ELSEVIER

Polymer 40 (1999) 4279–4288

polymer

Highly soluble polyimides from sterically hindered diamines

Tina L. Grubb[a], Victoria L. Ulery[a], Tara J. Smith[a], Gordon L. Tullos[a], Havva Yagci[a], Lon J. Mathias[a,*], Michael Langsam[b]

[a]*University of Southern Mississippi, Hattiesburg, MS 39406-0076, USA*
[b]*Air Products and Chemical Company, 7201 Hamilton Boulevard, Allentown, PA 18195-1501, USA*

Received 1 July 1998; received in revised form 2 September 1998; accepted 10 September 1998

Abstract

Polyimides with enhanced solubility have been synthesized from various aromatic tetracarboxylic dianhydrides and sterically hindered diamines. Intrinsic viscosities in 1-methyl-2-pyrrolidinone (NMP) ranged from 0.28 to 1.05 dL/g. Most of the polyimides were soluble in common solvents such as N,N-dimethylacetamide, NMP, chloroform and tetrahydrofuran. Polyimides derived from thianthrene-2,3,7,8-tetracarboxylic dianhydride (TDAN) and diamino mesitylene (DAM) or diethyltoluene diamine (DETDA) were insoluble in all solvents indicating that polyimide solubility decreased as anhydride rigidity increased. Glass transition temperatures ranged from 252 to 398°C and above with the polymers showing little or no weight loss by TGA up to 400°C in both air and nitrogen. The glass transition temperatures of the polyimides increased 15 to 98°C (compared to unhindered polyimide analogs) when one or more methyl group was placed ortho to the imide nitrogen, hindering backbone rotation, chain packing and flexibility. Tough, transparent films of the soluble polyimides were cast from solution. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide; Steric hindrance; Glass transition temperature

---

1. Introduction

Aromatic polyimides are important commercial polymers possessing outstanding thermal behavior combined with excellent mechanical properties. However, commercial use of these materials is often limited due to low solubility and/or poor processability [1,2]. Those polyimides that are processable usually incorporate flexible linkage groups to enhance dissolution and thermal processing [3–6]. Such groups often reduce glass transition temperatures, compromising ultimate performance. One successful approach to increasing solubility and processibility without sacrificing polyimide thermal stability has been through the synthesis of alternating copolyimides [7]. Recent work has also shown that incorporation of pendant groups that inhibit close packing and/or reduce backbone rotation facilitate dissolution without sacrificing thermal properties. For example, some researchers have incorporated bulky aromatic pendant groups [8–10]. Eastmond and coworkers have also shown that placing bulky substituents ortho to the ether linkage on the phthalimide residue in poly(ether imide)s can hinder rotation about the ether linkage, raising the glass transition temperature and hindering chain packing [11].

Several new families of polyimides are described here containing strategically placed substituents to promote increased solubility while maintaining excellent thermal and mechanical properties. These polymers were synthesized from 2,4-diaminomesitylene (DAM), diethyltoluenediamine (DETDA) or 4,4′-methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) and bisphenol A dianhydride (BPADA), thianthrene-2,3,7,8-tetracarboxylic dianhydride (TDAN), 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PIMA), 3,3′4,4′-diphenylsulfone tetracarboxylic dianhydride (DSDA), 3,3′4,4′-biphenyltetracarboxylic dianhydride (BPDA), or 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA).

While DAM has been investigated in several polyimides [12–15], MCDEA and DETDA (also known as Lonzacure and Ethacure 100, respectively) have not been extensively investigated in polyimides. Their use has mainly been limited to the curing of epoxy systems, and as chain extenders and crosslinkers in polyurethane systems [16–21]. A recent patent application revealed the synthesis of polyimides from MCDEA and PMDA, BTDA and 6FDA;

---

[*] Corresponding author. Tel.: +1-601-266-4868; Fax: +1-601-266-5504.

PII: S0032-3861(98)00663-6

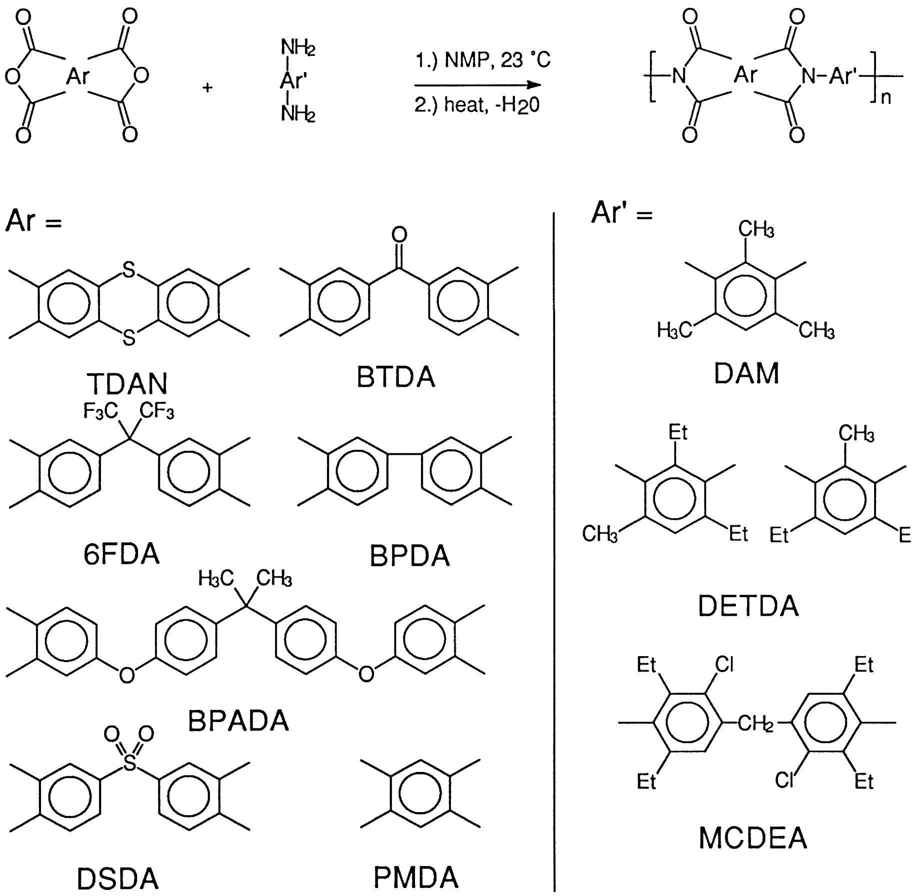


Fig. 1. Overall synthesis and structures of polyimides.

however, no T_g's were reported and polymer characterization was limited [22].

2. Experimental

All reagents were purchased from Aldrich Chemical Company unless specified otherwise. Bisphenol A dianhydride (BPADA) was donated by General Electric Company. 3,3′,4,4′-Biphenyltetracarboxylic dianhydride (BPDA) and pyromellitic dianhydride (PMDA) were purchased from CHRISKEV Company, Leawood, KS. 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 3,3′,4,4′-diphenylsulfonetetracarboxylic dianhydride (DSDA), 2,4-diaminomesitylene (DAM), and 1,5-naphthalene diamine (NAPDA) were donated by Air Products and Chemical Company. Diethyltoluenediamine (DETDA) was donated by Abermarle Corporation and was used as received. 1-Methyl-2-pyrrolidinone (NNP) was distilled from CaH_2 under reduced pressure. 2,4-Diaminomesitylene (DAM), and 1,5-naphthalene diamine (NAPDA) were sublimed under reduced pressure at 100°C and 160°C, respectively. 4,4′-Methylenebis(3-chloro-2,6-diethylaniline) (MCDEA) was recrystallized from ethanol. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was sublimed under reduced pressure at 250°C followed by recrystallization from acetic anhydride. BPADA, 6FDA, BPDA, DSDA and BTDA were all dried under vacuum at 120°C immediately before use. Thianthrene-2,3,7,8-tetracarboxylic dianhydride (TDAN) was synthesized as previously reported [23,24].

Solution ^1H and ^{13}C NMR spectra were obtained on a Bruker AC-300 instrument operating at frequencies of 300.133 MHz and 75.47 MHz, respectively, using standard acquisition parameters. Solid-state ^{13}C NMR spectra were acquired on a Bruker MSL-400 spectrometer operating at a frequency of 100.61 MHz using cross-polarization/magic angle spinning (CP/MAS) and high-power proton decoupling with sample spinning rates > 4.0 kHz. FTIR spectra were obtained on an ATI-Mattson Galaxy 5020 spectrometer on solution-cast thin films or KBr pellets. Molecular weight data were estimated by SEC relative to polystyrene standards with THF as solvent and using four AM gel, mixed-bed columns 7.5 mm i.d. × 300 mm, 10 mm particle diameters (American Polymer Standard Corporation). DSC and TGA analyses were conducted on TA Instruments 2920 and 2960 modules, respectively, controlled by a Thermal Analyst 2100. The differential scanning calorimetry results were obtained on the precipitated and vacuum dried polyimide powders.

2.1. Polyimide synthesis

Polyimides were prepared through a conventional two-step process (Fig. 1). For example, a round-bottom flask equipped with a mechanical stirrer and N$_2$ purge was charged with BTDA (5.02 g, 15.58 mmol), MCDEA (5.91 g, 15.58 mmol) and NMP (44 mL). The mixture was stirred for 24 h at 23°C. Xylenes (20 mL) were added and the reaction was heated to reflux for 10 h. A Dean-Stark trap was used to remove water from the reaction. The polymer was precipitated into methanol, filtered, washed with methanol, and dried under vacuum; yd 9.95 g, 96%; FTIR (film): 2974, 2937, 2879, 1780, 1714, 1684, 1456, 1367, 1296, 1246, 1190, 1105, 852, 752, 729, 648 cm^{-1}; ^{1}H NMR (CDCl$_3$): δ 8.35 (d) and 8.33 (s, 2H total), 8.20 (d, J = 8.1, 1H)), 6.99 (s, 1H), 4.33 (s, 1H), 2.42 (m, J = 7.0, 2H), 2.42 (m, J = 7.0, 2H), 1.10 (m, J = 7.3, 6H); ^{13}C NMR (CDCl$_3$): δ 192.8, 166.7, 142.0, 141.2, 141.1, 139.1, 135.8, 134.9, 132.7, 132.0, 128.5, 127.7, 124.8, 124.6, 38.4, 24.4, 24.1, 14.1, 13.3; ^{13}C CP/MAS NMR: δ 191.2, 163.8, 138.9, 130.1, 21.0, 9.9.

Other polyimides were synthesized similarly in essentially quantitative yields and isolated in the same manner as above. Characterization data for each polymer are listed separately below, while comparisons of the members of the various polyimide families are made in Section 3 and in several tables discussed later. For two of the insoluble polyimides, solution NMR data of their polyamic acids are included along with the solid state NMR data of the polyimides.

TDAN–MCDEA ^{1}H NMR (CDCl$_3$): δ 8.09 (s, 2H), 6.94 (s, 1H), 4.30 (s, 1H), 2.63 (d, J = 6.4, 2H), 2.34 (d, J = 7.2, 2H), 1.05 (m, 6H); ^{13}C NMR (CDCl$_3$): δ 166.5, 141.7, 141.3, 141.2, 139. 1, 132.8, 131.9, 128.6, 127.9, 124.1, 38.5, 24.5, 24.1, 14.2, 13.3; FTIR (KBr): 2972, 2937, 2877, 1780, 1722, 1691, 1456, 1402, 1365, 1309, 1198, 1111, 901, 866, 791, 746, 627, 594 cm^{-1}.

TDAN–DETDA ^{13}C CP/MAS NMR: δ 163.5, 140.5, 129.2, 125.5, 21.3, 15.0; FTIR (KBr pellet): 2968, 2935, 2875, 1780, 1720, 1603, 1477, 1452, 1346, 1223, 1184, 1105, 897, 744, 592 cm^{-1}.

TDAN–NAPDA (polyamic acid) ^{1}H NMR (CDCl$_3$): δ 13.35 (broad), 10.49 (s), 8.15 (d), 8.09 (s), 8.01 (s), 7.80 (d), 7.41 (d); ^{13}C NMR (CDCl$_3$): δ 166.9, 166.6, 139.1, 137.8, 137.7, 134.8, 134.5, 133.8, 130.5, 129.5, 128.3, 125.3, 122.9, 121.6; ^{13}C CP/MAS NMR: δ 168.6, 128.1; FTIR (KBr): 3237 (broad), 1711, 1664, 1533, 1500, 1412, 1338, 1254, 1118, 1099, 903, 793 cm^{-1}; (**polyimide**) ^{13}C CP/MAS NMR: δ 165.7, 142.3, 125.0; FTIR (KBr): 3066, 2924, 1778, 1718, 1636, 1599, 1510, 1415, 1346,1306, 1238, 1213, 1078, 964, 897, 771, 741, 617, 592, 511, 441 cm^{-1}.

TDAN–DAM (polyamic acid) ^{1}H NMR (CDCl$_3$): δ 9.89 (s, 2H), 7.99 (s, 2H), 7.84 (s, 2H), 7.02 (s, 1H), 3.40 (s, broad), 2.27 (s, 3H), 1.96 (s, 6H); ^{13}C NMR (CDCl$_3$): δ 166.9, 165.4, 138.3, 137.0, 136.8, 135.0, 134.7, 134.3, 134.0, 132.6, 131.6, 131.4, 129.3, 128.8, 128.0, 18.1, 13.6; ^{13}C CP/MAS NMR: δ 167.4, 130.4, 18.2; FTIR (KBr): 3203 (broad), 2925 (broad), 2578 (broad), 1720, 1630, 1514, 1454, 1363, 1281, 1111, 1016, 899, 777, 744, 715, 596, 455 cm^{-1}; (**polyimide**) ^{13}C CP/MAS NMR: δ 165.2, 138.0, 131.4, 123.4, 17.7; FTIR (KBr): 1780, 1722, 1483, 1346, 1311, 1227, 1188, 1107, 1030, 895, 866, 781, 744, 700, 621, 592, 496, 447 cm^{-1}.

6FDA–DETDA ^{1}H NMR (CDCl$_3$): δ 8.07(d, J = 7.5) and 7.98 with shoulder (s) 6H total, 7.29 (s, 1H), 2.51 (m), 2.34 (m), 2.23 (s), and 1.98 (d, J = 10.2) 7H total, 1.22 (s) and 0.95 (s) 6H total; ^{13}C NMR (CDCl$_3$): δ 166.5, 166.2, 166.0, 165.7, 144.4, 144.2, 142.4, 139.0, 136.0, 132.5, 132.1, 128.9, 127.8, 127.4, 127.3, 126.8, 125.2, 124.2, 121.3, 117.5, 66.0(m), 24.7, 24.4, 22.0, 18.4, 14.5, 13.9, 13.7; ^{13}C CP/MAS NMR: δ 163.3, 135.1, 130.0, 125.6, 21.8, 10.8; FTIR (film): 2974, 2941, 2881, 1788, 1732, 1479, 1435, 1360, 1298, 1257, 1209, 1194, 1144, 1105, 985, 725 cm^{-1}.

6FDA–MCDEA ^{1}H NMR (CDCl$_3$): δ 8.07 (d, J = 8.0), 8.01 (s), and 7.94 (d, J = 7.4), 3H total, 6.98 (s, 1H), 4.33 (d, 1H), 2.68 (m, J = 7.3, 2H), 2.37 (m, J = 7.3, 2H), 1.11 (m, J = 7.4, 6H); ^{13}C NMR (CDCl$_3$): δ 166.8, 166.5, 141.3, 141.2, 139.3, 139.2, 136.2, 132.8, 132.6, 132.3, 128.5, 127.7, 125.5, 124.4, 121.5, 117.5, 66.5 (m), 38.4, 24.4, 24.2, 14.1, 13.4; FTIR (film): 2973, 2938, 1787, 1727, 1455, 1367, 1267, 1211, 1145, 1105, 983, 725 cm^{-1}.

BTDA–DETDA ^{1}H NMR (CDCl$_3$): δ 8.30 (s, with shoulder) and 8.16 (d, J = 7.1) 6H total, 7.29 (s, 1H), 2.50 (t, J = 7.2), 2.36 (t, J = 7.6), and 2.22 (s) 7H total, 1.21 (s) and 0.93 (s) 6H total; ^{13}C NMR (CDCl$_3$): δ 192.9, 166.6, 166.2, 166.0, 144.4, 144.3, 142.3, 142.0, 139.1, 135.8, 134.9, 132.1, 129.1, 128.0, 127.6, 127.4, 124.8, 124.6, 24.9, 24.6, 22.2, 18.4, 14.4, 14.1, 13.9; FTIR (film): 2974, 2939, 2879, 1780, 1726, 1684, 1477, 1361, 1296, 1246, 1105, 729 cm^{-1}.

BPADA–MCDEA ^{1}H NMR (CDCl$_3$): δ 7.90 (d, J = 8.0, 1H), 7.43 (s), 7.41 (s), and 7.34 (d, J = 8.1) 4H total, 7.06 (d, J = 7.9) and 6.93 (s) 3H total, 4.29 (s, 1H), 2.65 (d, J = 6.9, 2H), 2.36 (d, J = 7.3, 2H), 1.76 (s, 3H), 1.06 (m, 6H); ^{13}C NMR (CDCl$_3$): δ 167.5, 167.4, 164.0, 152.4, 147.7, 141.4, 138.8, 134.2, 132.6, 128.8, 128.2, 125.9, 124.9, 123.0, 120.1, 111.7, 42.5, 38.4, 31.0, 24.4, 24.0, 14.1, 13.3; FTIR (CHCl$_3$ cast film): 2971, 2877, 1778, 1722, 1691, 1617, 1477, 1367, 1276, 1238, 1101, 800, 752 cm^{-1}.

BPADA–DETDA ^{1}H NMR (CDCl$_3$): δ 7.90 (d, J = 8.0, 2H), 7.41 (s), 7.33 (d, J = 8.5), and 7.24 (d, J = 11.4) 8H total, 7.05 (d, J = 8.2, 4H), 2.50 (m), 2.45 (m), and 2.17 (s) 7H total, 1.16 (t, J = 7.0, 3H), 0.88 (t, J = 7.4, 3H); ^{13}C NMR (CDCl$_3$): δ 167.3, 167.0, 166.8, 163.9, 152.5, 147.6, 144.2, 144.0, 142.6, 138.9, 134.2, 128.7, 128.3, 128.0, 127.8, 126.8, 125.8, 125.0, 122.9, 120.1, 111.6, 42.5, 31.0, 24.8, 24.5, 22.0, 18.3, 14.3, 14.0, 13.8, 13.7; FTIR (film): 2972, 2937, 2877, 1778, 1724, 1618, 1601, 1504, 1477, 1446, 1361, 1275, 1238, 1173, 1101, 850, 752 cm^{-1}.

BPDA–MCDEA ^{1}H NMR (CDCl$_3$): δ 8.30 (s, 2H), 8.15

(s, with shoulder, 4H), 6.99 (s, 2H), and 4.34. (s, 2H), 2.72 (t, $J = 7.0$, 4H), 2.42 (t, $J = 7.8$, 4H), 1.12 (m, $J = 7.6$, 12H); ^{13}C NMR ($CDCl_3$): δ 167.5, 145.8, 141.5, 139.2, 133.7, 133.1, 132.9, 131.7, 128.7, 128.2, 125.1, 123.0, 38.7, 24.6, 24.3, 14.4, 13.5; FTIR (film): 2972, 2939, 2879, 1776, 1782, 1686, 1522, 1456, 1368, 1267, 1198, 1105, 1078, 891, 860, 748 cm^{-1}.

BPDA–DETDA ^{1}H NMR ($CDCl_3$): δ 8.28 (s, 2H), 8.12 (s, with shoulder, 4H), 7.30 (s, 1H), 2.50 (m, $J = 7.4$), 2.39 (t, $J = 8.1$), and 2.24 (s) 6H total, 1.98 (s, 1H), 1.21 (t, $J = 76.7$), and 0.88 (t, $J = 7.4$) 6H total; ^{13}C NMR ($CDCl_3$): δ 167.4, 167.1, 166.9, 145.7, 144.5, 144.4, 142.6, 139.2, 136.2, 133.8, 133.0, 131.6, 129.2, 128.4, 1278.0, 127.8, 1245.0, 122.9, 25.0, 24.7, 22.3, 18.5, 17.7, 14.5, 14.3, 14.1, 12.8; FTIR (film): 3629, 3485, 2974, 2937, 2879, 1776, 1718, 1620, 1477, 1421, 1361, 1228, 1103, 889, 845, 746, 546 cm^{-1}.

DSDA–MCDEA ^{1}H NMR ($CDCl_3$): δ 8.46 (m) and 8.12 (m) 3H total, 6.88 (s, 1H), 4.22 (s, 1H), 2.54 (s) and 2.25 (m) 4H total, 0.97 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 165.8, 146.5, 141.1, 141.0, 139.3, 135.8, 134.3, 132.9, 128.6, 127.4, 125.4, 123.7, 38.4, 24.4, 24.1, 14.1, 13.3; FTIR (film): 3456, 3421, 2972, 2939, 2879, 1784, 1728, 1612, 1454, 1421, 1367, 1327, 1265, 1176, 1149, 1103, 1059, 920, 858, 783, 744, 673, 634, 563 cm^{-1}.

DSDA–DETDA ^{1}H NMR ($CDCl_3$): δ 8.76 (s) and 8.44 (s) 6H total, 7.40 (s, 1H), 2.51 (s), 2.41 (s), 2.23 (s), 2.11 (s), and 1.84 (s) 7H total, 1.07 (s) and 0.70 (s) 6H total; ^{13}C NMR ($CDCl_3$): δ 166.3, 166.1, 165.9, 165.7, 165.5, 145.6, 144.4, 142.4, 139.1, 135.6, 135.0, 132.6, 129.0, 127.4, 127.2, 125.5, 123.7, 24.1, 23.9, 21.1, 17.6, 14.5, 14.3, 13.3; FTIR (film): 3095, 2972, 2939, 2879, 1784, 1730, 1604, 1475, 1422, 1362, 1327, 1177, 1149, 1103, 1057, 920, 744, 673, 634, 563 cm^{-1}.

PMDA–MCDEA ^{1}H NMR ($CDCl_3$): δ 8.58 (s, 2H), 7.00 (s, 2H), 4.35 (s, 2H), 2.68 (d, $J = 4.6$) and 2.39 (d, $J = 7.1$) 8H total, 1.11 (m, 12H); ^{13}C NMR ($CDCl_3$): δ 165.9, 141.4, 141.3, 139.6, 137.5, 133.1, 128.9, 127.8, 120.1, 38.8, 24.7, 24.4, 14.4, 13.6; FTIR (film): 2972, 2879, 1778, 1730, 1689, 1456, 1402, 1361, 1296, 1263, 1161, 1111, 1076, 1024, 845, 798, 733, 633 cm^{-1}.

PMDA–DETDA ^{13}C CP/MAS NMR: δ 165.3, 144.0, 137.7, 128.3, 117.0, 24.7, 13.7; FTIR (KBr): 2972, 2881, 1780, 1734, 1477, 1456, 1369, 1347, 1261, 1111, 1032, 845, 802, 731 cm^{-1}.

BTDA–DAM ^{1}H NMR ($CDCl_3$): δ 8.30 (d), 8.26 (s), and 8.24 (d) 6H total, 7.36 (s, 1H), 2.16 (s) and 1.92 (s) 9H total; ^{13}C NMR ($CDCl_3$): δ 193.3, 165.9, 141.9, 138.2, 136.2, 134.4, 131.7, 130.2, 128.3, 124.4, 17.6, 13.4; FTIR (film): 3629, 3492, 3066, 2927, 1779, 1726, 1682, 1620, 1485, 1425, 1361, 1296, 1250, 1228, 1159, 1105, 862, 729 cm^{-1}.

DSDA–DAM ^{1}H NMR ($CDCl_3$): δ 8.71 (s) and 8.67 (shoulder) 4 H total, 8.25 (d, $J = 7.4$, 2H), 7.31 (s, 1H), 2.10 (s) and 1.85 (s) 9H; ^{13}C NMR ($CDCl_3$): δ 165.2, 165.1, 145.4, 138.3, 136.3, 135.8, 134.7, 132.8, 130.2, 128.0, 125.4, 123.5, 17.6, 13.3; FTIR (film): 3491, 3048, 2925, 1781, 1724, 1485, 1458, 1421, 1363, 1325, 1176, 1149, 1106, 1059, 1028, 922, 862, 744, 690, 638, 565 cm^{-1}.

PMDA–DAM ^{13}C CP/MAS NMR: δ 164.8, 137.4, 129.2, 119.0, 17.2; FTIR (KBr): 2981, 2927, 1778, 1730, 1484, 1458, 1371, 1348, 1308, 1267, 1230, 1113, 872, 841, 731, 436 cm^{-1}.

BPDA–DAM ^{13}C CP/MAS NMR: δ 165.9, 145.4, 132.5, 129.4, 123.6, 17.4, 13.2; FTIR (KBr) 3479, 2927, 1778, 1724, 1620, 1485, 1421, 1352, 1230, 1188, 1099, 1027, 906, 860, 742, 694, 627, 534 cm^{-1}.

6FDA–DAM ^{1}H NMR ($CDCl_3$): δ 8.06 (d, $J = 7.5$) and 7.96 (s) 6H total, 7.25 (s, 1H), 2.23 (s) and 1.99 (s) 9H; ^{13}C NMR ($CDCl_3$): δ 165.7, 165.4, 139.1, 138.6, 136.1, 136.0, 132.7, 132.3, 130.8, 129.0, 128.2, 125.5, 124.3, 121.4, 117.6, 65.5, 65.2, 64.9, 18.4, 14.0; FTIR (film): 2927, 1786, 1730, 1689, 1487, 1435, 1360, 1298, 1255, 1209, 1194, 1144, 1107, 982, 864, 750, 725 cm^{-1}.

BPADA–DAM ^{1}H NMR ($CDCl_3$): δ 7.88 (d, $J = 7.9$, 1H), 7.40 (d, $J = 10.3$), 7.33 (d, $J = 8.5$), and 7.19 (s), and 7.04 (d, $J = 7.8$) 7H total, 2.17 (s), 1.92 (s), and 1.75 (s) 8H total; ^{13}C NMR ($CDCl_3$): δ 166.4, 163.9, 152.5, 147.6, 138.3, 136.3, 134.3, 130.5, 128.7, 128.6, 125.8, 125.1, 122.9, 120.1, 111.7, 42.5, 31.0, 18.2, 13.1; FTIR (film): 3064, 2970, 2929, 2871, 1778, 1724, 1618, 1601, 1504, 1479, 1444, 1361, 1273, 1240, 1173, 1103, 1014, 849, 750, 540 cm^{-1}.

3. Results and discussion

As in any polyimide synthesis, monomer purification and drying were important in order to obtain high molecular weight polymers. This was especially important here because the hindered diamines react more slowly than typical unhindered amine monomers and side-reactions, especially anhydride hydrolysis by adventitious moisture, compete effectively with amic acid formation. Once monomers were pure and dry, polyimides were prepared through a conventional two-step process in which the dianhydride was reacted with the diamine at room temperature to give the polyamic acid that was then thermally cyclized in solution to the polyimide in high yields.

The rate of the initial reaction was found to be much lower for hindered diamines, taking several hours at room temperature or even requiring extended reaction at elevated temperatures before a viscosity increase was noticed. A mild exotherm was seen upon initial addition of the diamine to the dianhydrides when DAM was used as the diamine, but not with MCDEA or DETDA, indicating lower reactivity for the more sterically hindered diamines containing ortho ethyl substituents. Differences in diamine reactivity are also attributed to the nucleophilicity of the amino nitrogen atom and have been shown to follow a Hammet relationship in unhindered diamines [25]. Thus, in addition to bulky ortho ethyl substituents, MCDEA contains electron withdrawing

Table 1
Molecular weight and viscosity data for THF soluble polyimides synthesized. ns—not soluble

Polymer	M_n	M_w	Pk Max	η^a (dL/g)
TDAN–MCDEA	49,300	127,400	105,000	1.05
PMDA–MCDEA	33,000	99,700	77,400	0.61
BPDA–MCDEA	22,700	55,800	47,900	0.74
DSDA–MCDEA	40,200	84,000	58,000	0.67
BTDA–MCDEA	33,400	136,600	70,000	0.86
6FDA–MCDEA	29,400	96,300	84,400	0.93
BPADA–MCDEA	26,900	74,200	56,200	0.70
TDAN–DETDA	ns	ns	ns	ns
PMDA–DETDA	ns	ns	ns	0.76
BPDA–DETDA	13,100	54,200	55,000	0.66
DSDA–DETDA	19,200	27,100	23,300	0.28
BTDA–DETDA	17,400	32,800	32,600	0.59
6FDA–DETDA	21,500	84,100	76,900	0.91
BPADA–DETDA	41,500	111,200	83,100	0.84
TDAN–DAM	ns	ns	ns	ns
PMDA–DAM	ns	ns	ns	0.85
BPDA–DAM	ns	ns	ns	ns
DSDA–DAM	ns	ns	ns	0.53
BTDA–DAM	ns	ns	ns	0.60
6FDA–DAM	56,100	184,000	120,000	0.97
BPADA–DAM	19,000	41,300	37,800	0.45

[a] Intrinsic viscosities measured in NMP at 35°C.

chlorine groups resulting in a less nucleophilic amine, rendering it even less reactive.

Despite lower reactivity for the hindered diamine monomers, moderate molecular weights were obtained for all polyimides. Intrinsic viscosities in NMP of the soluble polyimides ranged from 0.28 to 1.05 dL/g and M_ns varied from 13,100 to 56,100 relative to polystyrene standards (Table 1). The SEC traces often displayed a low molecular weight tail. Intrinsic viscosities correlated better with the peak maximum in the SEC trace than either the M_n or M_w.

For insoluble polyimides (those from TDAN–DAM, TDAN–DETDA and BPDA–DAM monomer pairs), complete imidization was confirmed by FTIR analysis of the precipitated and dried polymers (Fig. 2). Upon imidization, the broad acid peak at 2925 cm^{-1} disappeared along with the acid and amide carbonyl stretches at 1720 and 1630 cm^{-1}. Characteristic imide symmetric and asymmetric carbonyl stretches at 1780 and 1726 cm^{-1} appeared in their place. Further characterization with solid-state ^{13}C NMR showed an upfield shift from the broad, combined peak of the amide and acid carbonyl carbons from 167 ppm to a single sharp peak at 165 consistent with imidization (Fig. 3). Additional changes in the 115–145 ppm region are also confirmation of imidization.

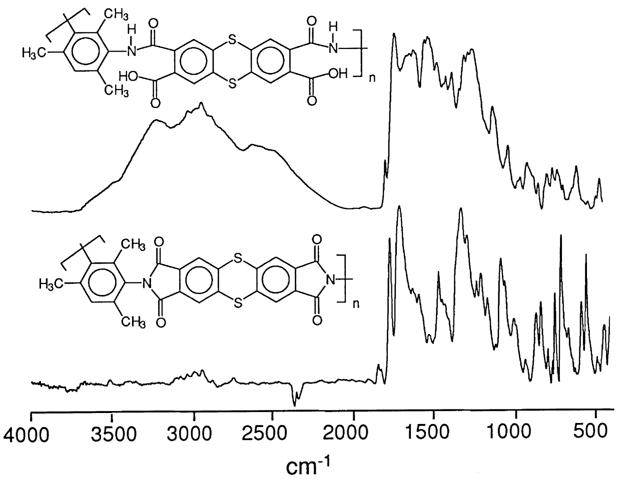


Fig. 2. FTIR spectra of polyamic acid from TDAN–DAM (top) and corresponding polyimide (bottom).

Fig. 4 shows representative solution ^{13}C NMR spectra for soluble polyimides from hindered diamines with BPADA. Each spectra shows an imide carbonyl around 166 ppm. In the case of the BPADA–DETDA polyimide, three imide carbonyls can be seen as a result of the use of the isomeric diamine mixture of the commercial monomer. DETDA consists of a 1:4 mixture of two isomers (shown in Fig. 1) with the unsymmetrical isomer predominating.

All polyimides showed good thermal and thermo-oxidative stability with little or no weight loss in N_2 or air occurring until > 400°C (Table 2). Fig. 5 shows typical TGA traces in nitrogen for polyimides from the hindered diamine MCDEA. These thermograms are similar to the thermograms for the polyimides made from DETDA and DAM. Char yields ranging from 30 to 67% were observed in nitrogen at 1000°C with the lowest for DSDA-containing polyimides and the highest for polyimides made from TDAN, PMDA, and BPDA. Within each family, polyimides from the dianhydride DSDA gave the least thermally stable polyimides and the lowest char yields (Table 2). Low thermal stabilities for DSDA containing polyimides have been reported by others [26,27].

Polyimides containing pendent alkyl groups displayed onsets of thermal degradation approximately 20–75°C lower than analogous unsubstituted polyimides. Table 3 illustrates this for polyimides made from thianthrene-2,3,7,8-tetracarboxylic dianhydride (TDAN). Thermal stability in air decreased by approximately 50°C due to the presence of pendent alkyl substituents on the diamine moieties. However, thermal stabilities in nitrogen were comparable for all polymers in the TDAN series. In general, no noticeable weight gain was seen in air as a result of alkyl group oxidation to carbonyls and alcohols for most of the polyimides, signifying no appreciable oxygen uptake by the alkyl substituents before degradation. PMDA-containing polyimides were the exception with polymers from DETDA and MCDEA diamines showing a weight gain of approximately 0.5% as observed in the TGA traces in air.

Glass transition temperatures are listed in Table 2 for all polyimides synthesized. No T_gs were detected for polymers from TDAN–MCDEA, TDAN–DETDA, TDAN–DAM, PMDA–DETDA, PMDA–DAM, DSDA–DAM, BPDA–DETDA or BPDA–DAM up to 430°C (degradation onset) by DSC. Apparently, the rigidity of the anhydride moiety

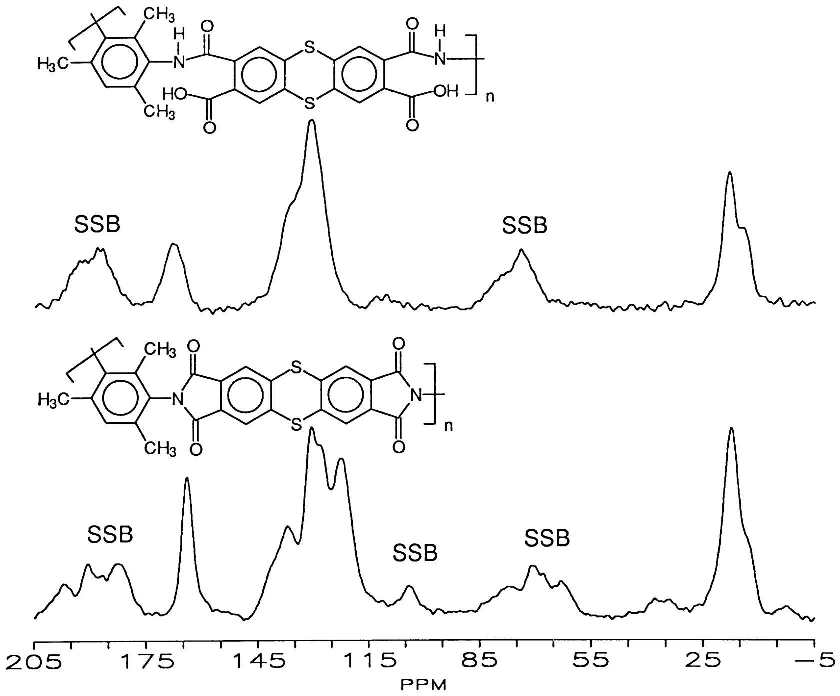


Fig. 3. CP/MAS ^{13}C NMR spectra of polyamic acid from TDAN–DAM (top) and corresponding polyimide (bottom).

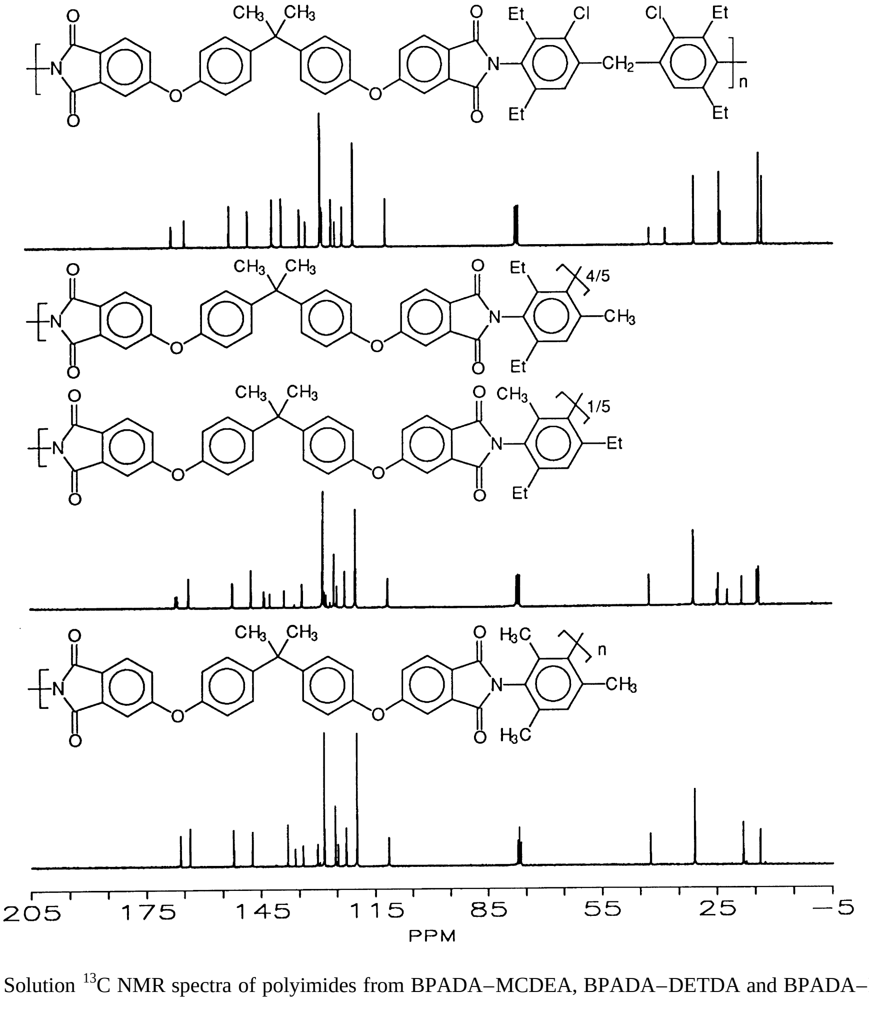


Fig. 4. Solution ^{13}C NMR spectra of polyimides from BPADA–MCDEA, BPADA–DETDA and BPADA–DAM.

Table 2
Thermal properties of polyimides synthesized here

Polymer	T_g[a] (°C)	TGA 5% wt. loss (°C)[b]		Char yield at 1000°C in N_2 (%)
		Air	N_2	
TDAN–MCDEA	nd	465	496	55
PMDA–MCDEA	373	422	504	58
BPDA–MCDEA	345	450	505	60
DSDA–MCDEA	307	400	439	39
BTDA–MCDEA	300	415	503	53
6FDA–MCDEA	294	438	512	53
BPADA–MCDEA	252	478	513	52
TDAN–DETDA	nd	470	528	60
PMDA–DETDA	nd	440	485	49
BPDA–DETDA	nd	470	545	63
DSDA–DETDA	388	423	455	30
BTDA–DETDA	385	499	511	60
6FDA–DETDA	376	470	527	52
BPADA–DETDA	295	487	516	50
TDAN–DAM	nd	463	495	63
PMDA–DAM	nd	511	538	59
BPDA–DAM	nd	480	564	62
DSDA–DAM	nd	442	477	45
BTDA–DAM	398	464	527	52
6FDA–DAM	392	455	522	53
BPADA–DAM	295	441	502	53

[a] Heating rate of 10°C/min in N_2—T_g reported as inflection point of trace.
[b] Heating rate of 20°C/min.nd—none detected up to decomposition temperatures.

(and thus the polyimide backbone) pushes the glass transition temperatures of these polymers beyond degradation temperatures. Glass transition temperatures for some of the more rigid polyimides may be observable by other techniques (e.g., DNIA, TMA), however, no T_gs were observed for any of the TDAN based polyimides by DMA and further studies using these techniques were not attempted. All other polyimides showed T_gs between 250 and 400°C.

Incorporation of methyl groups in positions ortho to an imide ring increasingly inhibits rotation around the bond between the phenyl ring and the nitrogen, resulting in more rigid polymer chains which in turn increase T_g. This can been seen in Table 4, where the T_g of the unsubstituted polyimide from BTDA-*m*-PDA is 300°C [28]. As ortho methyl substitution on the PDA residue increases, there is observed an incremental increase in the glass transition temperature of the polyimides. Introduction of one ortho methyl pendent group onto the diamine raises the T_g by 15°C. Incorporation of a second methyl group again raises T_g by an additional 70°C. In the case of three ortho methyl substituents, a dramatic total increase in T_g of 98°C is seen compared to the unsubstituted BTDA-*m*-PDA polyimide. Analogous polyimides derived from 6FDA (also shown in Table 4) display the same trend of increasing glass transition temperature upon addition of methyl substituents ortho to the imide heterocycle, evidence that steric interactions are decreasing polymer chain mobility.

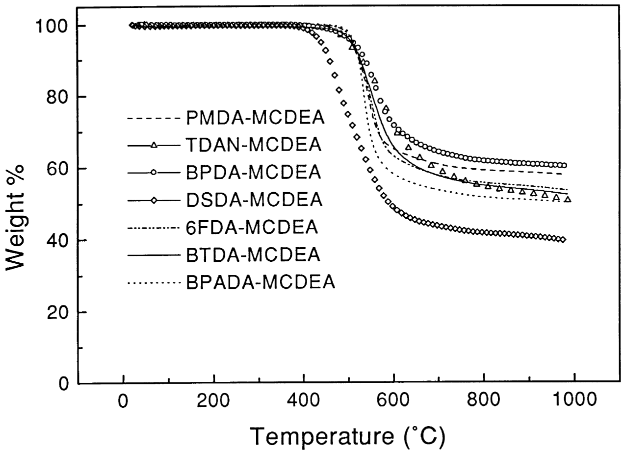
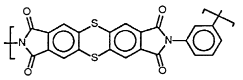
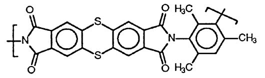
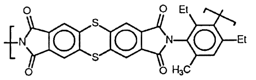
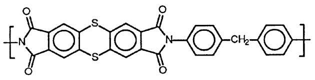
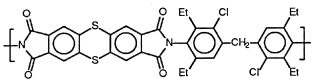


Fig. 5. Representative TGA thermograms in N_2 with a heating rate of 20°C/min for MCDEA-containing polyimides.

Replacing methyl groups with larger ethyl groups does not further increase T_g, but actually causes a slight depression in T_g due to internal plasticization. Comparing polyimides in Table 4 made from DAM and DETDA, T_g values were approximately 15°C lower for the latter. Differences for other polyimides made from more rigid dianhydrides are not available because T_g values are apparently above decomposition temperatures of the polymers. This slight decrease in T_g is probably the result of increased free volume in the polymer system caused by two effects. First, ethyl groups occupy more space than methyls, and second, the isomeric DETDA mixture leads to configuration and sequence isomers in the polymer backbone that reduce

Table 3
Effect of ortho-substituents on TDAN polyimide thermal properties

Polymer	TGA 5% wt. loss (°C)[a]		Char yield at 1000 °C in N_2 (%)
	air	N_2	
	512	508	61
	463	495	63
	470	528	60
	511	512	67
	465	496	55

a - Heating rate of 20 °C/min.

symmetry. Other researchers have shown that, as the volume of the ortho substituent is increased, the macroscopic density decreases [29]. This is consistent with an increase in free volume when methyl groups are replaced with ethyl groups. Also, polyimides containing DETDA display better solubility than those made with DAM (Table 5Table 6). The polyimides from the more rigid dianhydrides (PMDA, BPDA, and DSDA) and DETDA exhibited good solubility in polar aprotic as well as halogenated solvents, whereas PMDA–DAM and DSDA–DAM polyimides are only soluble in polar aprotics and the BPDA–DAM polyimide is insoluble.

Table 5 further compares the T_g values of more flexible polyimides, based on MDA, with increasing number and size of ortho substituents. The methylene bridge between the phenyl rings of MDA and its pendent substituted derivatives allows for facile rotation, resulting in inherently lower T_gs for these polyimides compared to the polyimides in Table 4 with the same pendant substitutions. Values for T_gs of polyimides based on substituted methylene dianilines showed only a slight T_g enhancement with methyl substitution. Replacing methyl groups with ethyl groups caused a significant decrease in T_g, approximately 60°C for the polyimide [30] from BTDA and 4,4′-methylenebis(2,6-diethylaniline) and 30°C for the polyimide from 6FDA and 4,4′-methylenebis(2,6-diethylaniline). This is believed to be due to an increase in free volume resulting from internal plasticization by the ethyl groups. Addition of chloro substituents ortho to the methylene spacer of 4,4′-methylenebis(2,6-diethylaniline) once again raises the T_g by decreasing mobility around the spacer group. Solubility was greatly enhanced in this series by the presence of pendant substituents. For example, the polyimides from

Table 4
Effect of ortho-substituents on T_g's of polyimides based on BTDA or 6FDA and *m*-phenylene diamines

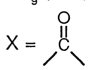
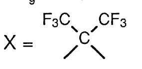
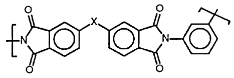
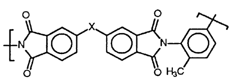
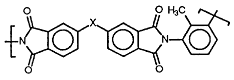
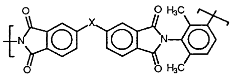
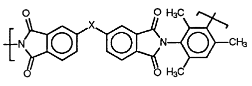
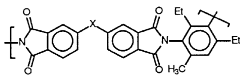
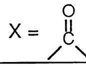
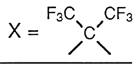
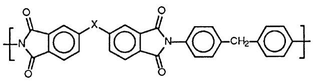
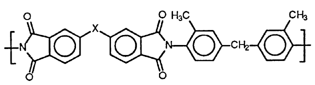
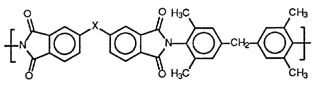
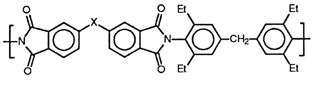
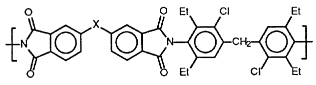
Polymer	T_g (°C) X =  $C{=}O$	T_g (°C) X =  $C(CF_3)_2$
	300[28]	298[12]
	315[13]	-----
	------	335[12]
	384[13]	-----
	398	392
	385	376

Table 5
Effect of ortho-substituents on T_g's of polyimides based on BTDA or 6FDA and methylene dianilines

Polymer	T_g (°C) X =  $C{=}O$	T_g (°C) X =  $C(CF_3)_2$
	290[28]	289[29]
	285[13]	-----
	309[13]	299[29]
	249[30,a]	270[a]
	300	294

a - measured in our labs

Table 6
Solubility of polyimides in 1—$CHCl_3$, 2—CH_2Cl_2, 3—THF, 4—methanol, 5—NMP, 6—DMAc, 7—acetone, 8—toluene, and 9—xylene. + soluble, − insoluble, +− swells

Polymer	1	2	3	4	5	6	7	8	9
TDAN–MCDEA	+	+	+	−	+	+	−	+	+
PMDA–MCDEA	+	+	+	−	+	+	−	+	+
BPDA–MCDEA	+	+	+	−	+	+	−	+−	+−
DSDA–MCDEA	+	+	+	−	+	+	−	−	−
BTDA–MCDEA	+	+	+	−	+	+	−	+−	+−
6FDA–MCDEA	+	+	+	−	+	+	+	+	+
BPADA–MCDEA	+	+	+	−	+	+	−	+	+
TDAN–DETDA	−	−	−	−	−	−	−	−	−
PMDA–DETDA	+−	+	−	−	+	+	−	−	−
BPDA–DETDA	+	+	+	−	+	+	−	−	−
DSDA–DETDA	+	+	+	−	+	+	−	−	−
BTDA–DETDA	+	+	+	−	+	+	−	−	−
6FDA–DETDA	+	+	+	−	+	+	+	+−	+−
BPADA–DETDA	+	+	+	−	+	+	−	+−	+−
TDAN–DAM	−	−	−	−	−	−	−	−	−
PMDA–DAM	−	−	−	−	+	+	−	−	−
BPDA–DAM	−	−	−	−	−	−	−	−	−
DSDA–DAM	+	+−	−	−	+	+	−	−	−
BTDA–DAM	+−	+	−	−	+	+	−	−	−
6FDA–DAM	+	+	+	−	+	+	+	+−	+−
BPADA–DAM	+	+	+	−	+	+	−	−	−

TDAN–MDA and PMDA–MDA are generally insoluble [23,31] (the latter did dissolve in concentrated H_2SO_4), while polyimides from TDAN–MCDEA and PMDA–MCDEA were highly soluble in polar aprotic solvents, halogenated solvents, and even toluene and xylene (Table 6). Other polyimides made using MCDEA were also extremely soluble.

Within a given diamine family, the T_gs of the polyimides decreased with decreasing rigidity of the dianhydride in the order TDAN $>$ PMDA $>$ BPDA $>$ DSDA $>$ BTDA $>$ 6FDA $>$ BPADA (Table 2). One surprising fact is that TDAN appears to be even more rigid than PMDA (i.e., TDAN polyimides showed no T_gs by DSC or DMA, apparently because their T_gs are greater than the decomposition temperatures). While T_gs were not detectable for PMDA–DAM and PMDA–DETDA polyimides, the more flexible PMDA–MCDEA exhibited a T_g at 373°C by DSC.

Most of these polyimides were soluble in common organic solvents including NMP, DMAc, CH_2Cl_2 and THF. Exceptions were the polyimides from TDAN–DETDA, TDAN–DAM, and BPDA–DAM for which no suitable solvents were found (Table 6). Surprisingly, the polyimides containing 6FDA were soluble in acetone and the polyimides containing MCDEA were even soluble in non-polar organic solvents such as toluene and xylene. Incorporation of ortho ethyl substituents prevents planarity and packing of the imide rings even more than the methyl groups of DAM. This causes both an increase in free volume and a decrease in intermolecular interactions. The ethyl groups also provide additional ‘handles’ for interaction with solvents. While the two polyimde series based on DETDA and MCDEA both contain ethyl substituents, MCDEA also contains a flexible methylene bridge and aromatic chlorine substituents that contribute to the enhanced solubility of MCDEA-containing polyimides. DAM-containing polyimides were the least soluble of those studied here, showing solubility only in polar aprotic solvents like NMP and DMAc, except for TDAN–DAM and BPDA–DAM which were insoluble.

It was originally hoped that incorporation of the non-planar thianthrene moiety would enhance solubility without loss of other properties [23,24]. However, polyimides containing thianthrene were even less soluble than those made from pyromellitic dianhydride. This is surprising since PMDA-containing polyimides are necessarily planar and should pack in highly ordered, usually crystalline, arrays. Cross-linking of the TDAN units is one possible explanation but the fact that the TDAN–MCDEA polymer was soluble argues against this. Another possibility is crystallinity despite a bent backbone. However, the thianthrene-containing polyimides showed no crystalline scattering by X-ray diffraction performed on thin films, suggesting they exist as amorphous polymers in the solid state. It may be that localized interactions involving TDAN units are enhanced. For example, polythioethylene melts at $>$200°C while polyoxyethylene melts $<$70°C [32]. Longer bond lengths and angles for the former induce a 2_1 glide-plane conformation that allows close packing of dipole-aligned C–S–C units. Similar packing of pairs of bent thianthrene rings might lead to combined sulfur dipole alignment and π–π stacking interactions. This is reflected in the crystalline packing of the parent unsubstituted thianthrene which has a melting point of 157–159°C versus 108–110°C for the all carbon analog 9,10-dihydroanthracene [33].

Films cast from $CHCl_3$ or CH_2Cl_2 for all soluble polyimides were tough, transparent and creasible. In addition, polyimide films from 6FDA–DETDA and 6FDA–MCDEA were colorless. In general, fluorine-containing polyimides with hexafluoroisopropylidene groups either in the dianhydride or the diamine are reported to display increased solubility, ultraviolet stability, transparency, and decreased dielectric constant and color [34]. Such properties make these fluorine-containing polymers attractive for opto-electronic and micro-electronic devices where charge transfer complexes (a source of optical loss) are of significant concern [35–38].

Solubility in weak organic solvents allows for unique fabrication opportunities not available to insoluble or less soluble polyimides. One such application is gas separation, where the combination of solubility, plus excellent mechanical and thermal properties, make these polyimides good candidates for fabrication into asymmetric membranes. Gas separation studies are currently being investigated on the polyimide films described in this research.

4. Conclusions

Polyimides with enhanced solubility have been synthesized from various aromatic tetracarboxylic dianhydrides and sterically hindered diamines. Despite this increase in solubility, glass transition temperatures and thermal stabilities of the polyimides were retained. More importantly, tough, transparent films of the soluble polyimides could be cast from solution, confirming a key discovery that ortho substitution provides a unique mechanism for increasing T_g without sacrificing solubility and mechanical properties.

Acknowledgements

This research was funded in part by a grant from Air Products and Chemical Company. We also thank NASA's Microgravity Materials Science Program for a graduate student fellowship that provided partial support for one of us (TLG). Summer fellowships for Tara J. Smith and Victoria L. Ulery were provided by the National Science Foundation through a Research Experience for Undergraduates grant (DMR-95-31507).

References

[1] Mittal KL, editor. Polyimides: Synthesis, characterization and applications, vols. 1 and 2. New York: Plenum, 1984.
[2] Cassidy PE. Thermally stable polymers: synthesis and properties. New York: Marcel Dekker, 1980; chap. 4 and 6.
[3] St Clair AK, St Clair TL, Smith EN. Polym Prepr (Am Chem Soc, Div Polym Chem) 1976;17:359.
[4] Bell VL, Stump BL, Gager HJ. J Polym Sci, Polym Chem Ed 1976;14:2275.
[5] Critchley JP, White MA. J Polym Sci, Polym Chem Ed 1972;10:1809.
[6] Matsuura T, Hasuda Y, Nishi S, Yamada N. Macromolecules 1991;24:5001.
[7] Park JW, Lee M, Lee MH, Liu JW, Kim SD, Chang JY, Rhee SB. Macromolecules 1994;27:3459.
[8] Imai Y, Malder MM, Kakimito MJ. J Polym Sci, Polym Chem Ed 1989;22:2189.
[9] Oishi Y, Ishida M, Imia J. J Polym Sci, Polym Chem Ed 1992;30:10.
[10] Yang CP, Chen WT. Macromolecules 1993;26:4865.
[11] Eastmond GC, Page PCB, Paprotny J, Richards RE, Shaunak R. Polymer 1994;35(19):4215.
[12] Tanaka K, Okano M, Toshino H, Kita H, Okamoto K. J Polym Sci, Polym Phys Ed 1992;30:907.
[13] Pfeifer J, Rohde O. In: Weber WD, Gupta MR, editors. Recent advances in polyimide science and technology. Brookfield, CT: SPE, 1987:336.
[14] Hayes RA. U.S. Patent 4 717 393, 1988.
[15] Hayes RA. U.S. Patent 4 705 540, 1987.
[16] Fujimoto M, Kudo M, Taniguchi N. Japanese Patent JP 05 132540 A2 930528, 1993.
[17] Voelker T, Althaus H, Schmidt A. Caoutch Plast 1992;69(714):106.
[18] Voelker T, Althaus H, Schmidt A. European Patent, EP 387894 A2 900919, 1990.
[19] Voelker T, Althaus H, Schmidt AJ. Elastomers Plast 1988;20(1):36.
[20] Dewhurst JE. European Patent application, EP383101 A2 900822, 1990.
[21] Inoue H, Muramatsu T, Hirano T. European Patent application, EP 304913 A2 890301, 1989.
[22] Hayes RA. European Patent application (881-07942.0), 1988.
[23] Yoneyama M, Johnson RA, Mathias LJ. J Polym Sci, Polym Chem Ed 1891;1995:33.
[24] Johnson RA, Mathais LJ. Macromolecules 1995;28:79.
[25] Zubkov VA, Koton MM, Kudryavtsev VV, Svetlichnyi VM. Zh Org Khim 1981;17(8):1682 English transl. 1982;17(8):1501..
[26] Liaw DJ, Liaw BY. J Polym Sci, Polym Chem Ed 1997;35:1527.
[27] Jeong HJ, Kakimoto MA, Imai Y. J Polym Sci, Polym Chem Ed 1991;29:1691.
[28] Bell VL, Kilzer L, Hett EM, Stokes GM. J Appl Polym Sci 1981;27:3805.
[29] Langsam M, Burgonyne WF. J Polym Sci, Polym Chem Ed 1993;31:909.
[30] Shindo Y, Hasegawa M, Sugimura T. J Photopolm Sci Tech 1993;6(1):75.
[31] Sroog CE. J Polym Sci: Macromol Rev 1976;11:161.
[32] Muthiah J, Mathias LJ. Macromolecules 1995;28:7806.
[33] Aldrich Chemical Co. Catalog. Milwaukee, WI: 1996–1997:532,1412.
[34] Cassidy PE, Aminabhavi TM, Farley JM. J Macromol Sci Rev Macromol Chem Phys 1989;C29:283.
[35] St Clair AK, St Clair TL, Slemp WS. In: Weber WD, Gupta MR, editors. Recent advances in polyimide science and technology. New York: Mid Hudson Sect. of Soc. Plast. Eng., 1978:16.
[36] Satou H, Makino D. In: Wong CP, editor. Polymers for electronic and photonic applications. New York: Academic Press, 1993:221.
[37] Senturia SD. In: Bowden MJ, Turner RS, editors. Polymers for high technology. ACS Symp. Ser., 1987;364:428.
[38] Jensen RJ. In: Bowden MJ, Turner RS, editors. Polymers for high technology. ACS Symp. Ser., 1987;364:466.