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Organo-soluble polyimides: synthesis and polymerization of 2,2'-disubstituted-4,4',5,5'-biphenyltetracarboxylic dianhydrides*

Frank W. Harris†, Sheng-Hsien Lin, Fuming Li and Stephen Z. D. Cheng
The Maurice Morton Institute of Polymer Science, The University of Akron, Akron, OH 44325-3909, USA
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The objective of this research was to investigate the effects of introducing pendant groups in the 2- and 2'-positions of 4,4',5,5'-biphenyltetracarboxylic dianhydrides on the properties of polyimides produced from the dianhydrides. Thus, the work was begun with the syntheses of 2,2'-dibromo-4,4',5,5'-biphenyltetracarboxylic dianhydride (DBBPDA) and 2,2'-diphenyl-4,4',5,5'-biphenyltetracarboxylic dianhydride (DPBPDA). The two new dianhydrides were polymerized with several substituted 4,4'-diaminobiphenyls including 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (PFMB) in refluxing *m*-cresol containing isoquinoline to afford two new series of soluble polyimides. The polyimides had intrinsic viscosities that ranged from 1.80 to 5.58 dl g^{-1} (*N*-methyl-2-pyrrolidinone or *m*-cresol at 30°C). Their glass transition temperatures (T_gs) ranged from 322 to 351°C (thermal mechanical analysis). Several of the polymers obtained from the new dianhydrides were soluble in acetone and tetrahydrofuran. The polymers formed water-white, tough films that were transparent above 350 nm. The films displayed negative birefringence, i.e. their in-plane refractive indices ($n_{\parallel}$) were higher than their out-of-plane refractive indices ($n_{\perp}$). For example, the DBBPDA/PFMB polymer, which was soluble in acetone and had a T_g of 330°C, formed films with $n_{\parallel} = 1.637$ and $n_{\perp} = 1.564$. The films had coefficients of thermal expansion that ranged from 1.05×10^{-5} to 2.12×10^{-5}°C^{-1}. The films may be useful as retardation layers in liquid crystal displays. Copyright © 1996 Elsevier Science Ltd.

(Keywords: soluble aromatic polyimides; substituted dianhydrides; polyimide films)

INTRODUCTION

Aromatic poly(pyromellitimides) are known for their excellent mechanical and electrical properties and their outstanding thermal stability[1,2]. They also display high softening temperatures and excellent chemical resistance. This combination of properties, however, makes them essentially impossible to fabricate. Thus, they must be processed in the form of their soluble poly(amic acid) (PAA) precursors, which are subsequently imidized in place. However, there are several drawbacks to this approach[3]. For example, water released during imidization at elevated temperatures creates strength-weakening voids in thick parts. Even in the case of thin films, the thermal imidization process must be carefully controlled in order to minimize depolymerization and maximize the degree of imidization[4]. Thus, there has been considerable research carried out aimed at the development of aromatic polyimides that can be melted and/or solution processed in the imide form[5]. Most of the structural modifications that have been used to attain processability have involved an increase in chain flexibility. Although this work has led to new commercial polyimides, the high-temperature performance associated with the rigid parent polymers has been compromised[6,7].

The overall goal of this ongoing research is to modify the structure of aromatic polyimides to attain solubility in common organic solvents without substantially decreasing the rigidity of their backbones. For example, a series of *para*-catenated, rigid-rod polyimides has been prepared from 3,6-diphenylpyromellitic dianhydride and 2,2'-disubstituted-4,4'-diaminobiphenyls that are soluble in phenolic solvents[8]. The rigid diamines have also been polymerized with commercial dianhydrides to produce polymers that are soluble in polar aprotic solvents[9,10]. The steric repulsion of the substituents in the 2- and 2'-positions of the biphenyl moieties twist the rings dramatically out of plane. The resulting twisted conformation inhibits chain packing and crystallization. The severe twist also breaks up the conjugation along the backbone and reduces colour.

The objective of this research was to investigate the effect of introducing twisted biphenyl structures in polyimide backbones through the synthesis and polymerization of appropriately substituted dianhydrides. It was postulated that polymers obtained from these substituted dianhydrides would be soluble in common organic solvents and would form optically clear films that would be transparent in the visible light region. Thus, two new dianhydrides, 2,2'-dibromo-4,4',5,5'-biphenyltetracarboxylic dianhydride (DBBPDA) and

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† To whom correspondence should be addressed

2,2′-diphenyl-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DPBPDA), were to be synthesized and polymerized with 2,2′-disubstituted-4,4′-diaminobiphenyls in refluxing *m*-cresol containing isoquinoline. The polyimides obtained were to be thoroughly characterized. In particular, the effects of introducing additional pendant groups at the 2- and 2′-positions of the biphenyl dianhydride on the solubility of the polymers and on the linear optical properties of the polymer films were to be examined.

EXPERIMENTAL

Instrumentation

Proton and carbon nuclear magnetic resonance (^{1}H and ^{13}C n.m.r.) spectra were measured at 200 and 50 MHz on a Varian Gemini-200 spectrometer. I.r. spectra were obtained with a Beckman FT-2100 Fourier transform spectrophotometer or with a Mattson Galaxy Series FTIR 5000 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Intrinsic viscosities were determined with Cannon-Ubbelohde No. 100 and 200 viscometers. Flow times were recorded for *N*-methyl-2-pyrrolidinone (NMP) or *m*-cresol solutions with polymer concentrations of approximately 0.50 g dl^{-1} to 0.25 g dl^{-1} at 30.0 ± 0.1°C. Thermogravimetric analyses (t.g.a.) were obtained in nitrogen and air with a TA Hi-Res TGA 2950 thermogravimetric analyzer using a heating rate of 10°C min^{-1}. The polyimide samples prepared for t.g.a. measurements were heated at 300°C for 20 min and cooled to 30°C before the measurements. Glass transition temperature (T_gs) and coefficients of thermal expansion (CTEs) of polyimide films were determined with thermal mechanical analysis (t.m.a.) using a TA TMA 2940 thermomechanical analyzer with a tension mode. Polyimide films with thicknesses between 10 and 30 μm were heated to 300°C under nitrogen at 1.0 MPa and held at this temperature for 20 min. After cooling to 30°C, the films were subjected to five different stresses with a heating rate of 10°C min^{-1}. The T_g was taken as the temperature at which a change in slope of a plot of film dimensional change *versus* temperature occurred. The T_gs obtained at each stress level were then extrapolated to zero stress. The CTE value was taken as the mean of the dimensional change between 50 and 150°C. The CTEs obtained at each stress level were then extrapolated to zero stress. Transmission u.v.-visible spectra were measured with a Perkin-Elmer Lambda 4B spectrometer in the transmittance mode. Refractive indices were measured using an optical waveguide method (Metricon) at 25°C with a wavelength of 632 nm.

Monomer syntheses

*2,2′-Dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride (**4**).* 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) (20.00 g, 67.98 mmol) was dissolved in a solution of 10.88 g (0.2720 mol) of sodium hydroxide in 150 ml of water in a three-neck, 500 ml, round-bottom flask fitted with a magnetic stirring bar, a condenser, and an addition funnel. Bromination was carried out in five steps. In the first step, 1.50 ml of bromine was slowly added to the solution at 50°C. After the addition was completed, the solution was heated at 90°C until most of the bromine had reacted. The mixture was then cooled to room temperature and neutralized with an aqueous sodium hydroxide solution to pH 7.0. For the second, third, and fourth steps, 2.00 ml of bromine was used, and the solution treated as in the first step. In the fifth step, 2.50 ml of bromine was added at 50°C. The solution was then heated at 90°C overnight. After the mixture was cooled to room temperature, the white precipitate that formed was collected by filtration, suspended in water, and acidified with conc. hydrochloric acid to pH 2.0. The white powder was collected by filtration and dried overnight at 200°C under reduced pressure. The material was then sublimed at 240°C under reduced pressure and recrystallized from a mixture of toluene and dioxane to afford 6.08 g (20%) of a white powder: mp 249–251°C; i.r. (KBr) 1841, 1779 (anhydride), 597 cm^{-1} (C-Br); ^{1}H n.m.r. (DMSO-d_6): δ 8.15 (*s*, 2H, aromatic), 8.64 (*s*, 2H, aromatic); ^{13}C n.m.r. (DMSO-d_6): δ 127.6, 129.9, 131.0, 131.3, 133.5, 147.1, 161.9, 162.6. Anal. Calcd for $C_{16}H_4Br_2O_6$: C, 42.51%; H, 0.89%; Found: C, 42.04%; H, 0.96%.

*Tetra(n-butyl) 2,2′-dibromo-4,4′,5,5′-biphenyltetracarboxylate (**5**).* A mixture of 13.83 g (30.60 mmol) of 2,2′-dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride, 80 ml of n-butanol, 70 ml of toluene, 1.5 ml of conc. H_2SO_4 in a one-neck, 300 ml, round-bottom flask fitted with a Dean–Stark trap was heated at reflux overnight. After the solution was cooled and washed with water, the solvents were removed under reduced pressure to give 21.70 g (99%) of a colourless viscous liquid. The crude product was used in the next reaction without purification: i.r. (neat) 1731 (C=O), 1285 cm^{-1} (C–O); ^{1}H n.m.r. ($CDCl_3$): δ 7.96 (*s*, 2H, aromatic), 7.56 (*s*, 2H, aromatic), 4.35–4.24 (*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 1.75–1.64 (*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 1.50–1.35 (*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 0.98–0.87 (*m*, 12H, -COO-CH_2-CH_2-CH_2-CH_3). Anal. Calcd for $C_{32}H_{40}Br_2O_8$: C, 53.94%; H, 5.66%; Found: C, 53.85%; H, 5.84%.

*Tetra(n-butyl) 2,2′-diphenyl-4,4′,5,5′-biphenyltetracarboxylate (**6**).* To a 100 ml, three-neck, round-bottom flask equipped with a nitrogen inlet tube, an addition funnel and a condenser were added 3.56 g (5.00 mmol) of the dibromotetraester **5**, 40 ml of toluene, 10 ml of 2 M sodium carbonate (0.02 mol), and 0.35 g (0.30 mmol) of $Pd(PPh_3)_4$ under nitrogen. After the mixture was vigorously stirred for 20 min under nitrogen, a solution of 1.82 g (15.0 mmol) of phenylboric acid in 8 mol of ethanol was added under nitrogen. The mixture was then heated at reflux for 24 h under nitrogen. After the mixture was cooled to room temperature, 2.5 ml of 30% hydrogen peroxide was carefully added, and the mixture was stirred for 1 h. The mixture was then filtered to remove insoluble materials. The organic layer of the filtrate was separated from the water layer and washed several times with water. The solvents were removed under reduced pressure to give 3.07 g (87%) of a brown viscous liquid: i.r. (neat) 1726 (C=O), 1288, 1242 cm^{-1} (C–O); ^{1}H n.m.r. ($CDCl_3$): δ 7.83 (*s*, 2H, aromatic), 7.46 (*s*, 2H, aromatic), 7.13 (*t*, 2H, aromatic), 7.00 (*t*, 4H, aromatic), 6.51 (*d*, 4H, aromatic), 4.36–4.26

(*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 1.76–1.66 (*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 1.48–1.34 (*m*, 8H, -COO-CH_2-CH_2-CH_2-CH_3), 0.99–0.89 (*m*, 12H, -COO-CH_2-CH_2-CH_2-CH_3). Anal. Calcd for $C_{44}H_{50}O_8$: C, 74.76%; H, 7.13%; Found: C, 74.52%; H, 7.22%.

*2,2′-Diphenyl-4,4′,5,5′-biphenyltetracarboxylic dianhydride (**8**).* To the brown liquid **6** dissolved in 45 ml of ethanol in a 100 ml flask was added 3.40 g of potassium hydroxide. The solution was heated at reflux for 3 h. The white pecipitate that formed was collected by filtration, dissolved in water and acidified with conc. hydrochloric acid to a pH of 1.0. The white precipitate was collected by filtration and dried at 200°C overnight and then sublimed at 270°C under reduced pressure to yield 1.74 g (90%) of light yellow powder. The product was recrystallized from a 1 : 1 (v/v) acetic acid/acetic anhydride mixture to give colourless crystals: mp 274–276°C; i.r. (KBr) 1842, 1780 cm^{-1} (anhydride); ^1H n.m.r. (DMSO): δ 8.34 (*s*, 2H, aromatic), 7.80 (*s*, 2H, aromatic), 7.24 (*t*, 2H, aromatic), 7.07 (*t*, 4H, aromatic), 6.54 (*d*, 4H, aromatic); ^{13}C n.m.r. (DMSO-d_6): δ 126.5, 128.3, 128.4, 129.1, 129.4, 130.4, 131.8, 137.4, 145.5, 148.4, 163.1. Anal. Calcd for $C_{28}H_{14}O_6$: C, 75.33%; H, 3.16%; Found: C, 74.88%; H, 3.40%.

*2,2′-Dichloro-4,4′-diaminobiphenyl (**9a**).* The compound was prepared from 3-chloro-1-nitrobenzene by the described procedure[11]: mp 164–166°C (Lit.[11] mp 165–166°C).

*2,2′-Dibromo-4,4′-diaminobiphenyl (**9b**).* The compound was prepared from 3-bromo-1-nitrobenzene by the described procedure[12]: mp 150–152°C (Lit.[13] mp 150–151.5°C).

*2,2′-Diiodo-4,4′-diaminobiphenyl (**9c**).* The compound was prepared from 1-iodo-3-nitrobenzene by the described procedure[36]: mp 170–171°C (Lit.[37] mp 169–170°C).

*2,2′-Bis(trifluoromethyl)-4,4′-diaminobiphenyl (**9d**).* The compound was prepared from 2-bromo-5-nitrobenzotrifluoride or 2-iodobenzotrifluoride by the described procedure[13,14]: mp 180–182°C (Lit.[13,14] mp 181–182°C).

*2,2′-Dimethyl-4,4′-diaminobiphenyl (**9e**).* The compound was prepared from 3-nitrotoluene by the described procedure[15]: mp 104–106°C (Lit.[15] mp 105–106°C).

*2,2′-Dichloro-6,6′-dimethyl-4,4′-diaminobiphenyl (**9g**).* The compound was prepared from 2-methyl-5-nitroaniline by the described procedure[16]: mp 166–168°C (Lit.[17] mp 167–168°C).

Polymer syntheses

The dianhydride (1.70 mmol) was added to a stirred solution of 1.70 mmol of the diamine in the appropriate amount of *m*-cresol containing five drops of isoquinoline under nitrogen at ambient temperature. After the solution was stirred for 3 h, it was heated to 200°C and maintained at that temperature for 3 h. During this time, the water of imidization was allowed to distil from the reaction mixture along with 1–2 ml of *m*-cresol. The *m*-cresol was continually replaced so as to keep the total volume of the solution constant. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of *m*-cresol and then slowly added to 1 l of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 h. The polymer was obtained in a 91–95% yield.

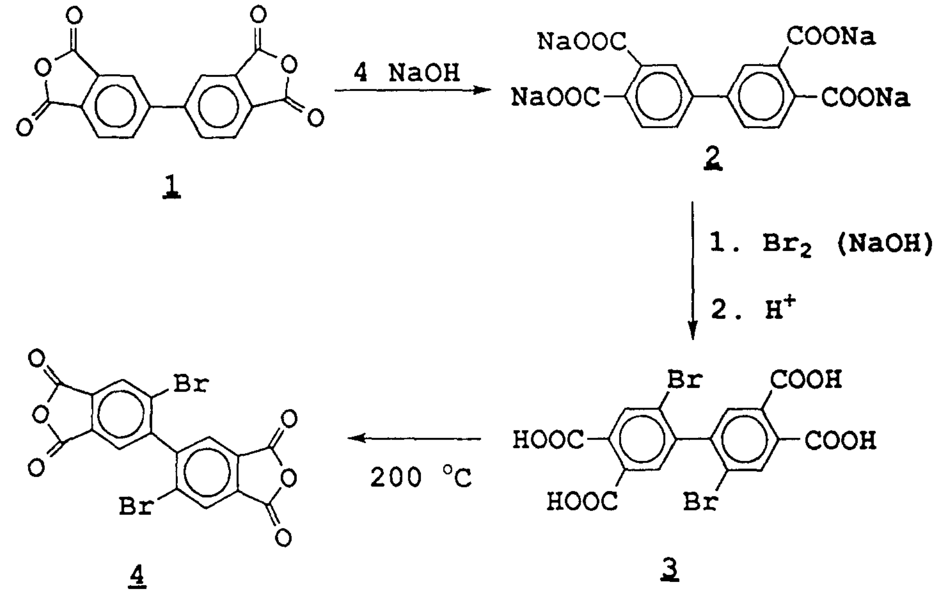
RESULTS AND DISCUSSION

Monomer syntheses[18]

2,2′-Dibromo-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DBBPDA). Several attempts to brominate BPDA (**1**) with silver sulfate/sulfuric acid/bromine, acetic acid/nitric acid/bromine, and acetic acid/sulfuric acid/potassium bromate mixtures[19] failed due to lack of reaction. This indicates that the electron-withdrawing anhydride groups are very effective in deactivating the aromatic rings towards electrophilic substitution reactions. Since the carboxylate ion is an electron donating group[20], the salts of aromatic carboxylic acids readily undergo bromination in water[21]. Thus, an attempt was made to brominate BPDA in the form of its tetracarboxylic salt (**2**) (*Scheme 1*). The dianhydride was converted to the sodium salt by stirring in aqueous sodium hydroxide at 50°C. Bromine was then added slowly. However, the hydrogen bromide (HBr) liberated during the bromination acidified the salt, which resulted in its precipitation. To overcome this problem, the bromination was carried out in five steps, where a sodium hydroxide solution was added to dissolve the precipitate after each bromine addition. The brominated salt was acidified and cyclodehydrated at 200°C to afford the dianhydride. The overall yield of pure monomer after sublimation at 240°C and recrystallization from a toluene/dioxane mixture was 20%.

In an attempt to simplify the bromination procedure, sodium bicarbonate was added to the neutral solution of the tetrasalt of BPDA prior to the bromination. The weak base had been used previously to neutralize the HBr liberated during the bromination of aniline[22]. This shortened the time required to obtain the product considerably. However, the dianhydride prepared by the procedure was considerably more difficult to purify.

2,2′-Diphenyl-4,4′,5,5′-biphenyltetracarboxylic dianhydride (DPBPDA). The synthetic route devised to DPBPDA (**8**) started with DBBPDA and involved the Suzuki cross-coupling reaction (*Scheme 2*)[23]. In order to obtain solubility in a suitable solvent for the coupling reaction, DBBPDA was first converted to the tetrabutyl ester **5** by treatment with *n*-butanol under acidic conditions. The cross-coupling reaction of the dibromotetraester **5** with phenylboric acid in the presence of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and sodium carbonate gave the diphenyltetraester **6** in 87% yield. Hydrolysis of the intermediate with potassium hydroxide in boiling ethanol and subsequent acidification with hydrochloric acid gave the biphenyltetracarboxylic acid **7**. The product was cyclodehydrated at 200°C under reduced pressure and sublimed at 270°C

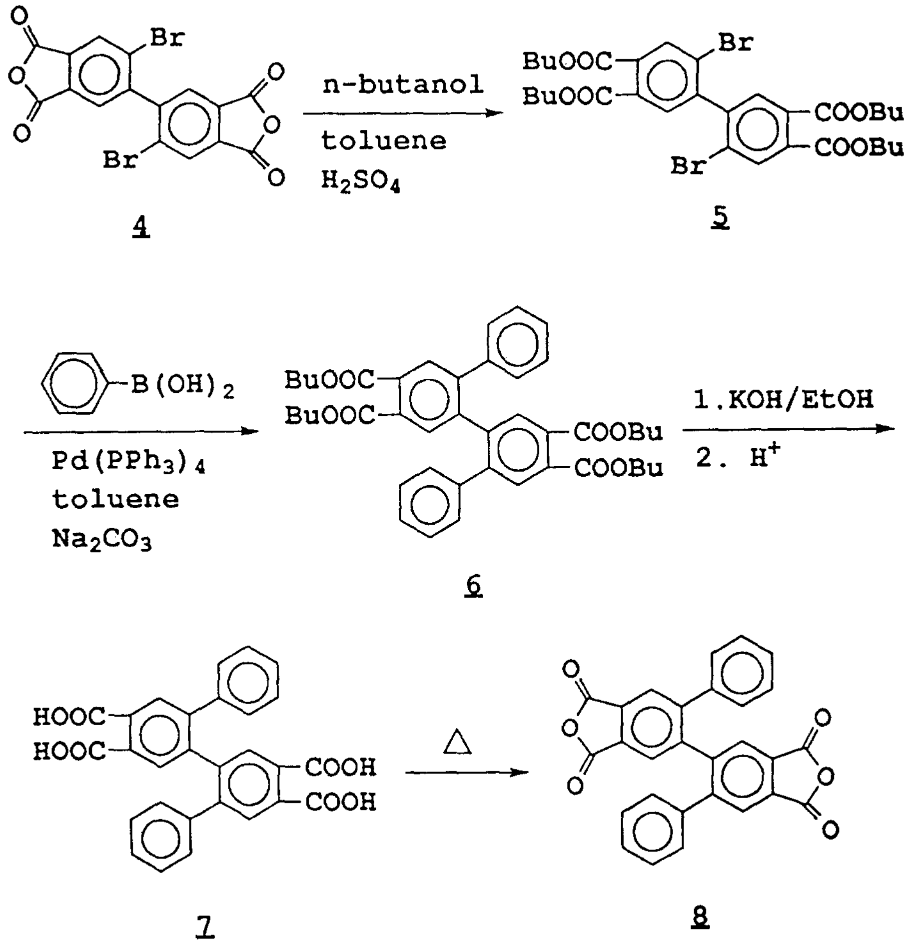


Scheme 1

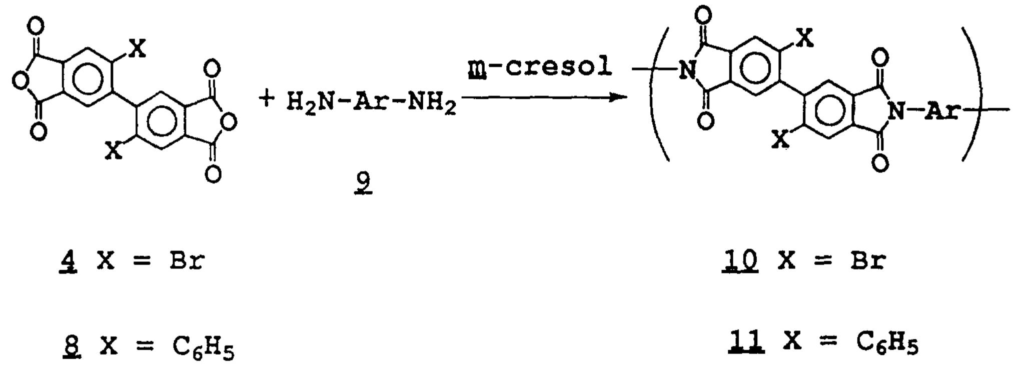
to give a 90% yield of a light yellow powder, which was recrystallized from an acetic acid/acetic anhydride mixture to give colourless crystals.

Polymer syntheses

DBBPDA and DPBPDA (**8**) were polymerized with several substituted 4,4′-diaminobiphenyls (**9**) in *m*-cresol containing a catalytic amount of isoquinoline (*Scheme 3*, *Tables 1* and *2*). The polymerizations were initially carried out at ambient temperature for 3 h. The resulting poly(amic acid) solutions were then heated at reflux for 3–6 h. During this time the water of imidization was allowed to distil from the reaction mixtures. The polyimide products, which remained in solution throughout the polymerization, were isolated by precipitation in ethanol.

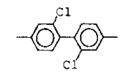
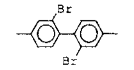
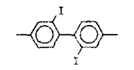
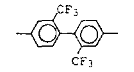
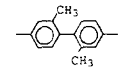
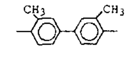
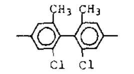
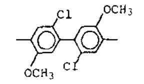


Scheme 2



Scheme 3

Table 1 Aromatic polyimides based on DBBPDA

PI	Diamine No.	Diamine -Ar-	$[\eta]^a$ (dl g^{-1})	T_g^b (°C)	CTE^c	T.g.a.^{d} (°C) N_2	T.g.a.^{d} (°C) Air
10a	**9a**		1.80	335	1.24	549	542
10b	**9b**		3.08	329	1.07	526	522
10c	**9c**		2.48	330	1.15	455	448
10d	**9d**		3.34	330	1.34	521	518
10e	**9e**		3.05	337	1.05	458	447
10f	**9f**		5.58^e	334	1.20	456	424
10g	**9g**		3.00	322	1.28	450	426
10h	**9h**		2.60	331	1.18	423	407

[a] Intrinsic viscosity determined in NMP at 30°C

[b] Temperature at which a change in slope occurred on a plot of film dimensional change vs temperature obtained by t.m.a. with a heating rate of 10°C min^{-1}. Films were subjected to initial stresses of 2.0–7.0 MPa and the results were extrapolated to zero stress

[c] The CTE ($\times 10^{-5}$°C^{-1}) values were determined as the mean between 50 and 150°C extrapolated to zero stress

[d] Temperature at which a 5% weight loss occurred when the polymers were subjected to t.g.a. with a heating rate of 10°C min^{-1}

[e] Intrinsic viscosity determined in *m*-cresol at 30°C

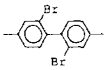
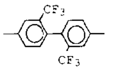
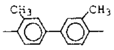
Polymer properties

The polyimides obtained from DBBPDA (**10**) had intrinsic viscosities that ranged from 1.80 to 5.58 dl g^{-1} in NMP and *m*-cresol at 30°C (*Table 1*). The polymers (**10a**,**b**,**d**) containing electron-withdrawing groups such as chlorine, bromine, and trifluoromethyl groups displayed good thermal and thermooxidative stabilities. Their thermogravimetric analysis (t.g.a.) thermograms showed 5% weight losses at 521–549°C in nitrogen and at 518–542°C in air. The polymers (**10e**–**h**) containing electron-donating groups such as methyl and methoxy groups were considerably less stable. Their t.g.a. thermograms showed 5% weight losses at 423–458°C in nitrogen and at 407–447°C in air.

The intrinsic viscosities of the polyimides based on DBBPDA (**11**) ranged from 1.81 to 2.38 dl g^{-1} in NMP at 30°C (*Table 2*). The polymers were slightly more thermally and thermooxidatively stable than the corresponding polymers based on DBBPDA. The TGA thermograms of polyimides **11b**,**d**,**f** showed 5% weight losses at 530–542°C in nitrogen and at 475–553°C in air.

The solubility behaviour of the polyimides based on DBBPDA is summarized in *Table 3*. The polymer (**10d**) obtained from 2,2′-bis(trifluoromethyl)-4,4′-diaminobiphenyl (PFMB), which was the most soluble polymer, was soluble in acetone, THF, DMF, DMSO, DMAc and NMP. Polymers **10a b**,**c**,**e**,**g**,**h** were soluble in THF, DMF, DMSO, DMAc and NMP. Polymer **50f** was soluble in DMSO, DMAc and NMP. The solubility behaviour of polyimides based on DPBPDA (**11b**,**d**,**f**) is summarized in *Table 4*. Polymers **11b**,**d** were soluble in THF, DMF, DMSO, DMAc and NMP. Polymer **11f** was soluble in DMAc and NMP. Thus, the polymers based on DPBPDA were soluble in fewer solvents than the polymers based on DBBPDA. However,

Table 2 Aromatic polyimides based on DPBPDA

	Diamine					T.g.a.[d] (°C)	
PI	No.	–Ar–	$[\eta]^a$ (dl g^{-1})	$T_g{}^b$ (°C)	CTE[c]	N_2	Air
11b	**9b**		1.81	334	1.76	530	526
11d	**9d**		1.87	351	1.89	542	553
11f	**9f**		2.38	332	2.12	542	475

[a] Intrinsic viscosity determined in NMP at 30°C
[b] Temperature at which a change in slope occurred on a plot of film dimensional change vs temperature obtained by t.m.a. with a heating rate of 10°C min^{-1}. Films were subjected to initial stresses of 2.0–7.0 MPa and the results were extrapolated to zero stress
[c] The CTE ($\times 10^{-5}$°C^{-1}) values were determined as the mean between 50 and 150°C extrapolated to zero stress
[d] Temperature (°C) at which a 5% weight loss occurred when the polymers were subjected to t.g.a. with a heating rate of 10°C min^{-1}

Table 3 Solubility of polyimides based on DBBPDA

Polymer	Acetone	THF	DMF	DMSO	DMAc	NMP
10a	–[a]	+[b]	+	+	+	+
10b	–	+	+	+	+	+
10c	–	+	+	+	+	+
10d	+	+	+	+	+	+
10e	–	+	+	+	+	+
10f	–	–	–	+	+	+
10g	–	+	+	+	+	+
10h	–	+	+	+	+	+

[a] – Solubility less than 2–3 g l^{-1} at room temperature
[b] + Minimum solubility of 2–3 g l^{-1} at room temperature

Table 4 Solubility of polyimides based on DPBPDA

Polymer	Acetone	THF	DMF	DMSO	DMAc	NMP
11b	–[a]	+[b]	+	+	+	+
11d	–	+	+	+	+	+
11f	–	–	–	–	+	+

[a] – Solubility less than 2–3 g l^{-1} at room temperature
[b] + Minimum solubility of 2–3 g l^{-1} at room temperature

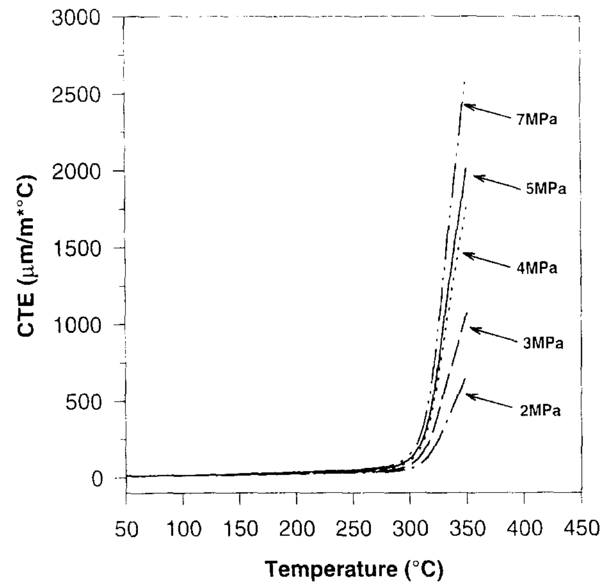


Figure 1 T.m.a. thermograms of polymer **10d** obtained in nitrogen with a heating rate of 10°C min^{-1} and applied stress of 2.0–7.0 MPa

the solubilities of the polyimides prepared from both the disubstituted dianhydrides were dramatically better than those of comparable polymers prepared from BPDA[9,10].

Relative to changes in structure in the diamine component, polymers based on 2,2′-dimethyl-4,4′-diaminobiphenyl (**10e**, **11e**) were soluble in THF, DMF, DMSO, DMAc and NMP, while polymers based on 3,3′-dimethyl-4,4′-diaminobiphenyl (**10f**, **11f**) were soluble in DMSO, DMAc and NMP. Thus, the effect of substitutents in the 2- and 2′-positions on solubility was greater than the effect of substitutents in the 3- and 3′-positions.

The T_gs and CTEs of the polyimides were obtained from t.m.a. measurements on 10–30 μm thick films. The films, which were cast from THF solutions, were annealed at 300°C under nitrogen at 1.0 MPa for 20 min to relieve any internal stress that was generated during their preparation. T.m.a. thermograms of polymer **10d**, which are typical of those obtained with a heating rate of 10°C min^{-1} and with different applied stress that ranged from 1.0 to 10.0 MPa, are shown in *Figure 1*. The T_g, which was taken as the extrapolated change in slope, and the CTE were dependent on the applied stress. A plot of T_g vs the magnitude of the applied stress (*Figure 2*) clearly shows that the T_g was linearly shifted to lower values as the applied stress increased. A linear extrapolation to zero applied stress gave a T_g of 330°C. The T_gs of the two series of polymers **10** and **11** are shown in *Tables 1* and *2*, respectively. The T_gs ranged from 322 to 337°C for the DBBPDA-based polyimides and from 332 to 351°C for the DPBPDA-based polyimides. Thus, the T_gs of the polyimides based on DPBPDA were higher than those of comparable polyimides based on DBBPDA.

The polyimides obtained from PFMB and DBBPDA (**10d**), and DPBPDA (**11d**) had T_gs of 330 and 351°C (TMA), respectively. These T_gs are much higher than that of the polyimide (290°C) prepared from BPDA and PFMB[24]. This is additional evidence that the introduction of bulky groups in the 2- and 2′-positions of BPDA hinders the rotation of the two phenyl rings and further increases the chain rigidity.

The CTEs were taken as the mean of the dimensional change between 50 and 150°C at each applied stress and extrapolated to zero stress. The CTE increased linearly as the magnitude of the applied stress increased

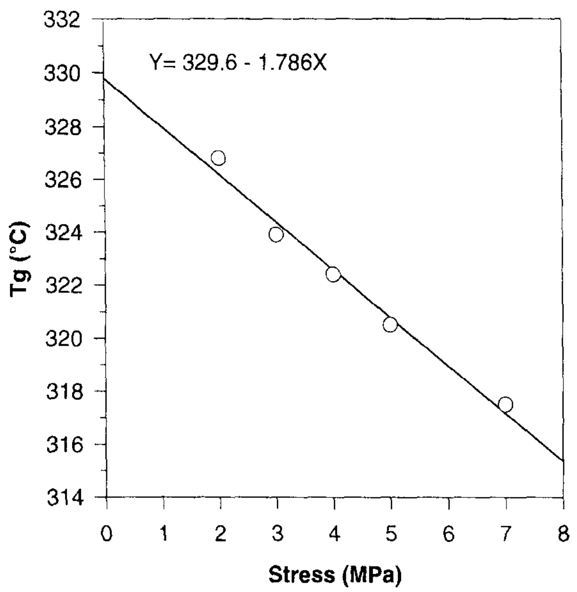


Figure 2 Dependence of the T_g of polymer **10d** on the applied stress

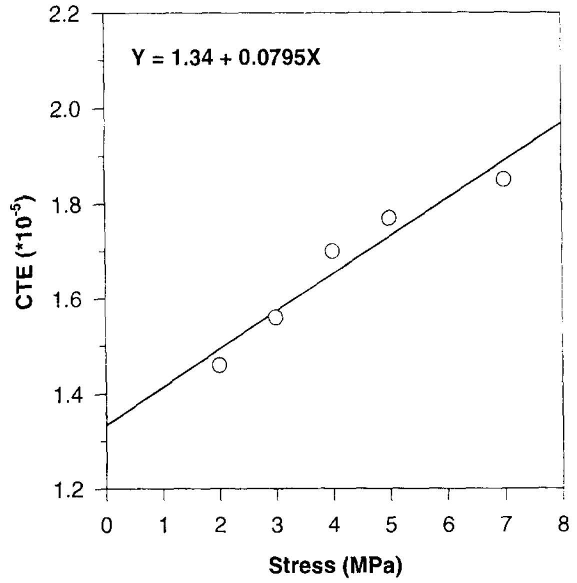


Figure 3 Dependence of the linear CTE of polymer **10d** on the applied stress

(*Figure 3*). The CTEs ranged from 1.05 to 1.28× 10^{-5}°C^{-1} for the DBBPDA series and from 1.76 to 2.12 × 10^{-5}°C^{-1} for the DPBPDA series (*Tables 1* and *2*). The CTEs of **10d** and **11d** were larger than that of the polyimide prepared from BPDA and PFMB (5.43× 10^{-6}°C^{-1})[24]. CTEs are associated with the rigidity and linearity of a polymer chain, which affect the chain packing. The twisted conformation in the substituted BPDAs disrupts the chain packing and increases the CTE. The fact that the CTE increased as the substituents at the 2- and 2′-positions of BPDA were changed from bromine to phenyl may be attributed to the increase in free volume. The incorporation of bulky groups along a polymer chain is known to inhibit close packing of polymer chains, thereby, increasing the free volume.

Most of the polymers could be cast into flexible, tough, transparent, colourless films from THF solutions at ambient temperature and atmospheric pressure. Polymers **10f** and **11f**, which were not soluble in THF, could be cast into similar films from DMAc solutions under reduced pressure at ambient temperature. The i.r. spectra of the films had characteristic polyimide absorption bands at 1780 (symmetrical stretch C=O), 1727 (asymmetrical stretch C=O), 1370 (C–N stretch), and 742 (C=O bending) cm^{-1} [25,26]. Films that were 5 μm thick began to transmit u.v. light in the range 328–345 nm. The films transmitted 80% of light above 416–448 nm (*Table 5*).

Table 5 U.v.-transmittance of films of polyimides based on DBBPDA and DPBPDA

	Transparency onset (nm)		80% transmission (nm)	
	Dianhydride		Dianhydride	
Diamine	DBBPDA	DPBPDA	DBBPDA	DPBPDA
9a	336	—	462	—
9b	325	341	429	448
9c	338	—	431	—
9d	341	329	403	416
9e	328	—	424	—
9f	341	344	417	443
9g	322	—	423	—
9h	345	—	417	—

The excellent transparency of the films can be attributed to the twisted conformations of the 2,2′-disubstituted BPDA moiety and the 2,2′-disubstituted, 3,3′-disubstituted, or 2,2′,6,6′-tetrasubstituted biphenyl diamine moieties. These conformations effectively interrupt the conjugation along the backbone and, therefore, dramatically reduce the chromophore length. For example, Beavan and Hall reported that 2,2′-difluorobiphenyl exhibited a u.v. absorption at λ_{max} 234 nm, compared to a λ_{max} of 249 nm for unsubstituted biphenyl[27]. They attributed this blueshift to decreased conjugation caused by steric hindrance at the 2- and 2′-positions of biphenyl. The lack of absorption of visible radiation by aromatic polyamides containing 2,2′-disubstituted biphenyl units has been attributed to their noncoplanar conformations, which prevent extended conjugation along their backbones[13].

Intermolecular charge transfer complexes in polyimides has also been suggested by Dine-Hart and Wright to affect their colour and solubility[28]. Frank and coworkers studied the u.v. and visible light absorptivity of a series of model compounds and BTDA-based polyimides in dilute solution[29]. They found that the intensity of the major absorption band was dependent on the torsional angle between the phenyl ring of the diamine component (donor fragment) and the imide component (acceptor fragment). The absorption band was attributed to intramolecular charge transfer complexes. The absorption was significantly reduced by introducing substitutents in the *ortho*-position of the diamine, which increased the torsional angle, and by separating the donor and acceptor fragments with spacer groups. Thus, the charge transfer complex formation was maximized when the torsional angle approached 0° and minimized at 90°. As discussed earlier, the CTE measurements in this study indicate that the polymers' pendant substituents and twisted conformations hinder chain packing, which should hinder the formation of intermolecular charge transfer complexes. The twisted conformations should also disrupt the formation of

Table 6 Refractive indices and birefringences of films of polyimides based on DBBPDA and DPBPDA

PI	$n_{\parallel}$	$n_{\perp}$	Δn^a
10a	1.713	1.628	0.085
10b	1.723	1.635	0.088
10c	1.732	1.656	0.076
10d	1.637	1.564	0.074
10e	1.698	1.606	0.092
10f	1.696	1.614	0.082
10g	1.672	1.596	0.076
10h	1.675	1.603	0.072
11b	1.704	1.635	0.069
11d	1.633	1.575	0.059
11f	1.684	1.614	0.069

[a] Birefringence $\Delta n = n_{\parallel} - n_{\perp}$

intramolecular complexes. However, no quantitative correlation between charge transfer complex formation and u.v.- and visible transparency has been attempted.

The refractive indices and birefringences of films of polyimides **10a–h** and **11b,d,f** are shown in *Table 6*. The birefringence, Δn, was taken as the difference between the inplane ($n_{\parallel}$) and out-of-plane ($n_{\perp}$) refractive indices. The $n_{\parallel}$ and $n_{\perp}$ of DBBPDA-based polyimides ranged from 1.637 to 1.732, and from 1.564 to 1.656, respectively. The $n_{\parallel}$ and $n_{\perp}$ of DPBPDA-based polyimides ranged from 1.633 to 1.704, and from 1.574 to 1.635, respectively.

The refractive index is related to the ratio of the induced dipole moment to the molar volume and is known to decrease as the polarizability of the chemical bonds decreases[30]. The refractive indices of polyimides **10** increased in the order of **10d** < **10e** < **10a** < **10b** < **10c**. This result is consistent with an increase in polarizability due to the incorporation of more polarizable bonds.

The birefringencies of the films ranged from -0.070 to -0.096 for the DBBPDA-based polymers, and from -0.051 to -0.065 for the DPBPDA-based polymers. A large negative birefringence indicates that the polymer molecules are preferentially aligned parallel to the surface of the film. In 1972, Sosnowski and Weber showed that the solvent casting process can produce birefringent films[31]. They speculated that the anisotropy resulted from drying-induced stress. In contrast to the negative birefringence (-13.3×10^{-3}) of a polycarbonate film, which contained polarizable aromatic groups in the main chain, a polystyrene film had a positive birefringence (6.1×10^{-3})[32]. The positive birefringence was attributed to the optically anisotropic phenyl groups lying perpendicular to the polymeric backbone, which was aligned parallel to the film's surface. The birefringences of polystyrene films were found to be a function of film thickness, drying temperature, and the molecular weight of the polymer[32]. The thicker the film was, the smaller the positive birefringence was, i.e. the molecule was more highly oriented in thin films. Higher drying temperature resulted in a smaller positive birefringence due to the molecular relaxation occurring easier at higher drying temperatures. The positive birefringence was larger for the higher molecular weight samples.

The optical properties of thin films of a polyimide prepared from BPDA and PFMB and copolymers of BPDA and PMDA and PFMB were studied by Arnold *et al.*[33]. The in-plane refractive index of a film of the homopolymer was 1.634, while it was 1.690 for a film of a copolymer containing equal amounts of PMDA and BPDA units. On the other hand, the out-of plane refractive index was 1.540 for the homopolymer film and 1.523 for the copolymer film. Thus, the absolute value of birefringence was 0.073 higher for the film of the copolymer. This was attributed to an increase in chain linearity and rigidity due to the PMDA moieties that resulted in an increase in the alignment of the molecular axes parallel to the surface of the film.

The higher birefringence of the DBBPDA-based polyimide films as compared to those of the corresponding DPBPDA-based films may be attributed to differences in chain packing as well as their intrinsic polarizabilities. The CTE studies showed that DPBPDA-based polymers do not pack as well as the DBBPDA systems. Thus, their backbones cannot align as well with the film surface. This is consistent with the fact that the $n_{\parallel}$ of the DBBPDA-based polymers are higher than those of the DPBPDA-based systems, while their $n_{\perp}$ are lower than those of the DPBPDA polymers.

Even though the negative birefringence of the films of the polyimides produced in this study is lower than those of films of BPDA-based polyimides, the new polymers should be extremely useful as retardation films in twisted nematic liquid crystal displays[34,35]. The solubility of the new materials in solvents such as acetone and THF is a major advantage since it greatly facilitates their use in commercial film casting operations.

CONCLUSIONS

2,2′-Disubstituted-biphenyl dianhydrides can be prepared and polymerized with aromatic diamines to afford polyimides with intrinsic viscosities as high as 5.58 dl g^{-1}. The introduction of bromine and phenyl substituents in the 2- and 2′-positions of the dianhydride component in BPDA-based polyimides results in dramatic changes in their properties. The T_gs and CTEs of the polymers are significantly increased. Phenyl substituents increase the T_gs and CTEs more than bromine substituents. The substituents also afford a dramatic improvement in solubility. Polymers that are only soluble in phenolic solvents can be made soluble in acetone and THF by the incorporation of the substituents in these positions. The wavelength range over which thin films of the polymers transmit light is also increased. Films can be prepared that transmit light as low as 350 nm. The substituents decrease the in-plane orientation of the polymer chains in the films. The difference in the in-plane refractive index and the out-of-plane refractive index, i.e. the optical birefringence, of the films is not as large as that of films of non-substituted analogues. Phenyl substituents result in a larger reduction in birefringence than do bromine substituents.

The increase in T_g provided by the 2- and 2′-substituents can be attributed to increased chain rigidity. The increase in CTE and solubility and the decrease in optical birefringence can be attributed to hindered chain packing, while the increase in the light transmittance of thin films can be attributed to the disruption of conjugation along the backbone that results from the twisted biphenyl structure.

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REFERENCES

1 Sroog, C. E., Endrey, A. L., Abramo, S. V., Berr, C. E., Edwards, W. M. and Oliver, K. L. *J. Polym. Sci., Part A* 1965, **3**, 1373

2 Sroog, C. E. *J. Polym. Sci., Macromol. Rev.* 1976, **11**, 161

3 Harris, F. W. in 'Polyimides' (Eds D. Wilson, H. D. Stenzenberger and P. M. Hergenrother), Blackie and Son, New York, 1990, p. 1

4 Boise, A. I. *J. Appl. Polym. Sci.* 1986, **32**, 4043

5 Harris, F. W. and Lanier, L. H. in 'Structure–Solubility Relationships in Polymers' (Eds F. W. Harris and R. B. Seymour), Academic Press, New York, 1977, p. 183

6 Bateman, J. H., Geresey, Jr., W. and Neiditch, D. S. *ACS Coatings Plastics Preprints* 1975, **35** (2), 77

7 Serfaty, I. W. in 'Polyimides Synthesis, Characterization and Applications' (Ed. K. L. Mittal), Wiley, New York, 1984, p. 149

8 Harris, F. W. and Hsu, S. L.-C. *High Perf. Polym.* 1989, **1**, 3

9 Harris, F. W. *U.S. Patent* 5, 071, 997, 1991

10 Harris, F. W., Hsu, S. L.-C. and Tso, C. C. *ACS Polym. Preprints* 1990, **31** (1), 342

11 Bilbo, A. J. and Wyman, G. M. *J. Am. Chem. Soc.* 1953, **75**, 5312

12 Lindley, P. M. and Reinhardt, B. A. *J. Polym. Sci., Polym. Chem. Ed.* 1991, **29**, 1061

13 Rogers, H. G., Gaudiana, R. A., Hollinsed, W. C., Kalyanaraman, P. S., Manello, J. S., McGowan, C., Minns, R. A. and Sahatjian, R. *Macromolecules* 1985, **18**, 1058

14 Schiang, W. R. and Woo, E. P. *J. Polym. Sci., Polym. Chem. Ed.* 1993, **31**, 2081

15 Everitt, P. M., Loh, S. M. and Turner, E. E. *J. Chem. Soc.* 1960, 4587

16 Su, W. C. and Harris, F. W., in preparation

17 Slocum, D. W. and Mislow, K. J. *Org. Chem.* 1965, **30**, 2152

18 Harris, F. W. and Lin, S. L.-H. *U.S. Patent* 5, 395, 918, 1995

19 Derbyshire, D. H. and Waters, W. A. *J. Chem. Soc.* 1950, 573

20 Spryskov, A. A. and Golubkin, L. N. *J. Gen. Chem. USSR* 1961, **31**, 833

21 Spencer, C. A. *U.S. Patent* 2, 394, 368, 1946

22 Wade, Jr., L. G. 'Organic Chemistry', Prentice-Hall, New Jersey, 1987, p. 668

23 Miyaura, N., Yamada, K., Suginome, H. and Suzuki, A. *J. Am. Chem. Soc.* 1985, **107**, 972

24 Arnold, Jr., F. E., Cheng, S. Z. D., Hsu, L.-C., Lee, C. J. and Harris, F. W. *Polymer* 1992, **33** (24), 5179

25 Tsimpris, C. W. and Mayhan, K. G. *J. Polym. Sci., Polym. Phys. Ed.* 1973, **11**, 1151

26 Krasovskii, A. N., Antonov, N. P., Koton, M. M., Kalninsk, K. K. and Kudryavtsev, V. V. *Polym. Sci. USSR* 1980, **21**, 1038

27 Beavan, G. H. and Hall, D. M. *J. Chem. Soc.* 1956, 4637

28 Dine-Hart, R. S. and Wright, W. W. *Makromol. Chem.* 1971, **143**, 189

29 Salley, J. M., Miwa, T. and Frank, C. W. in 'Materials Science of High Temperature Polymers For Microelectronics' (Eds D. T. Grubb, I. Mita and D. Y. Yoon), Materials Research Society No. 227, Pennsylvania, 1991, p. 117

30 Groh, W. and Zimmermann, A. *Macromolecules* 1991, **24**, 6660

31 Sosnowski, T. P. and Weber, H. P. *Appl. Phys. Lett.* 1972, **21**, 310

32 Prest, W. M. and Luca, D. J. *J. Appl. Phys.* 1979, **50**, 6067

33 Arnold, Jr., F. E., Shen, D., Lee, C. J., Harris, F. W., Cheng, S. Z. D. and Lau, S. F. *J. Mater. Chem.* 1993, **3**, 353

34 Harris, F. W. and Cheng, S. Z. D. *U.S. Patent* 5, 344, 916, 1994

35 Harris, F. W. and Cheng, S. Z. D. *U.S. Patent* 5, 480, 964, 1996

36 Theilacker, W., Braune, P. and Strobel, G. G. *Chem. Ber.* 1964, **97**, 880

37 Lindley, P. M. and Reinhardt, B. A. *J. Polym. Sci., Polym. Chem. Edn* 1991, **29**, 1061