3,3′-diaryloxy benzidines, (8a) and (8b), comprised the following three steps: (1) oxidation of a 3,3′-dichloro-benzidine to a *para*-dinitrobiphenyl intermediate, (5); (2) displacement of the chloride with aryloxy nucleophiles; and (3) catalytic reduction of the corresponding diaryloxy-dinitro-biphenyl, (7), to the desired diaryloxy-benzidine, (8) (see *Scheme 2*).

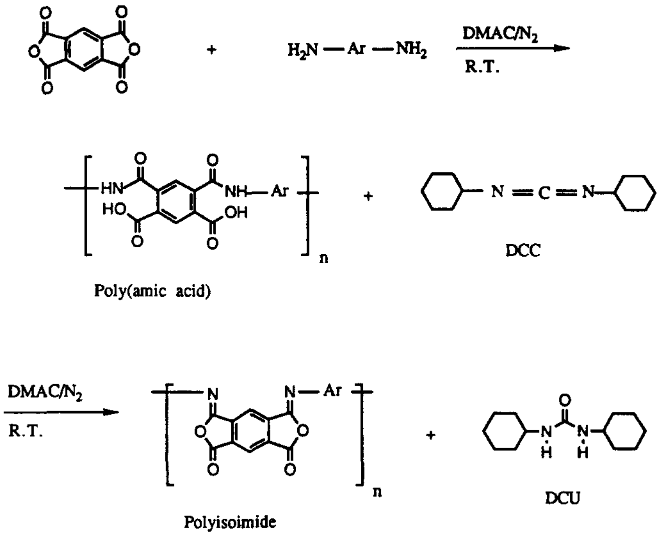
The procedure developed for the synthesis of 2-aryloxy-1,4-phenylenediamines, (11a) and (11b), is similar to that of the 3,3′-diaryloxy-benzidine, (8a) and (8b). Starting with 4-nitroaniline, the phenyl ring is brominated in the *ortho* position (some dibromo product is also formed), followed by aromatic nucleophilic displacement of the bromide, (9), with the desired aryloxy group. In the final step, the aryloxy-nitroaniline (10) is catalytically



Scheme 2 Synthetic route to 3,3′-diaryloxy benzidine monomers



Scheme 3 Synthetic route to 2-aryloxy-1,4-phenylenediamines



Scheme 4 Synthesis of aromatic polyisoimides

Table 1 Inherent viscosities for polymers[a]

Diamine[b]	Poly(amic acid)	Polyisoimide	Polyimide
TMB	1.11	1.89	[c]
(7a)	0.97	[d]	[c]
(7b)	0.85	0.93	[e]
(10a)	[f]	0.33	[e]
(10b)	[f]	0.25	[e]

[a] Inherent viscosity was measured at 30°C in DMAC at 0.50 g dl^{-1}

[b] Diamines: TMB, 3,3′,5,5′-tetramethyl benzidine; (7a), 3,3′-diphenoxy benzidine; (7b), 3,3′-diphenoxy-di(3-phenoxyphenoxy) benzidine; (10a), 2-phenoxy-1,4-phenylenediamine; (10b), 2-(3-phenoxyphenoxy)-1,4-phenylene-diamine

[c] Insoluble in aprotic solvents

[d] Very slightly soluble in aprotic solvents

[e] Not synthesized

[f] Not isolated

reduced, followed by acidic treatment to generate the hydrochloride salt of the amine, (11). The synthetic sequence is depicted in *Scheme 3*.

(11a) and (11b) were fairly stable but elemental analysis results (see Experimental section) seemed to indicate hydration had occurred. Attempts to dehydrate the diamines by drying at elevated temperatures (>80°C) under high vacuum over phosphorus pentoxide only resulted in decomposition. The loss of HCl along with water probably occurred. All attempts to isolate the free amines in high purity failed. The free diamines were found to be extremely susceptible to air oxidation.

Polymers

A procedure similar to that reported by Sroog[16] was used to synthesize the poly(amic acids). Polymerizations of the diamines with PMDA were carried out in DMAC (10 wt%) at room temperature in a dry nitrogen atmosphere. When hydrochloride salts of the diamines were used, lithium carbonate was added to liberate the free amines and generate lithium chloride which, in turn, enhanced the solubility of poly(amic acids) in aprotic solvents. Small aliquots of the poly(amic acids) solutions, in the case of the benzidine-based monomers, were withdrawn from the reaction mixtures and their inherent viscosities (η_{inh}) determined. After the mixture was stirred overnight, it was diluted with an additional amount of DMAC so that a poly(amic acid) concentration of approximately 2 wt% was attained. Subsequent cyclodehydration of the poly(amic acid) to the corresponding polyisoimide was effected by the addition of DCC (see *Scheme 4*). Upon addition of the DCC, the colour of the polymer solution changed from a pale yellow to bright orange and, after stirring for 1 h, to deep red, with the concomitant precipitation of *N,N′*-dicyclohexylurea (DCU). The polymers were isolated by precipitation in anhydrous isopropanol, which aided the removal of DCU. The precipitated material was collected on a coarse fritted funnel, great care being taken to keep the material covered with fresh anhydrous isopropanol at all times. The polyisoimides are sensitive to any water present during isolation and will revert to the poly(amic acid) if anhydrous conditions are not maintained. The precipitate was next washed several more times with fresh anhydrous isopropanol to remove any residual DCU and DMAC and finally with anhydrous benzene to remove the isopropanol. The resulting benzene/polyisoimide slurry was freeze-dried for about 72 h. The final material was a bright red–orange, light, spongy cake.

The polyisoimides prepared in this fashion exhibited varying degrees of solubility in aprotic solvents. The phenoxy pendent system showed the lowest solubility (only very dilute solutions could be made) and the tetramethyl pendent system the highest (up to 4% by polymer weight in DMAC). Inherent viscosities of the polyisoimides were measured in DMAC and span the range 0.25–1.89 dl g^{-1} (*Table 1*).

Films of the polyisoimides were cast from anhydrous DMAC at 55°C under reduced pressure (0.1 mm Hg ($\approx$10 Pa)). Casting the films under dry conditions using freshly freeze-dried material was found to be important because of the metastable nature of the polyisoimide systems. In all cases, thermally treated films were found to be insoluble in all common organic solvents tested. In an effort to substantiate that the insolubility did not arise from the annealing effect, polyisoimides were isomerized to polyimides at ambient conditions using sodium acetate[17] as a catalyst. We have also found that triethylamine alone can catalyse the isomerization. Thus, after a polyisoimide (TMB/PMDA) film had been immersed in a dry acetone solution containing a catalytic amount of triethylamine for ≈20 h, its colour changed from red to yellow. Complete isoimide–imide conversion was confirmed by i.r. analysis. The polyimides made in this manner were also insoluble.

Thermal isomerization by FT*i.r. analysis*

Fourier transform infrared (*FT*i.r.) spectra of cast films and KBr pellets of the poly(amic acids), polyisoimides and polyimides were consistent with their proposed structures. The TMB/PMDA system was studied in more detail. It was chosen primarily because of its good solubility and the easy access to its monomers in high purity. All the spectra referred to in the following discussion are associated with this system. The thermal isomerization of the isoimide function to imide moiety was evaluated as follows. A freshly prepared polyisoimide film was placed in a heatable sodium chloride cell and a baseline *FT*i.r. spectrum run at 25°C (*Figure 1a*). Significant bands in this spectrum are attributable to the isoimide carbonyl stretch (strong band at 1810 cm^{-1}) and vibration of the lactone ring with an exocyclic double bond (strong band at 920 cm^{-1}). After heating at 100°C for 1 h, the spectrum shown in *Figure 1b* was recorded. Examination of the spectrum indicates that the carbonyl band (1810 cm^{-1}) and lactone ring band (920 cm^{-1}) are greatly reduced in intensity. After heating for an additional 2 h at 215°C the spectrum shown in *Figure 1c* was recorded. Present in the spectrum are the bands which are characteristic of an imide (1790, 1720, 1380 and 730 cm^{-1}). The bands associated with an isoimide structure have completely receded. Thermally and chemically isomerized polyisoimide *FT*i.r. spectra were essentially identical, with only the band strengths varying slightly (probably due to slight differences in the rate and degree of isomerization).

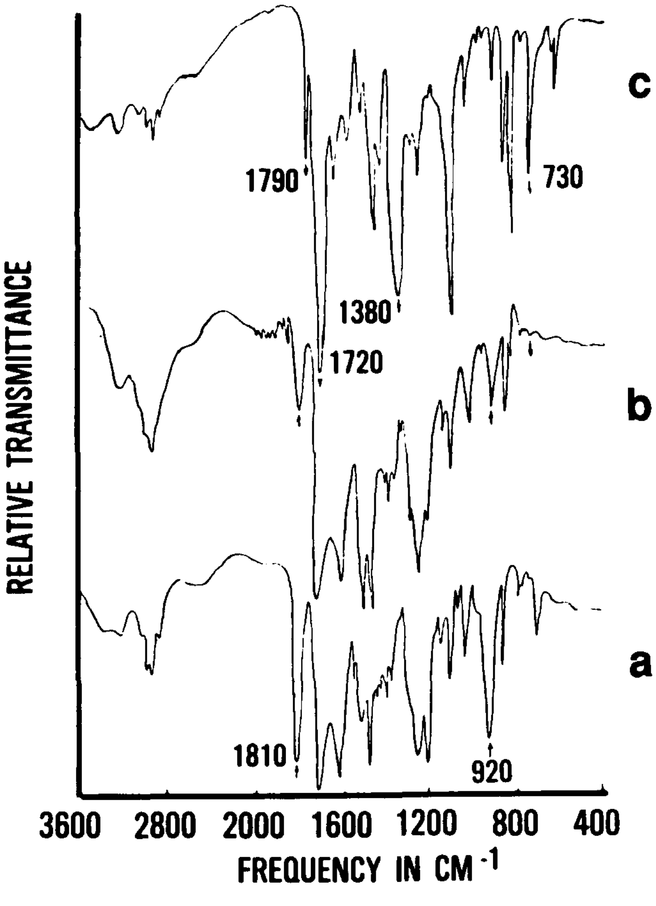


Figure 1 *FT*i.r. study of thermal isoimide–imide conversion: (a) polyisoimide film at 25°C; (b) after heating at 100°C for 1 h; (c) after heating at 215°C for 2 h

Composite films

The preparation of composite films and fibres was very important in achieving one of the primary objectives of this research: the development of a model polymer system which can be used to test the *in situ* generation of rigid-rod polymers for the fabrication of molecular composites. Composite films were produced with the polyisoimide derived from PMDA and TMB in the same manner as described for the pure films. Three commercial matrix systems were briefly investigated: a polyarylsulphone (Radel), a polysulphone (Udel), and an acetylene terminated isoimide thermosetting resin (IP-600). Films of the matrix and polyisoimide were cast from DMAC. Slightly cloudy films, indicating some phase separation, resulted with both the Radel and Udel systems. Composite films cast with IP-600, however, were completely clear and showed no signs of phase separation. The structural similarity of the IP-600 resin and the polyisoimide may account for the greater homogeneity of the system.

CONCLUSION

We have synthesized high molecular weight polyisoimides (rigid-rod precursors) which are soluble in aprotic solvents. Facile thermal isomerization of the TMB/PMDA-based polyisoimide to the corresponding polyimide has been demonstrated by *FT*i.r. analysis. Composite films using the TMB/PMDA polyisoimide system have been prepared using commercially available thermoset or thermoplastic resins. In one case, with IP-600, completely clear films, with no visually detectable phase separation, were cast. Property assessment of these films before and after thermal treatment is currently underway.

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