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N-Methylated copoly(imide amide)s containing hexafluoroisopropylidene

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A synthetic method was developed to produce *N*,*N*′-dimethylated diamines which were then used to prepare poly(imide amide)s. Thus, *N*,*N*′-dimethyl-4,4′-bis(4-aminophenoxy)biphenyl and *N*,*N*′-dimethyl-2,2-bis(4-aminophenyl)hexafluoropropane were condensed at 0°C in dimethylacetamide with 2,2-bis[*N*-(4-chlorocarboxyphenyl)phthalimidyl]hexafluoropropane. The yields were 76–92%, viscosities 0.28–2.26 dl g^{-1}, water absorptions 0.16–0.37 wt% and thermal stabilities around 460°C by thermogravimetric analysis. The addition of the methyl group caused lower molecular weights but superior thermal stability (isothermally) and decreased colour. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(imide amide); hexafluoroisopropylidene; fluoropolymer)

INTRODUCTION

In an effort to improve the strength-to-weight ratio for aerospace structures, composites of fibre-reinforced polymers are being investigated for use as replacements for metal components. These composites must withstand wide temperature ranges, fuels, oils, microcracking and mechanical degradation due to water and fatigue. Polyimide resin based composites have been used in these applications in spite of their inherent disadvantages, such as processing conditions and their tendency to darken with continued high-temperature exposure.

One approach to avoid the processing problems of polyimides is to make a copoly(imide amide). Such structures allow the complete development of the imide function in the monomer or reactive oligomer followed by polymerization via amide formation. Furthermore, the inclusion of an amide group into the polyimide backbone increases its processability, solubility and mouldability[1]. However, the thermal stability of the copolymer is typically intermediate between the thermal stabilities of the two homopolymers[2]. Some examples of commercially available copoly(imide amide)s are Kermel® (fibres), Torlon® (moulding materials), Amanin® (films), and AI® or Rhodeftal® (high-temperature electrical insulation varnishes).

Copoly(imide amide)s are commonly chain extended by one of three methods: amide formation, imide formation or both using trimellitic anhydride (TMA). By the first technique, a cyclized, imide-containing, diacid-terminated monomer is condensed with a diamine to form the final product[2]. In the procedure requiring an imidization, an imide-containing, diamine-terminated monomer is reacted with a dianhydride to form a copoly(amide amic acid). The amic acid must then be cyclodehydrated to form the final copolymer. The last of the three approaches is the classical copoly(imide amide) synthesis where TMA is condensed as a comonomer or as a functionalized comonomer with diamines[3–5].

The synthesis and characterization of a new series of copoly(imide amide)s incorporating a fully cyclized imide function into a monomer were recently reported[6]. The impetus for that research was to produce copoly(imide amide)s that did not require a chemical, thermal or light-induced cyclization step[7–10]. These polymers, composed of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride, 4-aminobenzoic acid and various diamines, showed good thermal stability (10% weight loss from 460°C to 540°C by thermogravimetric analysis (t.g.a.)) and solubility in polar aprotic solvents.

The purpose of the research reported in this paper was to increase the high-performance characteristics of the previously reported[6] polymer series by replacing the amide hydrogen with a methyl group. Compared to the non-methylated analogues, polymers with *N*-methyl substituents are known to show marked improvement in both solubility and oxidative stability[11–13], along with a decrease in glass transition and melting temperatures, film strength and colour due to a decrease in the interchain hydrogen bonding.

EXPERIMENTAL

Materials

The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride was provided by Hoechst Celanese and

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purified by sublimation. The 4-aminobenzoic acid was obtained from Aldrich and purified by recrystallization from 95% ethanol. The 4,4′-bis(4-aminophenoxy)biphenyl (BAPB) was obtained from Kennedy & Klim Inc. and used as received. The 2,2-bis(4-aminophenyl)hexafluoropropane (Bis-A-AF) was obtained from Central Glass Co. Ltd of Japan and purified by sublimation.

Monomer synthesis

*Synthesis of 2,2-bis[*N*-(4-carboxyphenyl)phthalimidyl]-hexafluoropropane (6F-DIA).* 2,2-Bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6F-DA) (10.00 g, 22.5 mmol) and 4-aminobenzoic acid (PABA) (6.12 g, 45.0 mmol) were placed in a 250 ml, three-necked, round-bottomed flask equipped with a reflux condenser and thermometer. Glacial acetic acid (100 ml) was added, and the mixture was stirred and heated to reflux. Within 15 min, all solids had dissolved. After 2.5 h, a white precipitate had formed, and the reaction was allowed to continue for 24 h to provide maximum yield. The reaction mixture was filtered hot to yield a slightly yellow solid which was rinsed with water to remove acetic acid. The product was dried *in vacuo* at 120°C for 12–14 h to yield 14.3 g (93.3%) of 6F-DIA (melting point 370–372°C). ^1H n.m.r. ($O{=}C(CD_3)_2$), δ (ppm) 7.2–8.0 (m, 12H), 12.4 (s, 2H).

*Synthesis of 2,2-bis[*N*-(4-chlorocarboxyphenyl)phthalimidyl]hexafluoropropane (6F-DIAC).* Under an argon purge, 6F-DIA (11.1042 g, 20.0 mmol) was placed in a 250 ml, three-necked, round-bottomed flask with thionyl chloride (50 ml) and one drop of pyridine catalyst. The mixture was heated to reflux for 12 h, and the HCl gas by-product was collected in a water trap. The mixture was cooled and filtered to give a crystalline powder which was rinsed with dry hexane. The white powder was dried in a vacuum desiccator for 12–14 h to yield 11.70 g (99%) of 6F-DIAC (melting point 310–311°C). ^1H n.m.r. ($O{=}S(CD_3)_2$), δ (ppm) 7.2–8.0 (m).

Synthesis of N,N′-di(methanesulfonyl)-4,4′-bis(4-aminophenoxy)biphenyl (BAPB-SA). BAPB (11.052 g, 30.0 mmol) was dissolved in dry pyridine (100 ml) in a 250 ml, three-necked, round-bottomed flask equipped with an argon purge, thermometer and condenser. The solution was cooled to 0°C with an ice bath, and methanesulfonyl chloride (5.1 ml, 65.9 mmol) was added dropwise using a constant-pressure addition funnel. The temperature was maintained at 0°C throughout the addition. The solution was subsequently heated at 50°C for 30 min and at 90°C for 2 h. The product was precipitated into an ice/HCl slurry. The precipitate was then collected by filtration and dried at 100°C for 24 h. The pale-tan product was purified by recrystallization in dimethylacetamide (DMAc)/water. The crystals were dried in an 80°C oven for 24 h to yield 14.79 g (94%) of BAPB-SA (melting point 313–315°C). ^1H n.m.r. ($O{=}S(CD_3)_2$), δ (ppm) 2.9 (s, 6H), 3.4 (b, 2H), 7.0–7.7 (m, 16H).

Synthesis of N,N′*-dimethyl-*N,N′*-di(methanesulfonyl)-4,4′-bis(4-aminophenoxy)biphenyl (BAPB-SA-Me).* In a 250 ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer and condenser, BAPB-SA (10.0 g, 19.1 mmol) was dissolved in DMAc (50 ml). Powdered 85% KOH (4.8 g) was added to the solution. The reaction mixture was heated to 90°C until all solids had dissolved (within 30 min). The solution was cooled to room temperature, and iodomethane (4.8 ml, 77.1 mmol) was added dropwise using a constant-pressure addition funnel. A precipitate formed and was dissolved by the addition of 30 ml additional DMAc. The mixture was then heated at 60°C for 1 h and precipitated into iced water (100 ml). The precipitate was collected by filtration, washed with methanol and dried at 100°C under vacuum. The crude product was purified by recrystallization from chloroform/hexane to yield 8.10 g (77%) of BAPB-SA-Me (melting point 221.7–221.9°C). ^1H n.m.r. ($CDCl_3$) δ (ppm) 2.9 (s, 6H), 3.3 (s, 6H), 7.0–7.6 (m, 16H).

Synthesis of N,N′*-dimethyl-4,4′-bis(4-aminophenoxy)-biphenyl (BAPB-Me).* In a 100 ml, three-necked, round-bottomed flask equipped with a magnetic stirrer, thermometer and condenser, BAPB-SA-Me (3.2 g, 5.8 mmol) was dissolved in H_2O (15 ml), phenol (1.68 g) and a 30 wt% solution of HBr in propionic acid (2.10 ml) at reflux. The reaction solution was heated at reflux for 24 h and precipitated into 100 ml of iced water. The precipitate was collected by filtration, washed with water and dried at 100°C under vacuum for 12 h. The crude product was purified by recrystallization from aqueous ethanol to yield 1.22 g (53%) of BAPB-Me (melting point 158.4–158.8°C). ^1H n.m.r. (C_6D_6), δ (ppm) 2.3 (s, 6H), 2.8 (b, 2H), 6.2–7.4 (m, 16H). Calculated for $C_{26}H_{24}O_2N_2$: C, 78.76%; H, 6.10%; N, 7.07%. Found: C, 78.96%; H, 5.96%; N, 7.14%.

Synthesis of N,N′*-di(methanesulfonyl)-2,2-bis(4-aminophenyl)hexafluoropropane (Bis-A-AF-SA).* By the procedure described for BAPB-SA, Bis-A-AF-SA was prepared from Bis-A-AF (10.0 g, 29.9 mmol) in 88% yield (melting point 256–258°C). ^1H n.m.r. ($O{=}C(CD_3)_2$), δ (ppm) 2.7 (s, 2H), 3.1 (s, 6H), 7.4 (s, 8H).

Synthesis of N,N′*-dimethyl-*N,N′*-di(methanesulfonyl)-2,2-bis(4-aminophenyl)hexafluoropropane (Bis-A-AF-SA-Me).* By the procedure described for BAPB-SA-Me, Bis-A-AF-SA-Me was prepared from Bis-A-AF-SA (10.0 g, 19.2 mmol) in 74% yield (melting point 173–175°C). ^1H n.m.r. ($CDCl_3$), δ (ppm) 2.9 (s, 6H), 3.4 (s, 6H), 7.4 (s, 8H).

Synthesis of N,N′*-dimethyl-2,2-bis(4-aminophenyl)-hexafluoropropane (Bis-A-AF-Me).* By the procedure described for BAPB-Me, Bis-A-AF-Me was prepared from Bis-A-AF-SA-Me (3.0 g, 5.8 mmol) in 48% yield (melting point 111–115°C). ^1H n.m.r. ($CDCl_3$), δ (ppm) 2.8 (s, 6H), 3.9 (b, 2H), 6.4–7.3 (q, 8H). Calculated for $C_{17}H_{16}F_6N_2$: C, 56.39%, H, 4.45%; N, 7.13%. Found: C, 56.60%; H, 4.41%; N, 7.40%.

Polymer synthesis

A clean, flame-dried, 100 ml, three-necked, round-bottomed flask fitted with a stopper, magnetic stir bar and two $CaCl_2$ drying tubes was cooled under a positive argon flow. The selected diamine and dry DMAc (20 ml) were added and stirred until all of the diamine had dissolved. The reaction flask was then lowered into a 0°C ice bath and allowed to equilibrate. The diacid chloride

(6F-DIAC) was added in three equal additions at 10 min intervals while the solution was rapidly stirred. The reaction flask was removed from the ice bath 30 min after the last addition of the diacid chloride and allowed to warm to ambient temperature. After 3 h, the reaction mixture was precipitated into a 10-fold excess of methanol. After drying for 12–14 h, the non-methylated polymers were redissolved in DMAc and reprecipitated into a 10-fold excess of water, filtered and washed with methanol (200 ml) for 2 h. The methylated polymers were reprecipitated from chloroform into a 10-fold excess of methanol and treated as above with methanol. All polymers were dried in a vacuum oven for 24 h at 100°C. Calculated for $C_{59}H_{36}F_6N_4O_8$ (N-Me-BAPB): C, 67.95%; H, 3.48%; N, 5.37%. Found: C, 65.79%; H, 3.38%; N, 5.12%. Calculated for $C_{50}H_{28}F_{12}N_4O_6$ (N-Me-Bis-A-AF): C, 59.53%; H, 2.80%; N, 5.55%. Found: C, 58.69%; H, 2.65%; N, 5.37%.

Polymer analysis

Viscosities of the non-methylated polymers were measured using a Cannon–Fenske 100 bore viscometer and solutions of 0.250 g dl^{-1} in DMAc at 25°C, while the methylated polymers were examined in a 50 bore viscometer with chloroform as solvent. Films of the copoly(imide amide)s were cast onto glass from DMAc at 70°C in an anhydrous environment. The *N*-methylated polymers were cast onto glass from chloroform at room temperature. Isothermal and water absorption data were collected on 2.5 cm diameter film samples. Isothermal ageing was performed at 350°C in air for 200 h. Water absorption samples were dried to a constant

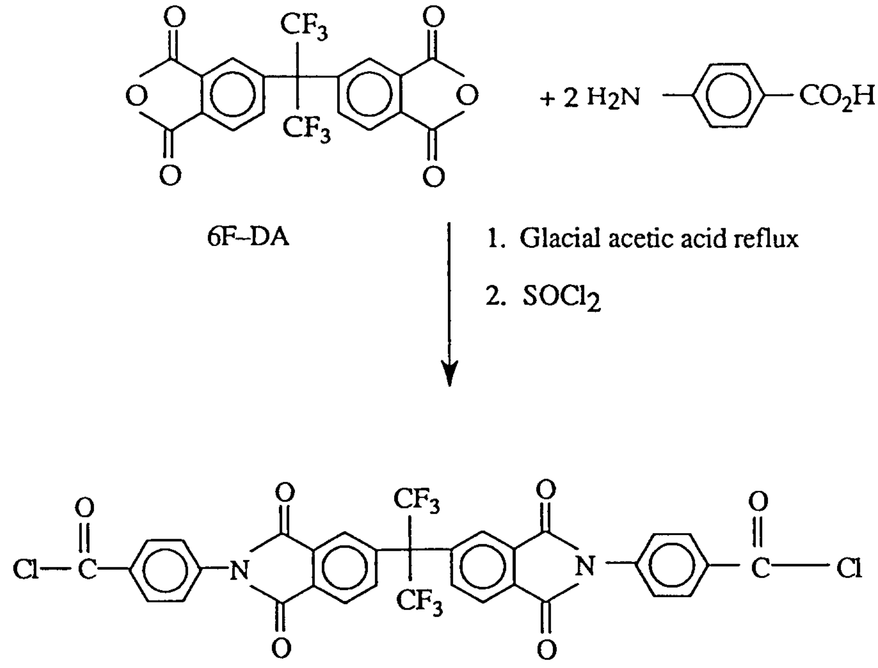

Figure 1 Preparation of 6F-DIAC

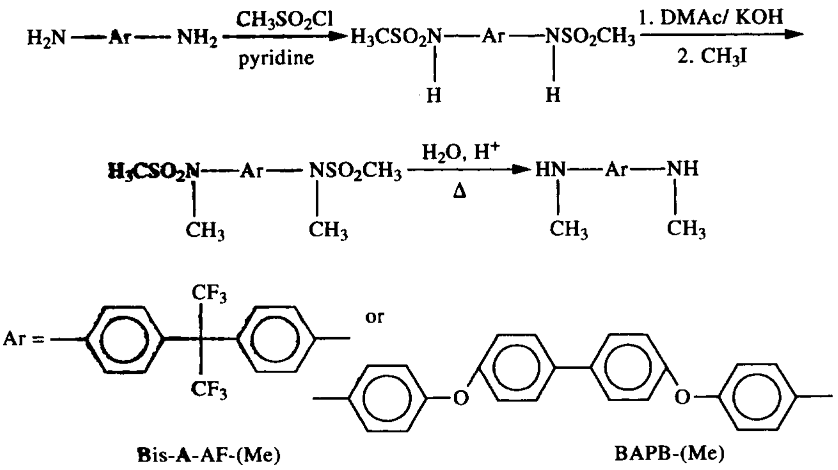

Figure 2 Synthesis of methylated diamines

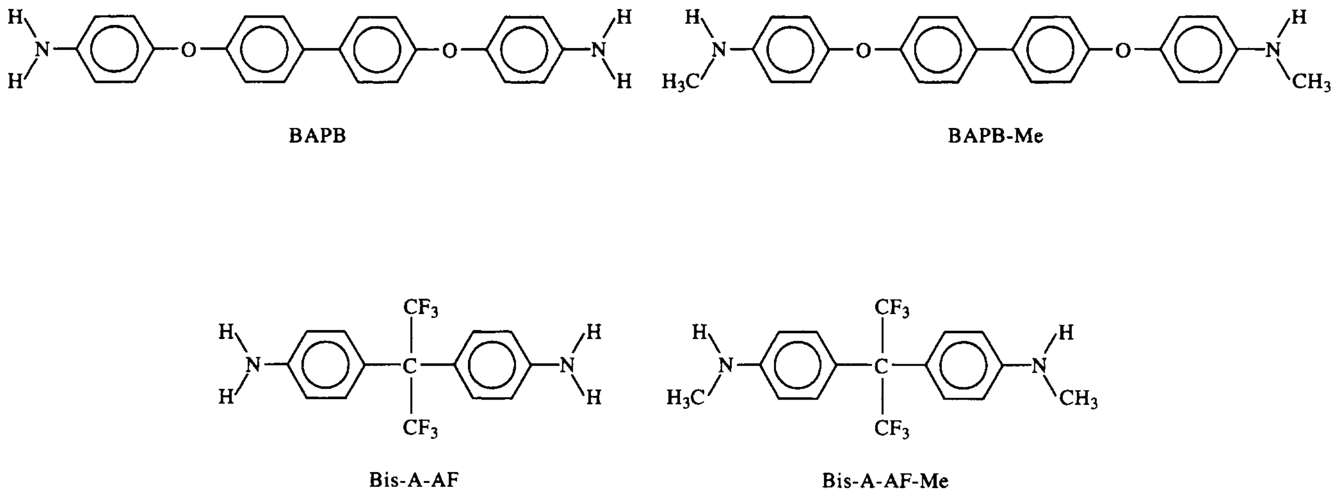

Figure 3 Diamine monomers

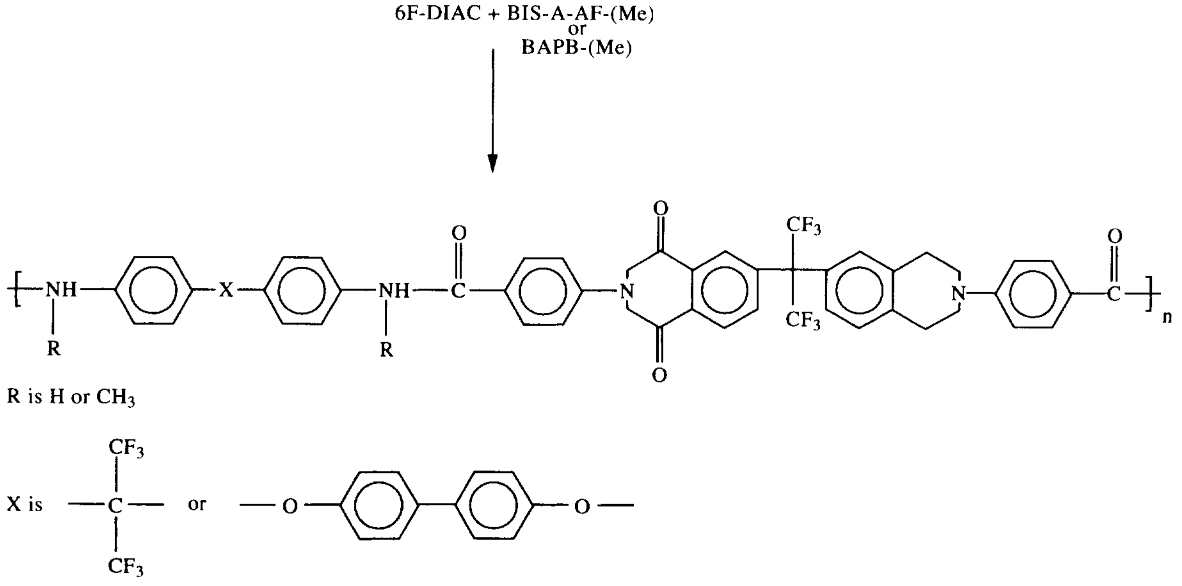

Figure 4 Preparation of the polyamides

Table 1 6F-DIAC derived poly(imide amide)s

Diamine	Yield (%)	Polymer viscosity[a] (dl g^{-1})	Temperature of 10% weight loss in air (°C)	Isothermal analysis: weight retention[b] (%)	Water absorption (wt%)	T_g/T_m (°C)
Bis-A-AF	86	1.17	460	66	0.37	–/–[c]
BAPB	88	2.26	464	40	0.35	297/–
Bis-A-AF-Me	92	0.28	468	84	0.16	246/360
BAPB-Me	76	0.41	463	48	0.18	240/420

[a] The base polymer viscosities were measured at 0.250 g dl^{-1} in DMAc; the methylated polymer viscosities were measured at 0.250 g dl^{-1} in chloroform

[b] Film samples tested in air at 350°C for 200 h

[c] Not found

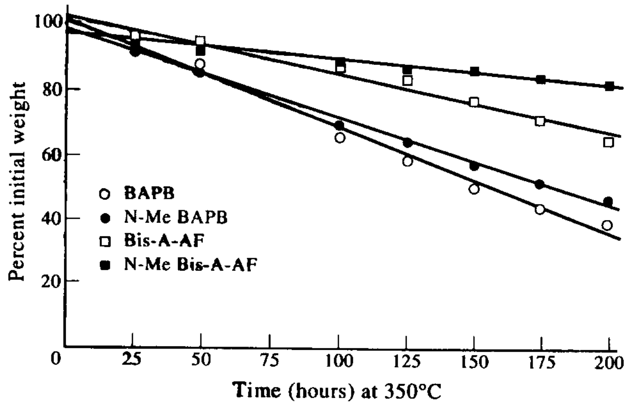

Figure 5 Isothermal ageing of film samples

weight in a 200°C oven, then immersed in deionized water to a constant weight (for around 24 h).

RESULTS AND DISCUSSION

Preparation and characterization of starting materials

The 6F-DIAC was prepared, as previously reported[14], by the condensation of the dianhydride (6F-DA) with 4-aminobenzoic acid and subsequent chlorination (*Figure 1*). The literature-prescribed reaction time of 96 h was reduced to 24 h without any effect on the yield of 6F-DIAC.

Alkylation of the diamines (*Figure 2*) using a methanesulfonamide intermediate was accomplished by a modification of the procedure reported by Greenwood *et al.*[11]. Dimethylacetamide (DMAc) was used as the solvent instead of hexamethylphosphoramide for the *N*-methylation step because of increased solubility of the diamines in this solvent.

The procedure for cleavage of the methanesulfonamide was also modified to use aqueous HBr in place of aqueous H_2SO_4 to hydrolyse the sulfonamide[15]. Yields were increased from 26% to 53%. See *Figure 3* for the monomer structures.

The infra-red spectra of both the diamine and the non-methylated sulfonamide showed a strong band at 3200 cm^{-1} attributed to the amine and sulfonamide hydrogens, respectively. The *N*-methylated sulfonamide showed no bands in this area other than the weak aromatic and aliphatic C–H stretches. The *N*-methylated amines showed a strong peak at 3500 cm^{-1} attributed to ν(N–H) in the secondary amines.

Polymer synthesis

The preparation of the polyamides (*Figure 4*) by amidation of the acid chloride proceeded well in DMAc at low temperature (0–25°C) to give good yields up to 92%. See *Table 1* for the properties of the new polymers. The higher-molecular-weight, non-methylated poly(imide amide) reaction mixtures became noticeably viscous during the first hour of the reaction. The reaction mixtures were precipitated into a 10-fold excess of water to give fibrous solids.

Polymer characterization

All polymers produced films that were creasable; those of the 6F-based diamines were colourless, while the BAPB-based polymers were a pale tan colour. The thermal stability data in *Table 1* (both the 10% weight loss temperature by t.g.a. and the isothermal weight retention data) indicate that the results from the dynamic method are nearly the same (460–468°C) for all four polymers. However, isothermal analysis showed that the methylated materials are superior to those containing the free amide functions. The isothermal ageing data are presented graphically in *Figure 5*, which shows that fluorine incorporation also improves stability. All samples were discoloured by isothermal ageing; the BAPB-based polymers became dark brown after 100 h in air at 350°C, and the 6F-based polymers became dark red after the same exposure.

The inherent viscosities of the non-methylated polymers are considerably higher than those of the methylated analogues. Higher molecular weights in the non-methylated series are probably obtained because of increased reactivity of the primary diamines over the sterically hindered, *N*-methylated secondary amines. In addition, hydrogen-bonding interactions, which cannot occur in the *N*-methylated polymers, probably also contribute to the observed difference in inherent viscosities. This absence of hydrogen bonding in the *N*-methylated polymers probably also accounts for their lowered T_g values compared to the BAPB-containing polymer (*Table 1*).

Film samples for water absorption studies reached constant weight after 24 h of exposure to liquid water at room temperature. The *N*-methylated polymers adsorbed less than 0.2 wt%, while the non-methylated versions adsorbed almost 0.4 wt%.

CONCLUSIONS

Highly soluble, *N*-methylated copoly(imide amide)s can be produced with low colour. Although the dynamic thermal stability of the series is not appreciably improved by *N*-methylation, the isothermal resistance is increased, and the water absorption is decreased.

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