New soluble polyimides prepared from 4,4′-(alkylenediyldioxy)dianilines

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New soluble aromatic polyimides have been prepared from 4,4′-(hexafluoroisopropylidene)bis(phthalic anhydride) (6FDA) and 4,4′-(alkylenediyldioxy)dianilines. Their structures were determined by i.r., ^{1}H n.m.r. and ^{13}C n.m.r. spectroscopic measurements, based on model compounds prepared by reacting 6FDA with *p*-anisidine. These polymers show low glass transition temperatures and good solubility in various solvents, and are stable up to 440°C in a nitrogen atmosphere.

(Keywords: polyimide; poly(amic acid); isomerism)

INTRODUCTION

Over the past few decades, polyimides have become attractive high-performance polymers as a result of their outstanding thermal stability, good radiation and chemical resistance, and excellent mechanical properties[1]. Polyimides have found many applications in microelectronics[1–4], and in the aircraft and space industries[1,5,6], and at the present time other studies of new applications in the field of separation techniques are currently in progress[7,8]. On the other hand, the presence of rigid aromatic moieties in the repeat unit, which are responsible for the majority of the above mentioned properties, render many of the polyimides infusible and insoluble in common solvents. This complicates their processability, so that these polymers are therefore usually processed at their precursor (poly(amic acid)s, or derivatives) stage. One of the few ways of improving the processability of fully cyclized thermoplastic polyimides is the incorporation of a short flexible chain between the stiff aromatic or heterocyclic sequences of the repeat unit[9]. We have previously reported the preparation of new poly(pyromellitimide)s based on 4,4′-(alkylenediyldioxy)dianiline[10] (DA-*n*) where $n \leqslant 10$. These polymers showed lower T_g values when compared with other poly(pyromellitimide)s, but they were insoluble in all solvents, with the exception of mineral acids.

Polyimides prepared from monomers containing hexafluoroisopropylidene groups, such as 4,4′-(hexafluoroisopropylidene)bis(phthalic anhydride) (6FDA), are attractive materials because of their high transparency, low dielectric constant, low moisture absorption, resistance to photochemical degradation, good solubility and gas permeation properties[11–15]. On the other hand, 6FDA is less reactive in the acylation of amines than pyromellitic dianhydride (PMDA) and gives polyimides with lower molecular weights[16], with the latter being strongly dependent on the diamine monomer that is used. According to the literature[15,16] these values vary over a wide range and the conditions of the polyaddition reaction may also be difficult to optimize. The structures of some of these fluorinated polyimides and their precursors, namely poly(amic acid)s (PAAs), have been studied by ^{13}C n.m.r. spectroscopy, including an estimate of the population of the amic acid isomers[17]. These isomers differ in reactivity, and probably also in hydrogen bonding and their solvent complexation behaviour[17–19].

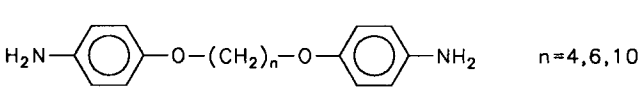
In this paper, we have used 6FDA as the dianhydride component in the polymerization reaction with various 4,4′-(alkylenediyldioxy)dianilines (see *Scheme 1*) in order to improve solubility while still retaining a relatively low glass transition temperature. Model compounds of both diamic acid and diimide were also prepared from 6FDA and *p*-anisidine in order to assist in the detailed characterization of the polymers by ^{1}H and ^{13}C n.m.r. and by i.r. spectroscopic methods.

EXPERIMENTAL

Materials

4,4′-(Hexafluoroisopropylidene)bis(phthalic anhydride) was purchased from TCI, and was used as received. *N*,*N*-dimethylformamide (DMF) was dried by azeotropic distillation with benzene and BaO and was then distilled at reduced pressure.

4,4′-(Alkylenediyldioxy)dianilines (DA-n). The synthesis of these compounds, but without any characterization of the products produced, has been published previously[10].



DA-n

Scheme 1

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Their melting points, yields and elemental analyses are summarized in *Table 1*, the characteristic i.r. bands are shown in *Table 2*, and the characteristic ^{1}H n.m.r. peaks are summarized in *Table 3*.

Poly(amic acid)s. To a solution of diamine in DMF, an equimolar amount of 6FDA was added with vigorous (magnetic) stirring, under argon at 20°C; the total monomer content was 15 wt%. After 40 h, the poly(amic acid) was precipitated in water and then dried.

Polyimides. The solid-state imidization reaction was carried out at 0.5 mmHg and 200°C for 2 h, followed by a further 5 min at 250°C.

Model compounds. To a solution of 4.5 mmol of *p*-anisidine in 6 ml of DMF, 2.25 mmol of 6FDA were added and the mixture was stirred under argon at 25°C for 40 h. The diamic acid (MMA) was precipitated by pouring the mixture into water. The MAA was heated (at 0.5 mmHg) at 100°C for 60 min, and then at 200°C for a further 90 min, to give 2.95 g (95% yield) of the diimide (MI) as a yellow powder (m.p. = 145°C). Elemental analysis: $C_{33}H_{20}F_6N_2O_6$ (654.53) requires C 60.55, H 2.92, N 4.32%; found C 60.20, H 3.08, N 4.28%.

Methods

N.m.r. spectroscopy. All of the n.m.r. spectra were recorded on a Bruker ACF-300 spectrometer, at resonance frequencies of 300.1 MHz for the ^{1}H and 75.5 MHz for the ^{13}C measurements. Dimethyl sulfoxide (DMSO)-d_6, dried over molecular sieve was used as the solvent. Most samples were measured as 10% (wt/vol) solutions, with the model compounds at ambient temperature and the polymers at 70°C. In the case of the polyimide PI-4 (see later), a homogeneous solution could not be produced after prolonged heating, so a 1% (wt/vol) solution was therefore prepared and measured at ambient temperature. Hexamethyldisiloxane ($\delta = 0.05$ ppm for ^{1}H and 2 ppm for ^{13}C) was used as the internal reference; the δ values given below were recalculated to the tetramethylsilane (TMS) reference. For the ^{1}H n.m.r. spectra, the pulse angle was 30°, with a pulse interval of 4.7 s. All of the ^{13}C n.m.r. spectra were recorded with the *J*-modulated spin-echo (APT) technique, using a ^{13}C relaxation delay of 20 s (10 s in the case of sample PI-4) and a refocusing delay of 8 ms for differentiating between the carbons with either an even (or zero) or an odd number of bound hydrogens. The long-range ^{1}H–^{13}C COSY (COLOC) spectrum[20] was measured at room temperature with 8192 points and 128 increments, 720 scans each, with zero filling up to 256 points in F1. The relaxation delay used was 1 s, with the two other delays in the sequence (antiphase coherence evolution and refocusing) being 20 and 30 ms, respectively. Sinebell weighting functions were used before Fourier transformation in both dimensions.

Infra-red spectroscopy. Infra-red spectra were measured by the KBr technique using a Perkin–Elmer 580-B spectrometer, connected on-line with a Tracor TN 4000 data analyser.

Viscometry. Viscometric measurements were made at 25°C by using an Ubbelohde viscometer. Intrinsic viscosities [η] were calculated by extrapolation from the data obtained for samples at five different concentrations[21].

Thermal analysis. Differential scanning calorimetry (d.s.c.) and thermogravimetric analysis (t.g.a.) were carried out by using Perkin–Elmer DSC-7 and TGA-7 instruments, respectively, with a heating rate in nitrogen of 10°C min^{-1} in both cases.

RESULTS AND DISCUSSION

Preparation of monomers and polymers

The 4,4′-(alkylenediylidioxy)dianilines (DA-*n*) were synthesized by the reaction of sodium 4-nitrophenolate with α,ω-dibromoalkanes and subsequent reduction of the nitro group. The respective nitro compounds were catalytically hydrogenated with PtO_2[10]. This method leads to higher yields than the corresponding reduction carried out with hydrazine hydrate in the presence of Raney nickel[22].

Table 1 Characteristics of 4,4′-(alkylenediyldioxy)dianilines

Code	*n*[a]	M.p. (°C)	Yield (%)		Elemental analysis (%) C	H	N
DA-4	4	137	50	Calcd	70.76	7.40	10.24
				Found	70.58	7.55	10.13
DA-6	6	135	52	Calcd	71.97	8.05	9.33
				Found	72.00	8.03	9.09
DA-10	10	117	51	Calcd	74.12	9.05	7.86
				Found	73.62	9.16	7.64

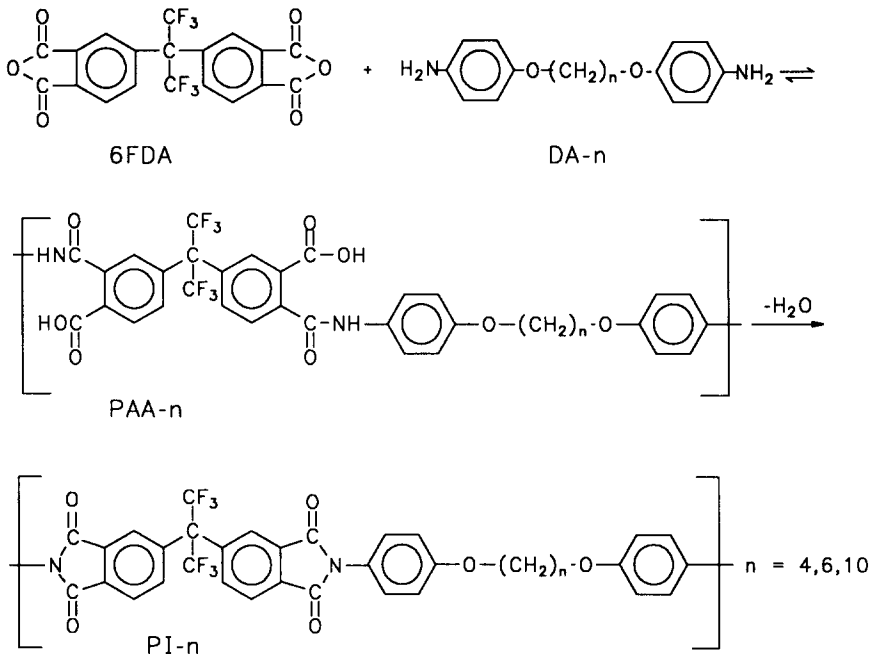
[a] Number of CH_2 groups (see *Scheme 1*)

Table 3 Chemical shifts (ppm) in the ^{1}H n.m.r. spectra of 4,4′-(alkylenediyldioxy)dianilines

Code	C_6H_4		NH_2	CH_2 protons 1′	2′	3′	4′, 5′
DA-4	6.63(d)	6.50(d)	4.58(s)	3.84(t)	1.70(m)	–	–
DA-6	6.63(d)	6.52(d)	4.58(s)	3.80(t)	1.65(m)	1.42(m)	–
DA-10	6.62(d)	6.50(d)	4.57(s)	3.78(t)	1.62(m)	1.37(m)	1.34(m)

Table 2 Characteristic bands (cm^{-1}) in the i.r. spectra of 4,4′-(alkylenediyldioxy)dianilines

Code	ν_{NH} (amide)	ν_{CH} (aromatic)	ν_{sCH} (aliphatic)	δ_{NH} (amine)	$\nu_{C=C}$ (aromatic)	ν_{COC} (ether)	ρ_{CH_2} (aliphatic)
DA-4	3395	3015	2875	1650	1510	1230	715
DA-6	3400	3010	2860	1640	1510	1235	720
DA-10	3405	3010	2850	1635	1510	1230	720



Scheme 2

Table 4 Yields and compositions of the polyimides PI-*n*

Polymer	Yield (%)		Elemental analysis (%) C	H	N
PI-4	97	Calcd	61.71	3.25	4.12
		Found	61.11	3.09	4.02
PI-6	92	Calcd	62.89	3.43	3.96
		Found	61.86	3.51	3.56
PI-10	95	Calcd	64.39	4.75	3.66
		Found	63.56	4.60	3.54

The polyimides (PI) were prepared by the usual two-step procedure from diamines and dianhydrides via poly(amic acid)s (PAAs) as precursors (see *Scheme 2*, where only one of the three possible isomeric structures of PAA (amide and hexafluoroisopropylidene groups in mutual *meta* or *para* positions) is shown).

The poly(amic acid)s are film-forming and quite soluble in alcohols, tetrahydrofuran and polar aprotic solvents. The solid-state imidization of poly(amic acid)s to the corresponding polyimides was carried out under reduced pressure in order to facilitate removal of water and traces of dimethylformamide, thus preventing hydrolysis[23] and transamidation reactions[24]. The reaction yields and compositions of the various polyimides are summarized in *Table 4*. The differences between the calculated and experimental elemental analysis data are comparable with those reported for other polyimides[25,26].

Chemical structure

Owing to the insolubility of many polyimides in common solvents, infra-red spectroscopy has been used almost exclusively for their routine characterization[27,28]. On the other hand, the good solubility of 6FDA-based polyimides makes it possible to also apply modern methods of high-resolution liquid-state n.m.r. spectroscopy, and thus to determine the detailed structures of all of the compounds being discussed here. In this work, the various assignments in the i.r. and n.m.r. spectra were based on comparisons with the spectra of the 6FDA–*p*-anisidine model compounds.

^1H n.m.r. spectra. The spectrum of the amic acid (MAA) model compound in *Figure 1a* shows in (addition to the DMSO solvent peak at 2.40 ppm, the strong peaks due to residual DMF at 2.65 and 2.80 ppm, and the OCH_3 peak at 3.68 ppm) the peak of amide NH at 9.98 ppm and the very broad band of COOH protons centred at ~12 ppm. In the aromatic range, the diagnostically important peaks are marked by arrows. The characteristic pattern of the aromatic protons of the anisidine ring appears as part of an AA'BB' system at 6.83 ppm; the second part of this system overlaps the complicated multiplet (7.3–8.1 ppm) of the 2,5,6 protons (for numbering see *Scheme 3*) of the 6FDA part of the molecules. The methine proton peak of residual DMF should also be concealed within this multiplet.

In the spectrum of the imide (MI) model compound in *Figure 2a*, the amide NH and COOH peaks of the *o*-carboxybenzamide groups have disappeared (as well as those of residual DMF). The peaks in the aromatic part of the spectrum are shifted so as to show clearly all proton signals of the *p*-anisidine ring, approximating to two doublets (with a spacing of 8.5 Hz) at 7.00 and 7.29 ppm. The protons of the 6FDA moiety of the MI are assigned on the basis of their coupling pattern, with protons 2 at 7.72 ppm (s), 6 at 7.87 ppm (d, 8 Hz), and 5 at 8.04 ppm (d, 8 Hz).

As can be seen in *Figures 1b–d* and *2b–d*, the general features of the spectra of the model compounds are reflected in the spectra of the polymeric products. In the spectra of the polyimides (PI), the NH and COOH bands are missing, and the aromatic protons of the diamine part show the typical two doublets that are observed in the imide model compound. Imidization of the precursor PAA is thus clearly proven in all cases. The somewhat more complicated pattern of the aromatic protons in the

6FDA units of all of the PI samples probably reflects certain specific details of their structures which will be discussed below in connection with their ^{13}C n.m.r. and i.r. spectra. The chemical shifts of the aliphatic protons in the PAA and PI products are summarized in *Table 5*.

^{13}C n.m.r. and ^{13}C–^{1}H 2D n.m.r. spectra. The ^{13}C n.m.r. spectrum of the MAA model compound in *Figure 3a* shows (in addition to the peaks of residual DMF at 28.8 and 35.8 ppm, and OCH_3 at 55.2 ppm) characteristic peaks in the low-field range. These could be assigned by using the ^{13}C–^{1}H 2D COSY (COLOC) technique (*Figure 4*): in substituted aromatic rings this produces cross-peaks, in addition to ^{1}J, predominantly by ^{3}J interaction, which is of the order of ~7 Hz[29]. The multiplet of

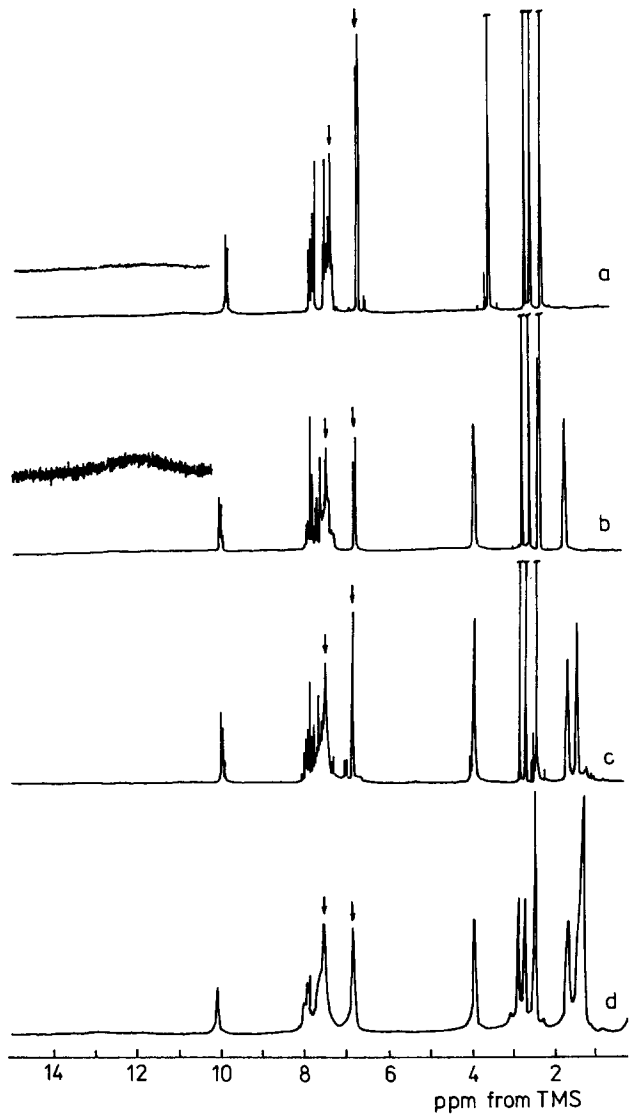


Figure 1 ^{1}H n.m.r. spectra of amic acids: (a) MAA model compound; (b) PAA-4; (c) PAA-6; (d) PAA-10

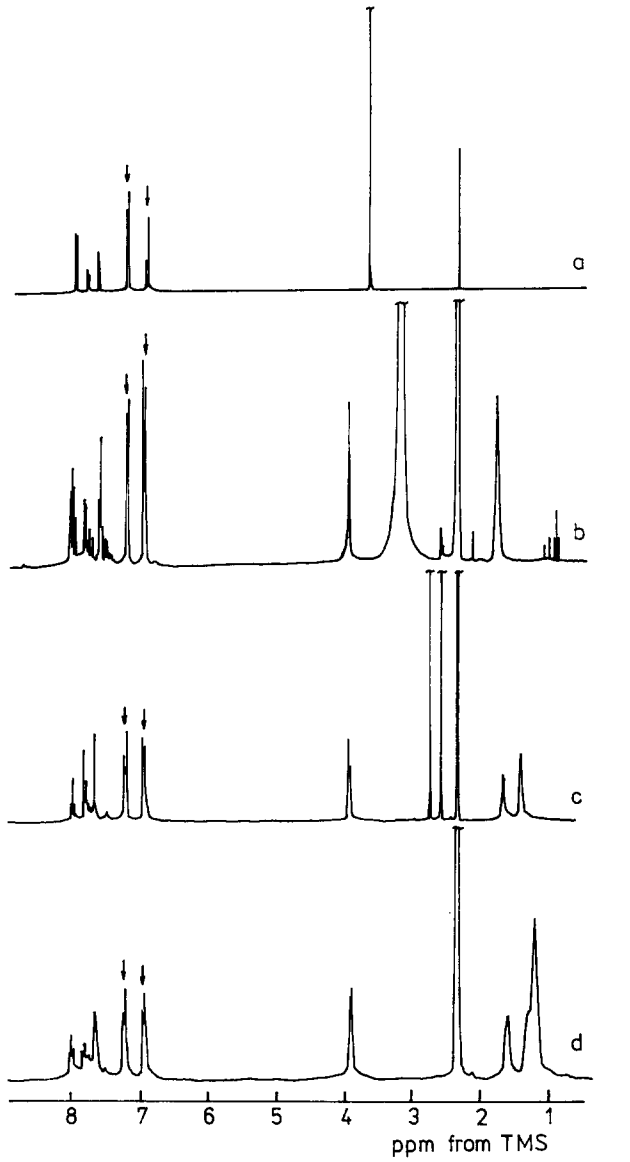
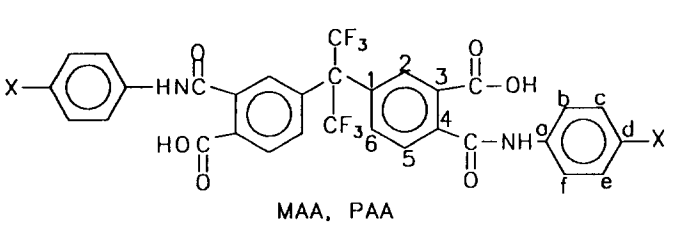
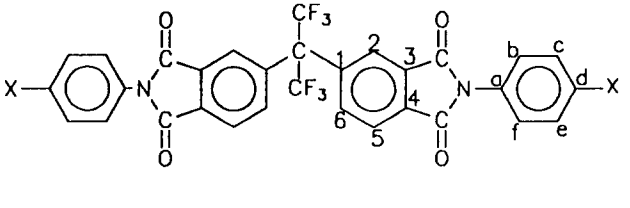


Figure 2 ^{1}H n.m.r. spectra of imides: (a) MI model compound; (b) PI-4; (c) PI-6; (d) PI-10 (there were no measurable peaks below 9 ppm)



X = OCH_3 (MAA, MI),



O-CH_2-CH_2-CH_2-CH_2-CH_2- (PAA, PI)
1′ 2′ 3′ 4′ 5′

Scheme 3

Table 5 ^{1}H n.m.r. chemical shifts (ppm) for 6FDA/DA-*n* poly(amic acid)s (PAA-*n*) and polyimides (PI-*n*) (for numbering see *Scheme 3*)

	n					
	PAA			PI		
Proton	4	6	10	4	6	10
1′	3.97	3.91	3.89	4.14	4.08	4.05
2′	1.81	1.67	1.66	1.97	1.82	1.76
3′	–	1.48	1.24	–	1.57	~1.40
4′,5′	–	–		–	–	1.31

aromatic protons at 6.83 ppm can be identified as that of b, f by giving a ^1J cross-peak with the ^{13}C signal at 113.7 (b, f carbons), and a ^3J cross-peak with the ^{13}C signal at 132.5 ppm (d carbon). The carbon peak at 155.5 ppm is identified as that of the a carbon by giving a ^3J cross-peak with the c, e proton multiplet at 7.55 ppm, which in turn gives a ^1J cross-peak with the ^{13}C signal at 121.1 ppm (c, e carbons). The 2D experiment has also made it possible to give a detailed assignment of the fine structure of the aromatic proton signals in the ^{1}H n.m.r. spectrum of the 6FDA moiety of MAA, which reflects the possible *p* and *m* isomeric structures of the amic acid (*Scheme 4*). This assignment was partly based on the fact that the protons in position 5, being the farthest from the fluorine atoms, give the sharpest peaks. Therefore, the sharp proton doublet (8 Hz) at 8.03 ppm gives a cross-peak with the carbon signal at 139.4 ppm, corresponding to a ^3J interaction between proton 5 and carbon 3 in a *m*-type ring. The carbon signal at 140.2 ppm gives ^3J cross-peaks with both the broadened proton singlet at 7.83 ppm and the broadened proton doublet (8 Hz) at 7.63 ppm, corresponding to a ^3J interaction between carbon 4 and protons 2 and 6 in a *p*-type ring. The two sharp (8 Hz) doublets at ~7.7 ppm give cross-peaks with the carbon signals at 132.5 and 128.3 ppm, respectively, by a ^3J interaction between proton 5 and carbons 1 and 3 in the *p*-type rings. (Proton 5p is sensitive to *p*- or *m*-substitution in the other ring of the 6FDA unit.) The broadened proton singlets at 7.35 and 7.40 ppm, as well as the 5p proton doublets, give a ^3J cross-peak with the carbon signal at 165.9 ppm, identifying the amide carbonyl carbon and the 2m proton in the *mm* and *mp* molecules. The 2p proton singlet at 7.8 ppm gives a ^3J cross-peak with the carbon signal at 166.5 ppm, thus identifying the latter as that of the carboxyl carbon. By integration of the ^{1}H n.m.r. spectrum of protons 2 and 5, the substitution preference could be accurately determined, with the populations of the *pp*, *pm* and *mm* molecules equal to 0.5, 0.4, and 0.1, respectively; within experimental error, this corresponds to a random distribution with $p{:}m = 0.7{:}0.3$.

In the ^{13}C n.m.r. spectrum of the MI model compound in *Figure 5a*, the peaks of the c, e and b, f aromatic carbons are shifted to 114.2 and 128.8 ppm, respectively, the peak of the d carbon to 124.2 ppm and the a carbon to 159.1 ppm. The peaks of the amide substituted carbons of the MAA model compound at ~140 ppm are missing (at the position indicated by the arrow), thus proving complete imidization. The carbons 3 and 4 in the imidized 6FDA unit resonate at 132.7 and 133.1 ppm, respectively, with carbon 1 at 137.3 ppm. The protonated carbons give peaks at 123.6 (2), 124.3 (5) and 135.8 ppm (6) (for numbering see *Scheme 3*). The imide carbons attached to positions 3 and 4 are very closely spaced at 166.26 and 166.38 ppm.

The ^{13}C n.m.r. spectra of the poly(amic acid)s (*Figures 3b–d*) show all the characteristic peaks of the MAA model compound. In addition, the pattern of the 6FDA aromatic carbons is somewhat more complicated and peaks of additional carbonyl carbons appear at 167.1 and 167.8 ppm. These correspond to carboxyl carbons in hydrolysed 6FDA. The presence of these carboxyl groups, which are probably produced by the hydrolysis of anhydride end-groups[30] during the isolation of PAA, may suggest lower molecular weights for the polymers, an effect which might also indicate the non-optimum conditions of the polyaddition reaction.

In the ^{13}C n.m.r. spectra of the polyimides (*Figures 5b–d*), the major peaks are fully analogous to those of the MI model compound, proving again complete imidization and the absence of any groups typical of PAA. Similar to those seen in the PAA spectra, weak peaks of carboxyl carbons are detectable at 167.1 and 167.7 ppm.

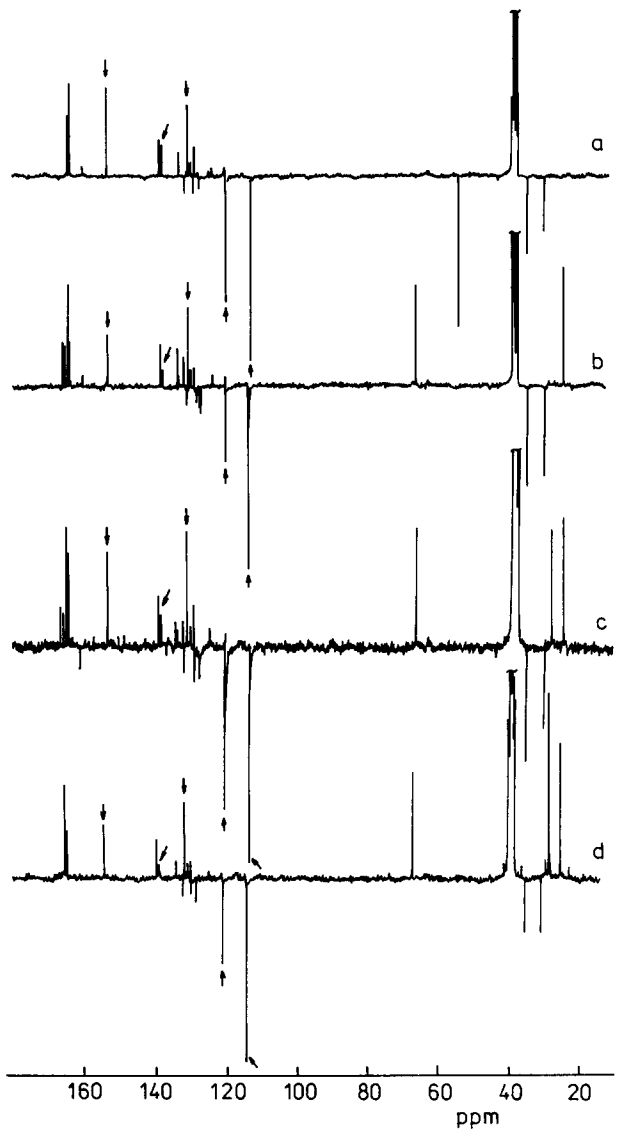


Figure 3 ^{13}C APT n.m.r. spectra of amic acids: (a) MAA model compound; (b) PAA-4; (c) PAA-6; (d) PAA-10

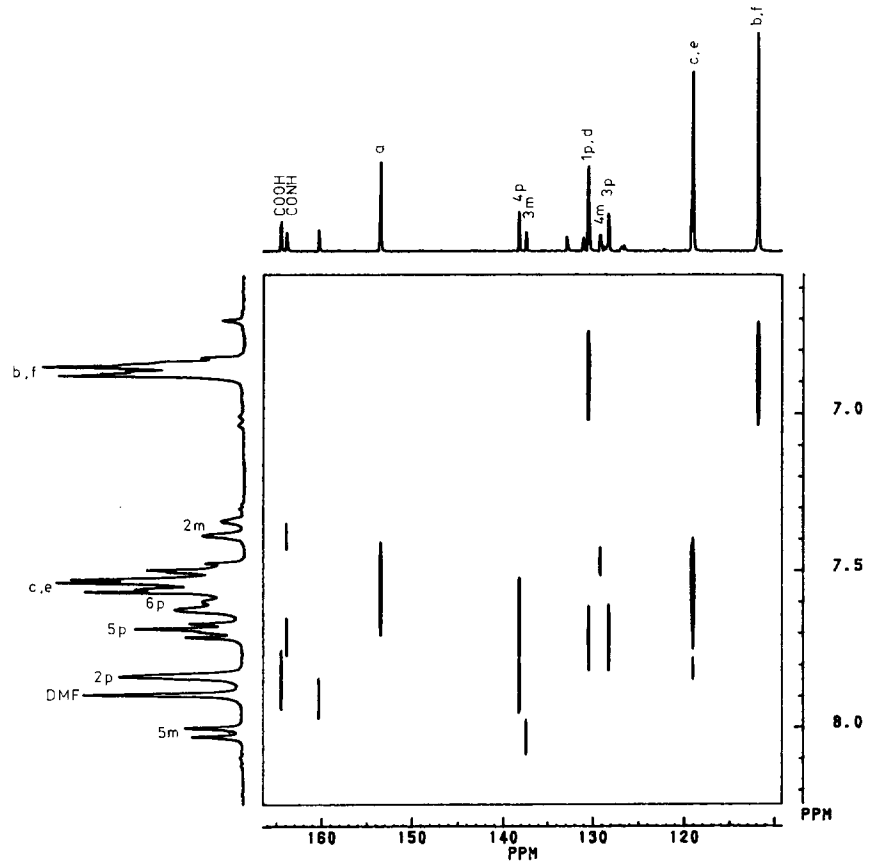
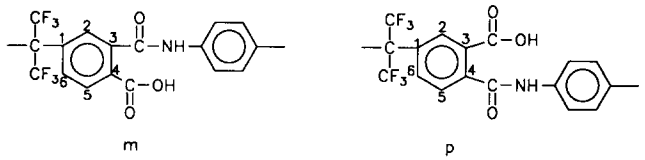


Figure 4 Long-range ^{1}H–^{13}C COSY (COLOC) n.m.r. spectrum of the diamic acid (MAA) model compound



Scheme 4

I.r. spectra. The infra-red spectra of the MAA and MI model compounds are shown in *Figures 6a* and *7a*, respectively. Both of the compounds studied show strong characteristic bands in the range from 1150 to 1300 cm^{-1}, corresponding to CF_3 stretching vibrations; bands characteristic of carboxyl, amide and imide structures appear in the range from 1500 to 1800 cm^{-1}. The characteristic peaks of the amic acid and imide structures are identified in *Figures 6* and *7* by arrows. MAA is characterized by one strong band at 1727 cm^{-1}, assigned to the C=O stretching vibration of a carboxyl group, two strong bands at 1655 and 1545 cm^{-1}, assigned to amide group vibrations (often designated as Amide I and Amide II), and the band at 1416 cm^{-1}. The broad absorption in the range from 2200 to 3700 cm^{-1} corresponds to the stretching vibrations of mutually hydrogen bonded amidic NH and OH groups. After imidization of the diamic acid (MAA) model compounds, the amide bands at 1655 and 1545 cm^{-1} disappear, as well as the band at 1416 cm^{-1} and the broad absorption between 2200 and 3700 cm^{-1}. In the spectrum of the MI imide there appear typical bands at 1726 and 1785 cm^{-1}, assigned to the stretching vibrations of C=O groups bound in a five-membered imide ring. There are almost no differences in the wavenumbers of all of the characteristic bands observed in MI when compared with the non-fluorinated polyimides or their corresponding model compounds.

The infra-red spectra of the poly(amic acid)s are shown in *Figures 6b–d*. The spectra of these polymers differ from those of the low-molecular-weight model compound mainly by the increased intensities of the bands in the 2800–3000 cm^{-1} range, because in the case of the polymers this range contains the bands of the asymmetrical and symmetrical stretching vibrations of the CH_2 groups in the aliphatic chain. The infra-red spectra of the precursors show the characteristic bands of MAA: the carboxyl C=O band at 1728 cm^{-1}, the amide bands at ~1660 and 1545 cm^{-1}, and the band at 1416 cm^{-1}, as well as the broad bands between 2200 and 3700 cm^{-1}, which are assigned to NH and OH vibrations of hydrogen-bonded amide and carboxyl groups.

After imidization of the PAA (*Figures 7b–d*) the absorption at ~ 1660 cm^{-1} is reduced, the bands at 1545 and 1416 cm^{-1} disappear, and the absorption between 2200 and 3700 cm^{-1} is also reduced. In the spectra of the polyimides there appears a new band at 1785 cm^{-1}, which as in the case of MI is similarly assigned to vibrations of the C=O groups in the imide ring. Imidization of the PAA is therefore also proven by infra-red spectroscopy, in accord with the n.m.r. results. The spectra of the PI materials exhibit additional weak bands, with the most remarkable of these being the weak band at 1857 cm^{-1}, indicating the presence of small amounts of anhydride structures, and the bands corresponding to residual DMF.

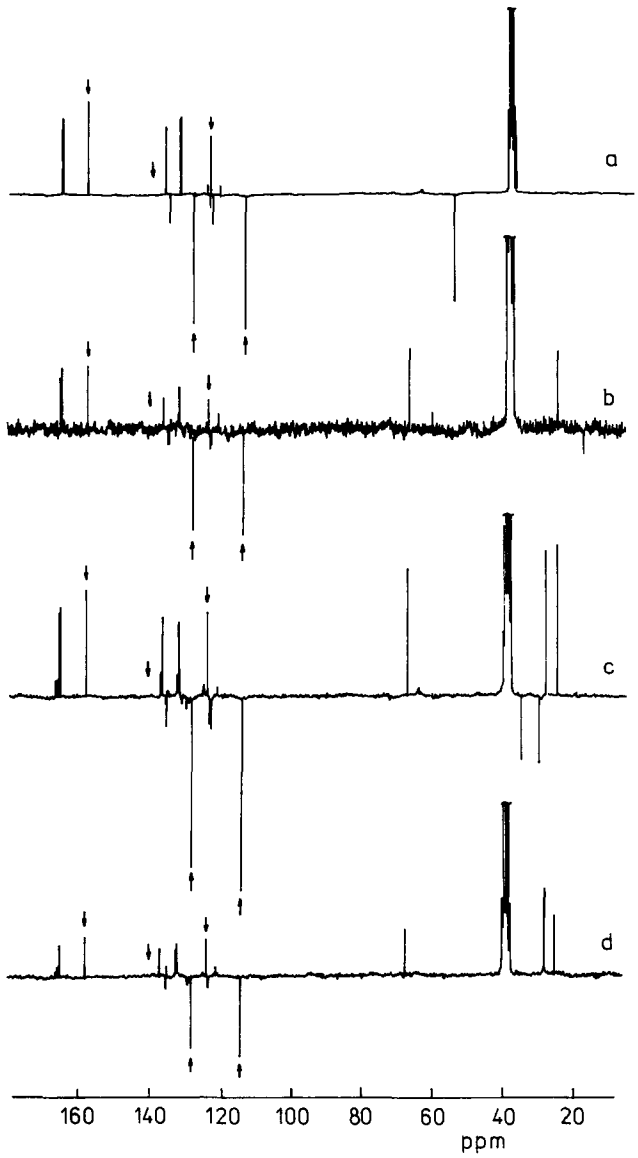


Figure 5 ^{13}C APT n.m.r. spectra of imides: (a) MI model compound; (b) PI-4; (c) PI-6; (d) PI-10

Some properties of the polyimides

The polyimide powders where $n=4$ and 10 are yellow, while the powder where $n=6$ is brownish; all polyimides are soluble in tetrahydrofuran and polar aprotic solvents. Only in the case of PI-10 (6FDA/DA-10) was the solubility in dimethyl sulfoxide at room temperature limited to 1 g l^{-1}. Films can be prepared for all of these presently described PI (6FDA/DA-*n*) materials by casting from DMF solution. The intrinsic viscosities (*Table 6*) are comparable with those of other 6FDA-based polyimides[15].

The results of thermal analysis of our 6FDA/DA-*n* polyimides are also shown in *Table 6*. Compared to other types of polyimides[9], these have very low and well pronounced glass transition temperatures (T_gs), as measured by d.s.c. The corresponding polyimides prepared from pyromellitic dianhydride and 4,4'-(alkylenediyldioxy)-dianiline[10] exhibited T_g values which were some 40–60°C higher than those reported here, while other polyimides based on 6FDA have T_gs which are usually above 230°C[15].

The thermal stability of the polyimides based on 6FDA and DA-*n*, measured using t.g.a. (in a nitrogen atmosphere), is comparable with the thermal stability of DA-*n*-based poly(pyromellitimides)[10]. Compared with highly aromatic polyimides without any flexible linkages[31], the polymers described here decompose at temperatures which are lower by about 50–150°, but nevertheless the thermal stability is still better than in many other polyimides or high-performance polymers[32].

Table 6 The intrinsic viscosity [η], glass transition temperature T_g, and temperatures for 5% (T_5) and 10% (T_{10}) weight losses of the PI-*n* polyimides

Polymer	[η] (dl g^{-1})	T_g (°C)	T_5 (°C)	T_{10} (°C)
PI-4	0.36	169	452	470
PI-6	0.40	167	450	467
PI-10	0.42	143	442	460

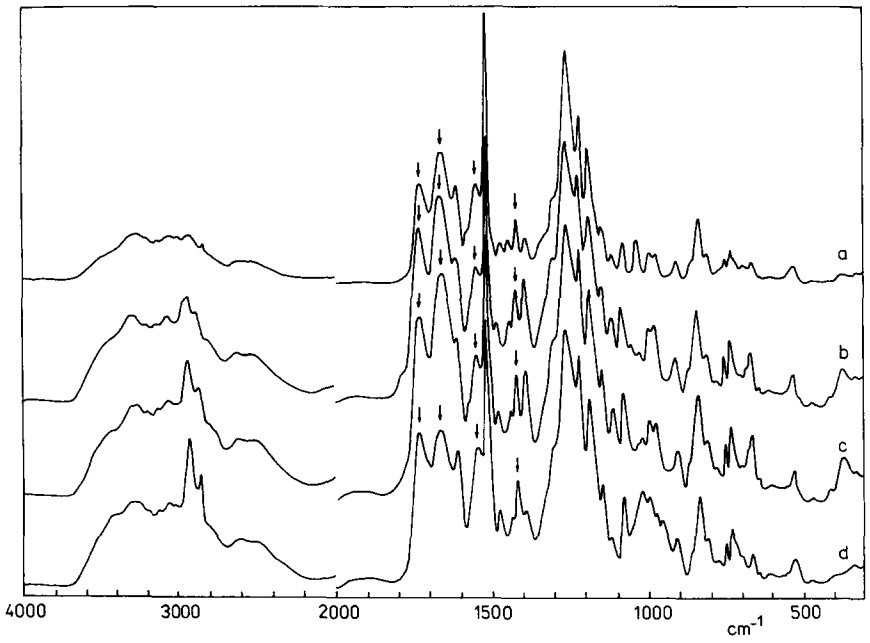


Figure 6 I.r. spectra of amic acids: (a) MAA model compound; (b) PAA-4; (c) PAA-6; (d) PAA-10

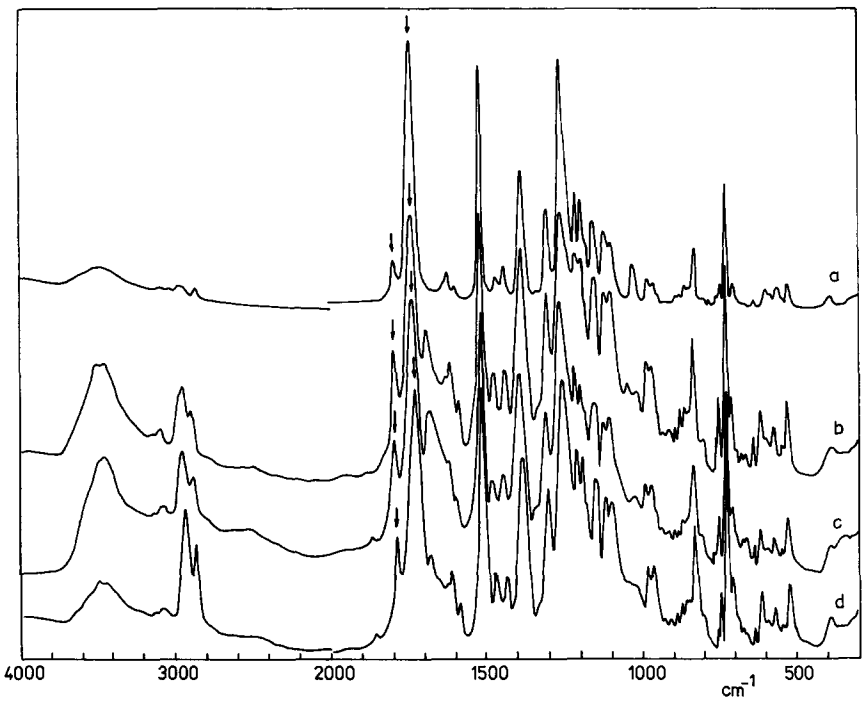


Figure 7 I.r. spectra of imides: (a) MI model compound; (b) PI-4; (c) PI-6; (d) PI-10

Based on the above established spectroscopic characteristics, the detailed structure of these polyimides in relation to the synthetic procedures that are employed in their production will be the subject of a forthcoming communication.

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