Synthesis and characterization of poly(amide–imides) from 3,4-dicarboxy-4′-chloroformylbiphenyl anhydride

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The synthesis of eight new poly(amide–imides) derived from the 3,4-dicarboxy-4′-chloroformyl biphenyl anhydride and aromatic diamines is reported. The poly(amide–imides) were characterized by i.r. spectroscopy, elemental analysis, differential scanning calorimetry and thermogravimetry. The T_g and the thermal decomposition temperatures were determined; the thermal stabilities of the polymers turned out to be higher than those reported for other poly(amide–imides).

Keywords Poly(amido–imides); 3,4-dicarboxy-4′-chloro-formylbiphenyl anhydride; 3,4,4′-trimethylbiphenyl; thermal stability; glass transition; polyelectrolyte

INTRODUCTION

In recent years a wide variety of polymers have been synthesized as a consequence of different technical requirements, particularly in relation to their thermal stability. Thus, polyamides, polyimides and poly(amide–imides) have been accepted and recognized as important groups of thermally stable polymers[1].

In earlier publications[2,3], we have described the synthesis, characterization and thermal properties of poly(amide–imides) (PAI) derived from the reaction of 3,4-dicarboxy-4′-chloroformyl-diphenylsulphone anhydride and 3′,4′-dicarboxy-4″-chloroformyl terephthalophenone anhydride with aromatic and aliphatic diamines. These polymers presented excellent thermal properties and acceptable molecular weights. Wrasidlo and Augl[4,5] synthesized polyimides-co-amides derived from trimellitic anhydride and aromatic diamines, and found that their behaviour was intermediate between polyamides and polyimides.

Continuing our work in this area we have synthesized poly(amide–imides) derived from the 3,4-dicarboxy-4′-chloroformylbiphenyl anhydride and aromatic diamines. The polymers were characterized by i.r. spectroscopy, their thermal properties were determined, and their molecular weights estimated.

EXPERIMENTAL

The diamines and solvents were obtained from Aldrich Chemical Co., and were purified by the usual methods. The melting points were not corrected.

The i.r. spectra were made with a Perkin-Elmer 337 i.r. spectrophotometer and the n.m.r. spectra were obtained with an XL-100 Varian n.m.r. spectrometer.

The elemental analyses were performed with a Perkin-Elmer model 240 CHN analyser at the Patronato Juan de la Cierva (Madrid, Spain). Viscosities were measured in a Desreux–Bischoff type dilution viscosimeter[6]. The T_g values were determined under N_2 flow with a Perkin-Elmer model DSC-1B differential scanning calorimeter, and the t.g.a. data were obtained by means of a Perkin-Elmer model TGS-1 thermobalance under air atmosphere.

Monomer synthesis

3,4-Dicarboxy-4′-chloroformylbiphenyl anhydride (I) was synthesized following the procedure described by Adduci *et al.*[7], in which 3,4,4′-trimethylbiphenyl is oxidized and then the triacid obtained is treated with thionyl chloride. The monomer obtained (m.p. 140°–142°C) showed characteristic i.r. bands for the carbonyl group at 1845, 1770 and 1720 cm^{-1}. The n.m.r. spectra presented only one complex signal corresponding to aromatic H between 7.1 and 8.45. Elemental analysis for $C_{15}H_7O_4Cl$: calc. C: 62.83%, H: 2.44%, Cl: 12.39%, found C: 62.71%, H: 2.67%, Cl: 12.16%.

3,4,4′-Trimethylbiphenyl was synthesized according to the following procedure: a solution of 12 g of 4-methylcyclohexanone in ether was added drop-by-drop to the Grignard reagent prepared by reaction of 37 g of 4-bromo-*o*-xylene with 8 g of Mg in 20 ml of anhydrous ether. The mixture obtained was hydrolysed with ice-HCl and the product was washed with 5% NaOH and then washed with water. The crude alcohol produced was mixed with 25 ml of acetic anhydride and then it was allowed to stand at room temperature for three days. The acetic acid produced was eliminated and the crude product was treated with sulphur at 200°–230°C for 2 h. The mixture was distilled and the fraction between 150° and 180°C was collected. This fraction solidified, and was recrystallized several times from methanol. 4.5 g of trimethylbiphenyl were obtained (m.p. 60°C). The n.m.r. spectra showed a signal corresponding to aromatic H between 7.1 and 7.55 and two signals corresponding to the methyl groups at 2.31 and 2.39 δ. Elemental analysis for $C_{15}H_{16}$: calc. C: 91.78%, H: 8.22%; found C: 91.88%, H: 7.94%.

Polymerizations

The polymerizations were carried out according to the methods described previously[2–3,8], in which a solution of

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Table 1 Intrinsic viscosities and elemental analysis for the PAI

Polymer	[η]*			Elemental analysis %C	%H	%N	%S
I	0.31	$C_{27}H_{16}N_2O_5S$	Calc	67.50	3.33	5.83	6.67
			Found	64.63	3.75	6.26	6.30
II	0.35	$C_{27}H_{18}N_2O_6S$†	Calc	65.06	3.61	5.62	6.43
			Found	61.87	4.09	5.34	5.74
III	0.30	$C_{21}H_{12}N_2O_3$	Calc	74.12	3.53	8.24	–
			Found	71.39	3.98	8.81	
IV	0.65	$C_{27}H_{18}N_2O_4$†	Calc	74.65	4.15	6.45	–
			Found	70.71	4.21	6.83	
V	0.64	$C_{27}H_{16}N_2O_4$	Calc	75.00	3.70	6.48	–
			Found	68.40	3.97	6.95	
VI	1.02	$C_{28}H_{18}N_2O_3$	Calc	78.14	4.19	6.51	–
			Found	76.46	4.21	6.67	
VII	–	$C_{21}H_{14}N_2O_4$†	Calc	70.39	3.91	7.82	–
			Found	66.41	4.48	8.02	
VIII	0.19	$C_{25}H_{14}N_2O_3$	Calc	76.92	3.59	7.18	–
			Found	70.75	3.92	7.45	

* in DMAc at 25°C (dl g^{-1})
† From the polyamic acids

the diamine in DMAc at −20°C was added with stirring to an equimolar amount of the monomer I. The temperature was kept at −20°C for 2–3 h, and then it was raised slowly up to room temperature maintaining stirring for 12 h. The viscous solution was poured on water and the polyamic acid precipitated. This solid was filtered, washed with water and acetone, and finally dried at reduced pressure until constant weight.

Poly(amide–imide) films

The PAI films were obtained by heating, under vacuum, a concentrated solution of the polyamic acid in DMAc. The temperature was raised slowly up to 100°C to eliminate the solvent, and then heated at 200°C under vacuum for 2 h. When the plate was at room temperature the film was separated.

RESULTS AND DISCUSSION

The PAI were synthesized by polymerization in solution according to the following reaction scheme, using DMAc as solvent:

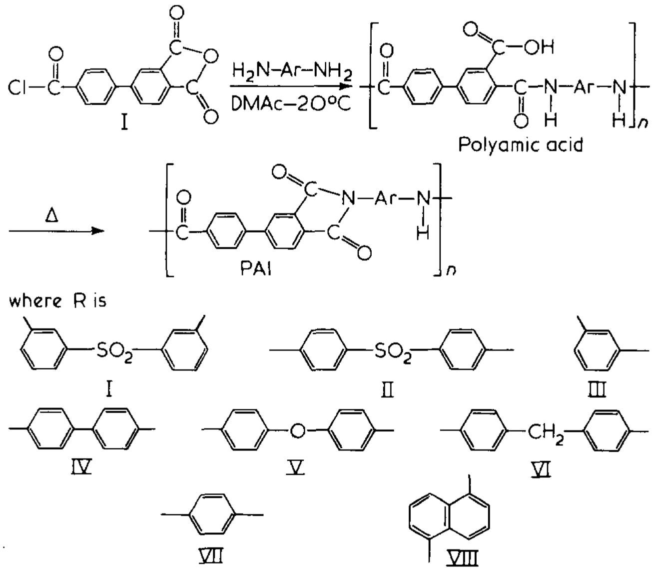

Table 2 Glass transition temperatures (T_g) and thermal decomposition temperatures (*TDT*) of the poly(amide–imides)

Polymer	T_g (°C)	*TDT* (°C)
I	207	478
II	215	496
III	204	500
IV	283	540
V	285	550
VI	313	555
VII	157	570
VIII	129	596

The polyamic acids were soluble in polar aprotic solvents like DMAc, DMF and DMSO, whereas the PAI were insoluble in these solvents. The polyamic acid obtained from the diamine VII was slightly soluble in the above mentioned solvents and for this reason it was not possible to estimate its molecular weight.

The molecular weights were estimated from viscosimetric measurements. A typical polyelectrolyte behaviour was observed, apparently due to the presence of a free carboxylic group in a highly polar solvent (DMAc). Using the Fuoss and Strauss method[9] it is possible to obtain the value of the intrinsic viscosity (plotting $(\eta_{sp}/c)^{-1}$ vs. $\sqrt{c}$, where the intercept with the ordinate axis corresponds to the reciprocal of the [η]). *Table 1* summarizes the values of [η] obtained.

The results of the elemental analyses are consistent with the theoretical values and are shown in *Table 1*.

The glass transition temperatures were studied by d.s.c. directly on the PAI films. The values of T_g were taken as the first evidence of a slope change in the baseline of the thermogram, and are summarized in *Table 2*. The T_g values of the PAI are quite high, which is in good agreement with those reported in the literature for other systems[2,3,8]. *Table 2* also summarizes the values of the thermal decomposition temperatures obtained by thermogravimetric analysis and taken as the temperature at which the polymer loses 10% of its weight. *Table 3*

Table 3 Thermogravimetric analyses of the poly(amide–imides) at temperatures (*T* °C)

	Weight loss (%)					
PAI	100	200	300	400	500	600
I	0.9	2.4	3.3	5.5	13.2	34.4
II	0.8	1.3	2.1	3.8	10.2	29.1
III	1.0	3.0	3.4	5.9	9.7	20.0
IV	–	0.3	0.9	2.8	4.0	29.7
V	–	1.3	2.5	3.8	4.8	21.2
VI	–	0.5	1.5	2.9	4.5	18.0
VII	–	0.7	2.6	3.7	6.7	19.3
VIII	0.8	1.7	4.1	6.6	11.5	41.1

summarizes the corresponding values of the weight loss at different temperatures.

All the polymers exhibit a weight loss of less than 10% at 400°C, which demonstrated their high thermal stability. The weight loss between 1 and 4% observed at 300°C may be due to a certain amount of solvent that is trapped during the polyimidation process. Anyhow, these PAI present a higher thermal stability than the previously reported ones[2–3,8,10] in which the monomer presented functional groups between the aromatic rings.

Therefore, the absence of functional groups between the aromatic rings of the monomeric unit is concluded to be the cause of the higher thermal stability shown by these PAI.

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