Synthesis and characterization of a linear CARDO polyimide from (5,5'-bisisobenzofuran)-1,1',3,3'-tetrone and 4,4'-(9*H*-fluoren-9-ylidene)bisphenylamine

Nathalie Biolley, Martine Grégoire, Thierry Pascal and Bernard Sillion
CEMOTA/UMR 102, CNRS-IFP, BP 3, 69390 Vernaison, France

(Received 2 March 1990; revised 18 July 1990; accepted 26 July 1990)

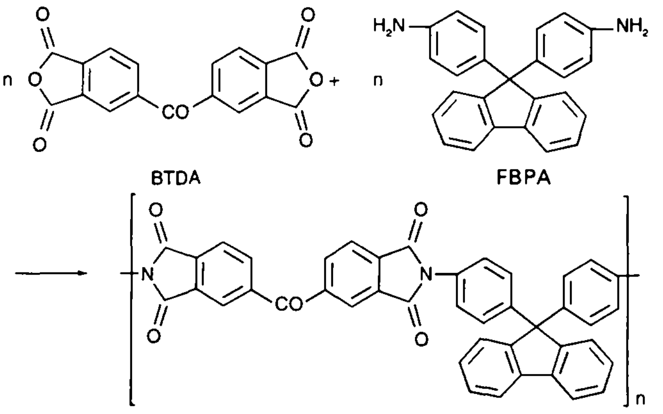
Starting from an aromatic diamine, 4,4'-(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA), we have synthesized a series of linear polyimides by polycondensation with different molar proportions of (5,5'-bisisobenzofuran)-1,1',3,3'-tetrone (BTDA). The polymers were anhydride end-capped or phenylimide end-capped. Owing to the presence of lateral fluorene groups (CARDO structure), the fully cyclized FBPA/BTDA polyimides exhibited good solubility in many solvents such as *N*,*N*-dimethylformamide, *N*-methylpyrrolidone, *m*-cresol, dimethylsulphoxide and *N*,*N*-dimethylacetamide. A detailed study of the FBPA/BTDA chemical structure and molecular weight was performed by ^{13}C nuclear magnetic resonance and size exclusion chromatography. The thermal and mechanical properties of polymer films were then investigated. The glass transition temperature determined from thermomechanical analysis ranged from 350 to 380°C and the Young's modulus measured from tensile tests was about 2.5 GPa at room temperature and 1.7 GPa at 200°C. Thermogravimetric analyses and water uptake determination showed the high decomposition temperature, near to 400°C under argon, and the low water absorption (lower than 1 wt%) of the FBPA/BTDA polyimides.

(Keywords: 4,4'-(9*H*-fluoren-9-ylidene)bisphenylamine; (5,5'-bisisobenzofuran)-1,1',3,3'-tetrone; linear polyimide; CARDO polymeric structure)

INTRODUCTION

The search for high-performance materials for electronic or structural applications requires the use of easily processable thermostable polymers with high glass transition temperature (T_g) and low water absorption. Standard polyimides represent a large field of investigation, but are generally poorly soluble in most organic solvents. Non-classical polyimide structures containing at least one bulky cyclic side-group in the repeat unit were reported by Korshak and coworkers[1] in the 1970s. These polymers, termed CARDO polyimides, showed promising properties such as very high T_g (300–350°C), high thermomechanical resistance and good solubility characteristics due to the steric hindrance caused by the presence of bulky lateral groups on the polymer backbone.

This paper deals with the study of a CARDO polyimide prepared by polycondensation between (5,5'-bisisobenzofuran)-1,1',3,3'-tetrone (BTDA) with 4,4'-(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA). The reaction was conducted in *N*-methylpyrrolidone (NMP) solution, with different molar proportions of both monomers. Polymerizations with subsequent addition of aniline were realized to transform anhydride chain ends into phenylimide chain ends. The solubility properties, the ^{13}C n.m.r. data and the molecular-weight characteristics from s.e.c. were then studied. The thermomechanical and thermogravimetric behaviours were also examined as a function of the molecular weight.



Poly (1,3-dihydro-1,3-dioxo-2*H*-isoindole-2,5-diyl)carbonyl(1,3-dihydro-1,3-dioxo-2*H*-isoindole-5,2-diyl)-9*H*-fluorenone-9-ylidene-bis(1,4-phenylene)

EXPERIMENTAL

Instrumentation

I.r. spectra were recorded with a Perkin–Elmer 377 spectrometer.

*FT*i.r. spectra were performed by a Nicolet 20 SX FTIR spectrophotometer.

N.m.r. spectra were obtained with a Brucker AC 250 apparatus using a Me_4Si reference (the frequencies were respectively 62.9 MHz for ^{13}C n.m.r. and 250 MHz for ^{1}H n.m.r.).

0032-3861/91/173256-06

Inherent viscosities were measured at 30 C from a NMP solution with 1 g dl^{-1} of polyimide using an Ubbelohde capillarity viscosimeter.

Melting points were determined from d.s.c. analyses using a Mettler TA 3000 apparatus. The heating rate was 10 C min^{-1}.

T.g.a. data were obtained from 50 mg samples using a Setaram TG 85 thermogravimetric analyser. The heating rate was 5 C min^{-1} with a flow rate of 100 ml min^{-1} of argon or air.

Water absorption was measured in a controlled-atmosphere oven at 25 C with 65% relative humidity.

S.e.c. analysis were performed by a Waters 150 C chromatograph apparatus. The detection device was a differential refractometer. The solvent was a 1:0.005 benzyl alcohol/2,6-di-t-butyl-4-methylphenol mixture with a flow rate of 0.5 ml min^{-1}. The temperature was maintained at 130 C. Two columns were used: a mixed one (porosity 500 4 × 10^{6} Å), diameter 10 μm, length 60 cm; a standard one (porosity 500 Å), diameter 10 μm, length 30 cm.

T.m.a. spectra were recorded at a 10 C min^{-1} heating rate with a 0.3 N penetrating strength or a 0.5 stretching strength, using a Mettler TMA 40 thermomechanical analyser.

Mechanical tensile tests were performed by an Instron 1175 analyser with a 1 mm min^{-1} crosshead speed. The polyimide specimens used for mechanical tests and thermomechanical analyses were self-supporting films made according to the procedure described below.

Synthesis

Reagents. (5,5′-Bisisobenzofuran)-1,1′,3,3′-tetrone (BTDA), aniline and common reagents were commercial and of analytical grade. *N*-Methylpyrrolidone (NMP) was distilled in an argon stream.

*Synthesis of 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine (FBPA).* In a 1000 ml three-necked flask fitted with a mechanical stirrer, thermometer and argon inlet tube, 73 g (0.405 mol) of fluoren-9-one, 222 g (1.71 mol) of aniline hydrochloride and 420 g (4.51 mol) of aniline were added. The reaction mixture was heated for 5 h at 165 C with stirring. The hot mixture was precipitated in 2 litres of aqueous potassium hydroxide solution (10 wt%). After boiling for 10 min, the red aqueous phase was decanted off. The reddish precipitate obtained was washed in 2 litres of water and filtered. The crude product was crystallized twice from a 1.5:1 anisole/xylene mixture, giving a total yield of 67% of diamine; m.p. 235.1 C. I.r. (KBr) = 3420, 3335, 3190, 3020, 1610, 1500, 1440, 1270, 830, 815, 810. Analysis calculated for $C_{25}H_{20}N_2$: C 86.175, H 5.785, N 8.039, O 0; found: C 85.60, H 5.99, N 7.86, O 0.54. ^{1}H n.m.r. (Me_2SO-d_6): 6.35–7.8 (m, 16H); 3.2 (s, 4H).

Synthesis of model compounds for ^{13}C n.m.r. Model compounds I and II were respectively 4,4′-(9*H*-fluoren-9-ylidene)bisbenzeneamine and commercial fluoren-9-one.

Model compound III was 2,2′-[(9*H*-fluoren-9-ylidene)-bis(1,4-phenylene)]bis(1,3-dihydro-1,3-dioxo-2*H*-isoindole). In a 100 ml three-necked flask fitted with a mechanical stirrer, thermometer and argon inlet tube, 5.248 g (0.0015 mol) of FBPA, 4.462 g (0.030 mol) of phthalic anhydride and 14.158 g of NMP were added. The mixture was heated to 80 C for 3 h, then to 120 C for 2 h and to 200 C for 3 h. The reaction mixture was then precipitated into a 1:1 methanol/water mixture. The resulting powder was filtered and dried for 4 h at 100 C under vacuum, giving a yield of about 85%.

Model IV was 5,5′-carbonylbis(2-phenyl-1,3-dihydro-1,3-dioxo-2*H*-isoindole). Following the preceding procedure, 14.279 g (0.044 mol) of BTDA, 8.253 g (0.088 mol) of aniline and 21.734 g of NMP were reacted, to obtain a yield of about 85%.

Model V was 5,5′-carbonylbis[2-(2-acetylphenyl)-1,3-dihydro-1,3-dioxo-2*H*-isoindole]. Following the preceding procedure, model V was synthesized by reaction of 10.477 g (0.032 mol) of BTDA with 8.008 g (0.064 mol) of *o*-anisidine in 15.710 g of NMP. A yield of approximately 85% was obtained.

The oligomers VI, VII, VIII and IX were synthesized following the procedure described for ^{13}C n.m.r. model products. Oligomer VI was obtained by reacting 13.561 g (0.0389 mol) of FBPA with 6.270 g (0.0194 mol) of BTDA in 19.5 g of NMP. Oligomer VII was synthesized by reacting 14.417 g (0.0414 mol) of FBPA with 6.666 g (0.0207 mol) of BTDA and 6.128 g (0.0414 mol) of phthalic anhydride in 31 g of NMP. Oligomer VIII was obtained by reacting 7.107 g (0.0204 mol) of FBPA with 13.144 g (0.0408 mol) of BTDA and 3.799 g (0.0408 mol) of aniline in 29.8 g of NMP. Oligomer IX was obtained by reacting 7.536 g (0.0216 mol) of FBPA with 10.724 g (0.0333 mol) of BTDA and 2.171 g (0.0233 mol) of aniline in 27.4 g of NMP. Considering the molar proportion of the reactants, we have calculated the theoretical molecular weights of the models (*DP* is the theoretical degree of polymerization):

Oligomer VI	$DP = 1$	$M_{VI(DP=1)} = 983.0$
Oligomer VII	$DP = 1$	$M_{VII(DP=1)} = 1243.3$
Oligomer VIII	$DP = 1$	$M_{VIII(DP=1)} = 1107.1$
Oligomer IX	$DP = 3$	$M_{IX(DP=3)} = 2376.4$

*Synthesis of the polyimide from (5,5′-bisisobenzofuran)-1,1′,3,3′-tetrone and 4,4′-(9*H*-fluoren-9-ylidene)bisphenylamine: standard procedure for polyimide FBPA/BTDA.* In a 150 ml three-necked flask fitted with a mechanical stirrer, thermometer and argon inlet tube, 12.253 g (0.035 mol) of FBPA was weighed. Then 20 g of NMP was added. After full solubilization of the diamine, 11.331 g (0.035 mol) of BTDA was gradually added followed by 14.227 g of NMP. During the polycondensation, the argon flow was maintained at 50 ml min^{-1}. The reaction mixture was heated to 80 C for 3 h, then to 120 C for 2 h and 200 C for 3 h. After cooling, 61.25 mg of aniline was added, and an additional thermal cycle of imidization was applied: 80 C for 3 h, 120 C for 2 h, 200 C for 3 h. During cooling, the mixture was diluted with NMP from a starting solid content of 40% to a solid content of 30%. Then the polyimide solution was precipitated in a 1:1 methanol/water mixture. The polymer powder was filtered and dried under vacuum for 1 h at 100 C and 3 h at 140 C.

Preparation of films

A NMP solution, 30% by weight in polyimide, was cast on a glass plate using a 200 μm thickness doctor

Table 1 Inherent viscosities of the FBPA/BTDA polyimides

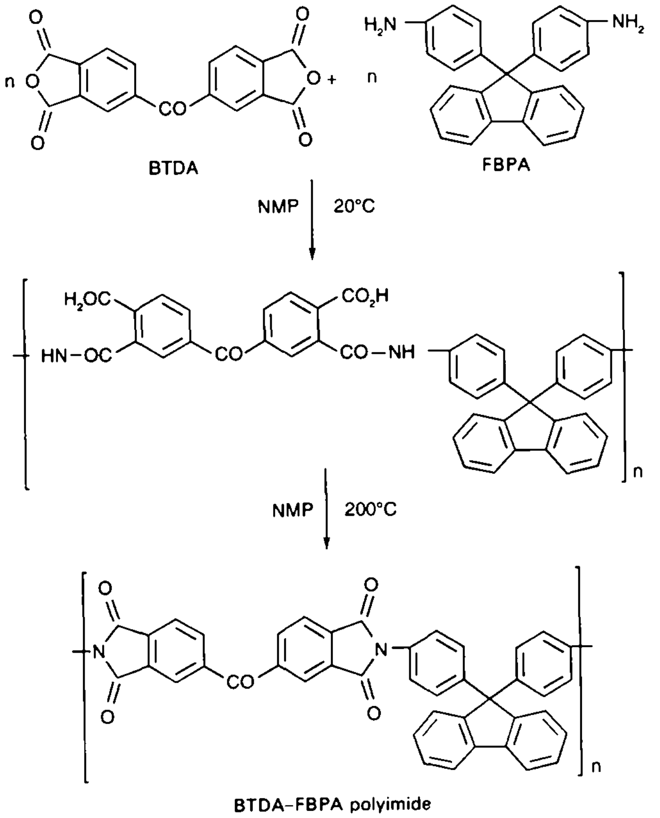
Experiment	FBPA/BTDA (mol:mol)	Moles of aniline per mole of BTDA	η_i (dl g^{-1})
1	1:1	0	0.57
2	1:1.02	0	0.57
3	1:1.04	0	0.41
4	1:1.06	0	0.36
5	1:1	0.0187	0.74
6	1:1	0.0935	0.5
7	1:1	0.187	0.4
8	1:1.02	0.183	0.39
9	1:1.04	0.180	0.38
10	1:1.06	0.176	0.23

blade. The solvent was evaporated in a convection oven at 100°C for 1 h and at 200°C for 1 h. Final drying was performed at 300°C for 2 h. The film was removed from the glass plate by soaking it in cold water. The final film thickness was about 0.05 mm.

RESULTS AND DISCUSSION

Synthesis of FBPA/BTDA polyimide

The aromatic diamine FBPA was prepared according to the procedure reported by Harris *et al.*[2]. A poly(amic acid) was first formed at room temperature by polycondensation between BTDA and FBPA in NMP solution. Imidization was then thermally achieved by gradual heating up to 200°C in solution.



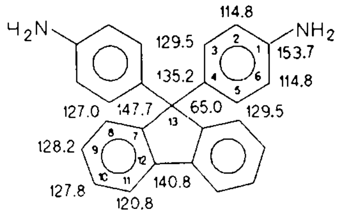
As reported in *Table 1*, variable molar excesses of BTDA (0 to 6 mol%) were used to change the molecular weight of the final polyimide. For experiments 5 to 10, the residual anhydride groups were deactivated by direct addition of aniline to the reaction mixture after polycondensation. An additional thermal cycle of imidization was then applied to obtain phenylimide chain ends. A decrease of the inherent viscosity was obtained as the amount of aniline increased (experiments 1, 5, 6 and 7). This corresponded to a reduction of the polymer average molecular weight.

Although ^{13}C n.m.r. determination showed full imidization before aniline addition (carbonyl amic acid carbon is located near to 172 ppm), the precision of the measurement is not so high as to refute the possibility of chain scission by nucleophilic attack of residual amic acid groups.

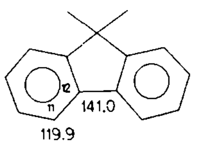
The solubility was checked at 40% solid content in different solvents at room temperature. Full dissolution was observed in *N*,*N*-dimethylformamide, *N*-methylpyrrolidone, *m*-cresol, dimethylsulphoxide, γ-butyrolactone, *N*,*N*-dimethylacetamide, anisole, dioxane, tetrachloroethane, dichloromethane and chloroform. Partial or complete insolubility was obtained with diglyme, methyl ethyl ketone, toluene and cyclohexanone. This good solubility could be attributed, first, to the high steric hindrance due to diphenylfluorene groups, which brings a decrease of molecular interactions and also an easier solvation pathway, and secondly, to the chain flexibility associated with the presence of carbonyl groups from benzophenone sequences.

^{13}C n.m.r. characterization

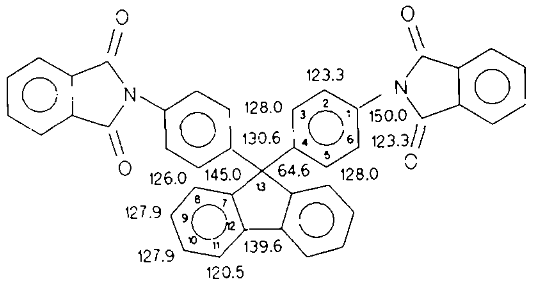
Apart from the solvent resonance centred at 39.5 ppm, 16 peaks can be observed in the 62.9 MHz ^{13}C n.m.r. spectrum of polyimide from experiment 5. Model products I, II, III, IV and V were used to assign these different resonances.



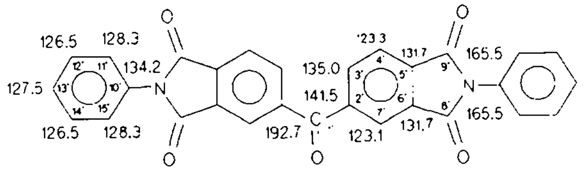
Model I



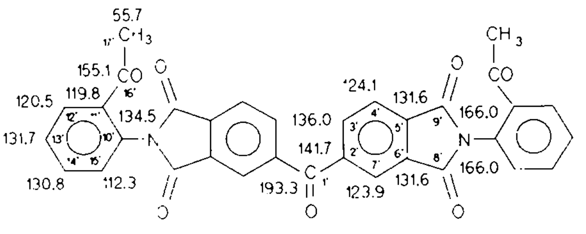
Model II



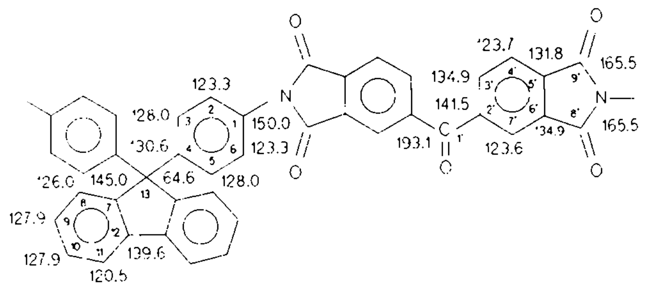
Model III



Model IV



Model V



Polyimide FBPA BTDA

The identification of the C atoms of the 9,9'-diphenylfluorene and benzophenone moieties located between two imide groups allowed the determination of the chemical shifts of the corresponding C atoms in the polymeric backbone.

The chemical shifts of C atoms for the FBPA/BTDA polyimide are also shown. A comparison of the ^{13}C n.m.r. spectra of polymers from experiments 1 to 10 showed no great differences.

S.e.c. characterization

The s.e.c. analysis was performed in benzyl alcohol at 130 C, according to the method developed by Boscher *et al.*[3]. The calibration curve obtained from FBPA/BTDA phenyl end-capped oligoimides (products described in 'Experimental' part) is presented in *Figure 1*. An extrapolation to higher molecular weights was achieved by means of a reference curve obtained from high-molecular-weight polystyrene standards. The resulting pattern is shown in *Figure 2*.

A Mark Houwink law in benzyl alcohol was thus determined:

$$\eta = 0.336 \times 10^{-2} \bar{M}_w^{0.98}$$

The exponent value is in agreement with that expected for a rigid macromolecule in benzyl alcohol solution[4].

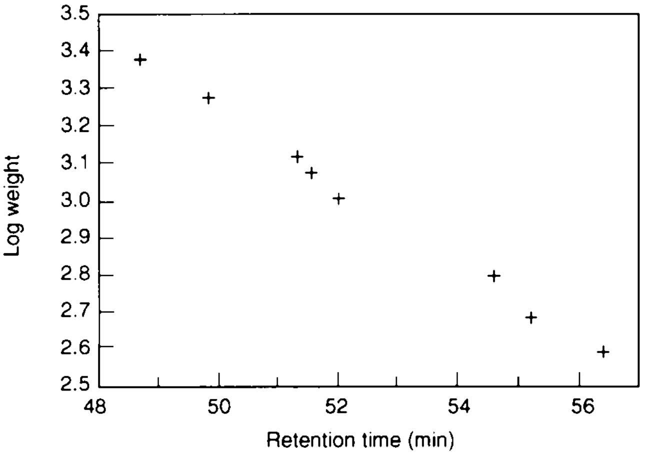


Figure 1 S.e.c. calibration curve from FBPA/BTDA oligomers

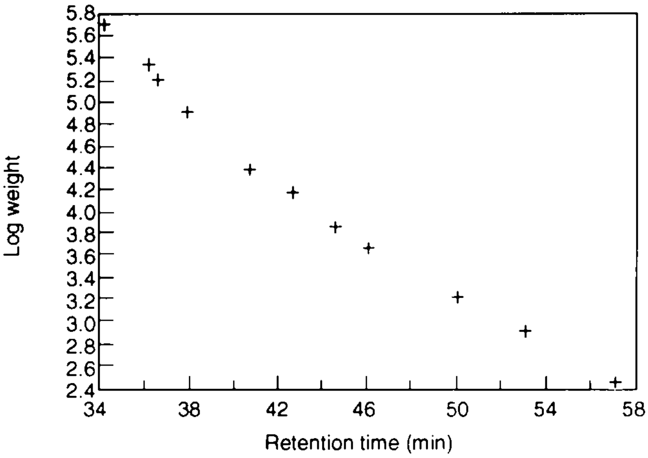


Figure 2 Reference curve for s.e.c. determinations: extrapolation of calibration curve to higher molecular weights by means of polystyrene standards

Table 2 S.e.c. analyses of FBPA/BTDA polyimides

Experiment	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w/\bar{M}_n$
1	9 525	22 322	37 011	2.34
5	10 707	26 618	46 518	2.49
6	8 480	19 475	33 074	2.30
7	4 748	13 352	24 552	2.81

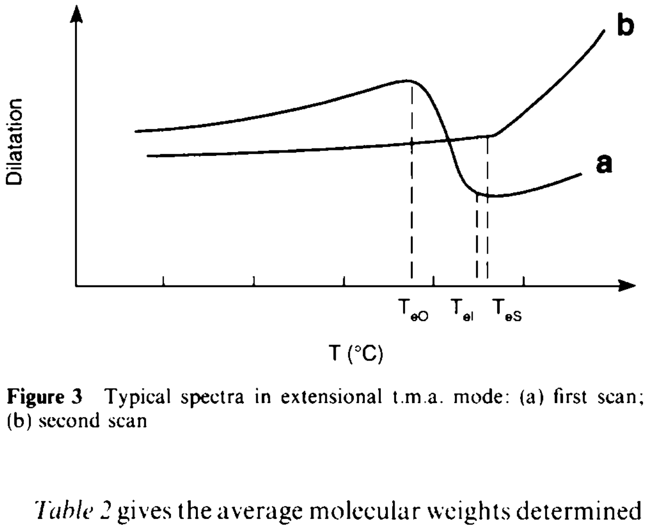


Figure 3 Typical spectra in extensional t.m.a. mode: (a) first scan; (b) second scan

Table 2 gives the average molecular weights determined for polyimides from experiments 1, 5, 6 and 7. The evolution of the molecular weights correlates with the values of inherent viscosities given in *Table 1*.

Thermomechanical analysis

T.m.a. analysis was performed in both extensional and penetrating modes on polymer films. In each mode, two successive scans were applied. The first was up to 400 C and the second to 450 C.

For the extensional mode, three steps were observed during the first scan, as shown in *Figure 3*: a first conventional step of thermal dilatation from 50 C to about 315 C; a second step corresponding to a retraction phenomenon (the starting temperature of retraction T_{eO} was about 315 C, and the maximum temperature of retraction T_{el} was between 330 and 370 C); a third step of thermal dilatation due to the softening of the

Table 3 T.m.a. data from extensional mode

Experiment	T_{e0} (°C)	T_{e1} (°C)	T_{eS} (°C)
1	315	372	381
2	313	365	378
3	314	356	377
4	313	340	348
5	312	364	385
6	315	364	378
7	313	346	351
8	314	340	346
9	314	330	340
10	–		–

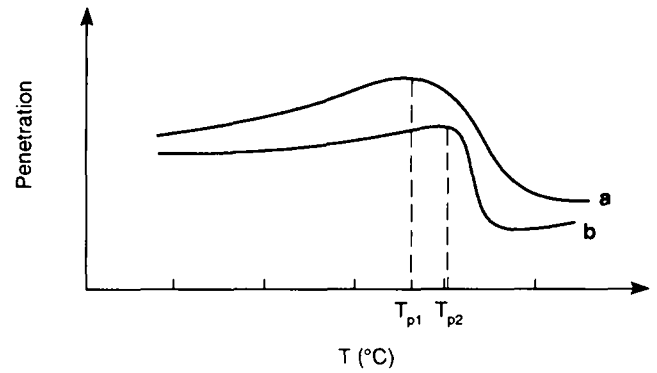


Figure 4 Typical spectra in penetrating t.m.a. mode: (a) first scan; (b) second scan

polyimide. In the second scan, the retraction phenomenon disappeared, and a conventional change of slope was observed when the polymer softening temperature T_{eS} was raised. The corresponding analytic data are given in *Table 3*.

The thermomechanical behaviour of films in the penetrating mode is shown in *Figure 4*. In this case, the softening of the sample during the first scan at T_{p1} seemed to be disturbed and occurred at a lower temperature than in the second scan, which showed a clear deviation of the signal at T_{p2}. The retraction phenomenon was not directly revealed compared to the extensional mode. T_{p1} and T_{p2} are given in *Table 4* for each analysed sample.

A good correlation was noticed between the two temperatures T_{eS} and T_{p2}, which could be associated with the glass transition of the polymer. A decrease of T_{eS} and T_{p2} was observed as the inherent viscosity of the polyimide decreased. The maximum value of T_{eS} was close to 380°C ($T_{p2} \simeq 375$°C) for the high-molecular-weight samples 1 and 5.

The T_g values of the aniline-treated polymers were generally lower, at the same inherent viscosity, than the T_g values of the polymers containing residual anhydride end-groups. This behaviour could be explained by a thermal growth of polyimide chains during film annealing at 300°C.

Concerning the retraction phenomenon, no chemical evolution of polyimide films thermally treated at 350–400°C was detected by *FT*i.r. or ^{13}C n.m.r. spectroscopy. Considering that this feature could not be attributed to chain growth because the aniline end-capped polymers underwent the same behaviour, this phenomenon was either a morphological rearrangement or a shrinking caused by internal mechanical stresses. The very high molecular rigidity of the FBPA/BTDA backbone probably induced this unusual behaviour.

Thermogravimetric analysis

T.g.a. was applied to polyimide films under dynamic conditions with a controlled argon flow. *Table 5* shows that the onset of decomposition was slightly dependent on the molecular weight. From this point of view, polyimide from experiment 5 exhibited the more interesting properties. However, the molecular weights of polyimides seemed to have no determining influence on their weight losses in an oxidative atmosphere. The char yield at 600°C was close to 80% for each sample.

Moisture regain

Water uptake at 25°C and 65% relative humidity was 2% for non-blocked polymer from experiment 1 and 0.8% for end-capped polymer from experiment 5, both polymers exhibiting the same inherent viscosity. These results indicate, first the strong influence of the nature of the chain ends on moisture regain, and secondly, the rather low water uptake of FBPA/BTDA polyimide probably due to the low polar character of its backbone.

Mechanical tensile tests

The results from the mechanical tensile study of polyimide films are given in *Table 6*. The tensile modulus values (*E*) were between 3 and 2 GPa at room temperature, depending on the molecular weight of the sample, and elongation at rupture (ε_R) was about 3 to 4%. The moduli of the end-capped polymers were lower than those of the non-blocked polymers, even if the inherent

Table 4 T.m.a. data from penetrating mode

Experiment	First scan T_{p1} (°C)	Second scan T_{p2} (°C)
1	356	378
2	348	372
3	342	365
4	339	354
5	336	372
6	329	361
7	340	354
8	336	351
9	334	350
10	–	–

Table 5 Dynamic thermogravimetric properties of polymer films

Experiment	T_d[a] (°C)	ΔP (%)[b]		
		400°C	500°C	600°C
1	390	0.16	1.05	18.3
2	–			–
3	–		–	–
4	390	0.21	0.98	18.6
5	401	–	0.7	18.2
6	373	0.16	0.97	20.4
7	381	0.14	0.97	19.25
8	375	0.14	0.84	16.04
9	387	0.14	0.97	19.25
10	–	–	–	–

[a] Onset of thermal degradation
[b] Weight loss at indicated temperature

Table 6 Mechanical characteristics from tensile tests

	Room temperature			200 C		
Experiment	E (GPa)	σ_R (MPa)	ε_R (%)	E (GPa)	σ_R (MPa)	ε_R (%)
1	2.9	99.1	4.91	1.6	55.3	4.4
2	2.45	93.9	4.88	1.6	45.9	3.8
3	2.75	70.2	2.87	1.8	38.6	2.3
4	2.34	35.0	1.64	1.7	38.0	2.8
5	2.3	67.5	3.93	1.4	47.2	3.4
6	1.9	74.4	4.4	1.7	46.5	3.0
7	2.1	59.5	3.32	1.8	31.3	2.11
8	2.2	58.7	3.0			-
9	2.1	19.5	0.88	-		
10		-			–	

viscosities were similar, indicating the same average molecular weight after polycondensation.

The evolution of stress at rupture (σ_R) values were quite analogous. This behaviour might be explained by the reaction of terminal reactive groups during thermal annealing of films. This hypothesis was confirmed by an appreciable reduction of the solubility of polymers from experiments 1, 2, 3 and 4 in NMP when they were in film form.

CONCLUSIONS

The polyimide prepared from 4,4′-(9*H*-fluoren-9-ylidene)-bisphenylamine (FBPA) and (5,5′-bisisobenzofuran)-1,1′,3,3′-tetrone (BTDA) showed good solubility in many solvents owing to the presence in the backbone of bulky lateral groups. The very high glass transition temperature ($T_g \geqslant 350^\circ$C) of the resulting films depended on the inherent viscosity of the starting polymer and so on the nature of chain ends. The aniline-treated polymer thus had lower T_g than the polymer containing residual reactive terminal functions.

The thermal resistance of films did not seem to be affected by the end-capping treatment with aniline, but moisture regain and mechanical tensile properties were clearly modified. The water uptake was increased by the stronger polar character of the non-blocked polymer and the tensile modulus was increased by the possibility of chain growth from residual reactive end-groups.

ACKNOWLEDGEMENTS

We would like to thank Mrs C. Lefebvre and Mr Y. Boscher (Institut Français du Pétrole, Rueil-Malmaison) for aiding with s.e.c. analyses.

REFERENCES

1 Korshak, V. V., Vinogradova, S. V. and Vygodskii, *J. Macromol. Sci.- Rev. Macromol. Chem. (C)* 1974, **11**(1), 45

2 Stille, J. K., Harris, R. M. and Padaki, S. M. *Macromolecules* 1981, **14**, 486

3 Bosher, Y., Renard, C. and Ballaguet, J. P. GPC Symposium Preprints, Pau, France, May 1989

4 Bessonov, M. I., Koton, M. M., Kudryavtsev, V. V. and Laius, L. A. 'Polyimides: Thermally Stable Polymers', Consultants' Bureau, New York, 1987, p. 167