Halogenated polymers with high thermal stability and flame-resistance

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A series of polyamides and poly(amido-imides) with variable chlorine content in the nitrogen monomer as in the carboxylic monomer have been prepared. All the polymers showed excellent thermal properties and fairly good flame-resistance characteristics.

INTRODUCTION

The development of polymeric molecules comes from the fact that they show a great mechanical resistance related to their relatively small weight, high chemical stability and easy handling. The use of these products spread to industries where the oxidative thermal stability of polymers was important.

The range of temperature where the materials should be stable are variable and dependent on the exposure time and environment. Thus, thermal stability has been defined as the temperature or range of temperature that a polymer or a material can withstand and still retain its useful properties in a given application[1].

Investigating these materials has brought experimental problems due mainly to their resistance to temperature between 500 to 1 000°C, which associated with their insolubility and indeterminate melting points made them difficult to handle and therefore limited in terms of their uses and applications.

However some polymers with good thermal and insulator electrical characteristics have been prepared in the last few years. These polymers include NOMEX (Polyphenyl isophtalamide, Dupont)[2], DURETTE (a polyamide)[3] and halogen containing fibres as PVC, TEFLON and PVC copolymers as SARAW, TEKLAN, etc.[4]

The thermal characteristics and the flame behaviour of the polymers prepared in our laboratory have been previously described[5-8] (*Table 1*).

Aromatic polyamides (PA) and poly(amide-imides) (PAI) containing a variable percentage of chlorine were used to analyse the increment in thermal stability and flame resistance[9]. The polymers also contain –O–, $-CH_2-$ and $-SO_2-$ groups which reduce the chain rigidity leaving the thermal stability unchanged[5,8,10].

The polymers were characterized by elementary analysis, infra-red spectroscopy, differential scanning calorimetry (d.s.c.), thermogravimetric analysis (t.g.a.) and viscosimetry techniques. A series of qualitative physical and chemical tests such as solubility, resistance to acids and bases and flame resistance were also carried out.

EXPERIMENTAL

The diamines, the trimellitic acid and the solvents were obtained from Eastman Kodak Rochester and Aldrich Chemical Co., and used after purifying. The other monomers were synthesized according to the data reported elsewhere[5].

The elementary analyses were carried out using a Perkin–Elmer model 240 microanalyzer at Patronato Juan de la Cierva, C.S.I.C. (Madrid, Spain).

The i.r. spectra were recorded using a Perkin–Elmer model 337 spectrophotometer. The T_g values were obtained using a Perkin–Elmer model DSC-1B Differential Scanning Calorimeter at 16°C min^{-1} under nitrogen flow and the t.g.a. curves, from a Perkin–Elmer model TGS-1 thermobalance at 16°C min^{-1}, under nitrogen flow.

The viscosity measurements were carried out using a viscosimeter type Desreux-Bischoff.

Polyamides and poly(amido-imides) polymerization

Polyamides were synthesized following the modified method, described by Beaman and Morgan[11]. To an aqueous solution of the diamine (2.5×10^{-3} mol) containing sodium hydroxide (5%), a benzene solution of

Table 1 Thermal characteristics and flame behaviour of some polymers

Polymer	T_m	TDT^a	Autoextinction	Ignition	Ref.
Aliphatic PA polychlorinated	400	440	Yes	Moderate	(5)
Aromatic PA polychlorinated	480	500	Yes	Moderate	(6)
Polyethylene terephthalate polychlorinated	430	450	Yes	–	(7)
Poly(amide-imide)	500	>500	Yes	Moderate	(8)
Poly(amide-imide) polychlorinated	–	540	Yes	Difficult[b]	

[a] Thermal decomposition temperature
[b] PAI_2 (Present work)

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Table 2 Microanalysis, intrinsic viscosities [η] vitreous transition temperature T_g and thermal decomposition position temperatures for polyamides and poly(amido-imides)

Polymer	Formula		%C	%H	%N	%Cl	[η]	T_g (°C)	*TDT* (°C)
PA_1	$C_{14}H_5O_2N_2Cl_5$	Calc.	40.93	1.22	6.82	43.23	0.055[a]	267	290
		Found	40.95	1.47	6.36	45.84			
PA_2	$C_{14}H_5O_2N_2Cl_5$	Calc.	40.93	1.22	6.82	43.24	0.084[a]	265	300
		Found	41.28	1.19	6.01	45.10			
PA_3	$C_{21}H_{10}O_2N_2Cl_6$	Calc.	47.10	1.87	5.23	39.81	0.069[a]	270	340
		Found	47.14	1.86	5.81	38.78			
PAI_1	$C_{15}H_7O_3N_2Cl$	Calc.	60.30	2.35	9.48	11.89	0,390[b]	327	410
		Found	59.73	2.90	11.35	11.94			
PAI_2	$C_{15}H_7O_3N_2Cl$	Calc.	60.30	2.35	9.48	11.89	0,370[b]	309	540
		Found	58.90	3.01	8.91	11.40			
PAI_3	$C_{22}H_{12}O_3N_2Cl_2$	Calc.	62.40	2.89	6.62	16.78	0,250[b]	312	420
		Found	60.37	3.10	6.72	17.69			

[a] (dl g^{-1}), DMSO at 25°C
[b] (dl g^{-1}), DMAc at 25°C

the monomer (2.5×10^{-3} mol) was added with strong stirring at room temperature.

The mixture was stirred for 90 min and the resulting polyamide precipitate filtered off, washed several times with hydrochloric acid (1%) followed by a sodium hydroxide solution (1%) and finally with distilled water and acetone. The product was air dried and then dried under vacuum at 80°C until constant weight.

Poly(amide-imides) were synthesized following the procedure, described by Wrasidlo and Augl[12,13]. An equimolar mixture of a diamine (5×10^{-4} mol) in 3 to 5 ml of DMAc and the monomer (5×10^{-4} mol) were left stirring at -15°C during $2\frac{1}{2}$ h. The temperature was kept constant for 2–3 h and then slowly raised to finish the reaction at 70°C in a period of 20 h.

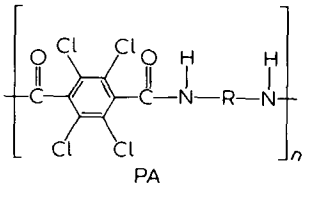
A viscous solution of polyamic acid was obtained from which the acid was precipitated by the addition of water. The solid was filtered off, washed with water, acetone and dried under vacuum.

Films of poly(amido-imides) were prepared by heating on a glass plate and under vacuum a viscous solution (20–25% in weight) of polyamic acid. The plate was heated up to 100°C to eliminate the occluded solvent, and then the temperature was raised to 200°C and kept there for 2–3 h. Finally, the system was cooled at room temperature.

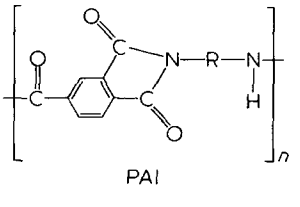
RESULTS AND DISCUSSION

Three polyamides (PA) from perchloroterephthaloil dichloride and three poly(amido-imides) (PAI) from trimellitic acid chloride with three chlorinated diamines were prepared.

The polymers with R group showed the following structures:



PA



PAI

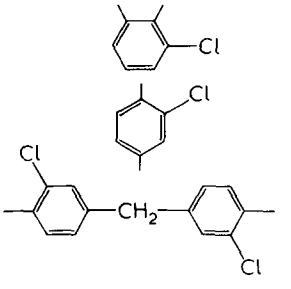
and the R groups were:

Polymer

PA_1 and PAI_1

PA_2 and PAI_2

PA_3 and PAI_3



The PA and PAI solubilities were fairly good in aprotic polar solvents such as *N,N*-dimethylacetamide (DMAc) dimethyl sulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) but were insoluble in other organic solvents.

The infra-red spectra obtained for PA and PAI showed the typical N–H bands at 3300–3400 cm^{-1} and C=O group vibrations between 1640–1670 cm^{-1}. The PAI spectra showed an additional band at 1720–1780 cm^{-1} corresponding to the imidic group.

The microanalysis data are given in *Table 2*.

As an estimation of the molecular weights, measurements of the intrinsic viscosity [η] were made for both PA and PAI. The behaviour of the PA have been found to be normal according to the classic Huggins relationship[14], but those of the PAI were shown to be similar to a polyelectrolyte and therefore it was necessary to apply the Fuos and Strauss[15] treatment for that type of polymer. *Table 2* summarized the [η] data obtained for the polymers as well as their percentage chlorine content.

Figure 1 shows the plot of intrinsic viscosity [η] *versus* percentage chlorine, showing a decrease in [η], and consequently the molecular weight, when the chloro content increases. This behaviour has been found in PA with the different chlorine content of dichlorides of chlorinated acids with different aliphatic diamines[5,16]. The [η] decreasing is the product of a lessening in the monomer reactivity when the chloro content is increased. Sokolov and Kroglova[17] reported that a perchlorinated diacid chloride had a lower reactivity than the unchlorinated diacidchloride. Attempts to polymerize two perchlorinated monomers were unsuccessful[18].

The polymers thermal properties were studied by differential scanning calorimetry (d.s.c.) and

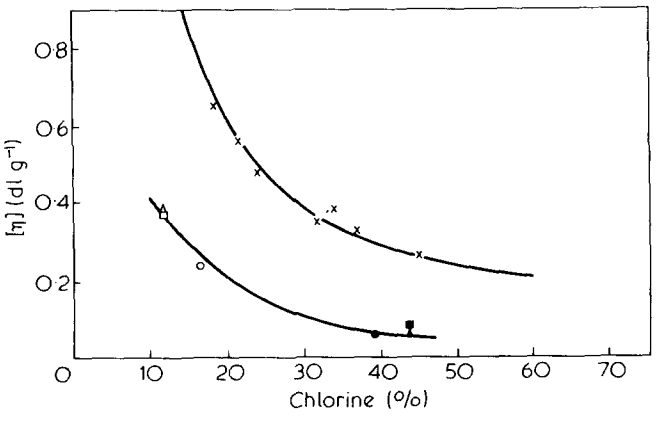


Figure 1 Plot of intrinsic viscosity vs. chlorine content (▲), PA_1; (■), PA_2; (●), PA_3; (△), PAI_1; (□), PAI_2; (○), PAI_3. (X), PA of several chlorides acids dichlorides and tetrachlorides and aliphatic diamines (ref 5)

thermogravimetric techniques using both powder and film.

The values for the vitreous transition temperature, T_g, and the thermal decomposition temperature (T DT) were taken as the first evidence of a sharp loss of weight and are observed in *Table 2*.

Also in *Table 2* an increase in the T_g values when the chloro content decreases can be observed though the values for the PA and PAI are found in a narrow range. The fact that the PAI show higher T_g values than the PA might be a consequence of their higher rigidity and due to the presence of the imidic ring in the chain.

In *Figure 2* the thermogravimetric analyses for the PA and PAI are shown and the corresponding data are summarized in *Table 3*. The PAI showed a higher thermostability than the PA, which is in agreement with the data already published for other systems[12,13].

However, it can be observed that both PA_1 and PAI_1, are derived from an *ortho* diamine and show lower thermal stability than polymers derived from a *para* diamine. The lower stability observed in the case of PA and PAI with *ortho* diamines was attributed to an increased steric hindrance to rotation and possibly intramolecular hydrogen bonding. These factors might facilitate bond cleavage[1]. The trend $p>m>o$ has been confirmed by recent studies[19].

Finally, qualitative tests were carried out to study the polymers flame behaviour (*Table 4*) and the results showed their auto-extinguishable capacity.

The PAI were hardly burnt and their residues keeping their original colours, though their physical appearance was shown to be a fragile melted mass.

ACKNOWLEDGEMENT

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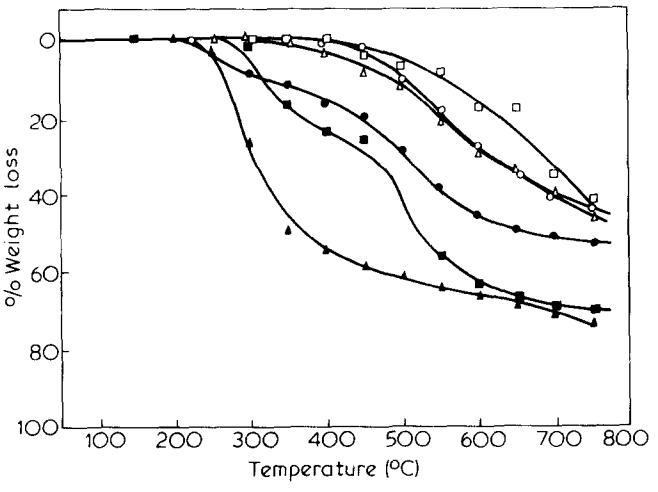

Figure 2 Thermogravimetric analysis: (▲), PA_1; (■), PA_2; (●), PA_3; (△), PAI_1; (□), PAI_2; (○), PAI_3

Table 4 Combustion qualitative determinations

Polymer	Ignition	Burning smell	Material behaviour	Residue
PA_1[a]	Moderate	Pungent	Melts and burns	Dark carbonize
PA_2[a]	Very diffic.	Pungent	Burns	Dark carbonize
PA_3[a]	Difficult	Pungent	Melts and burns	Dark carbonize
PAI_1[a]	Difficult	Faint	Melts and drips	Dark and porous solid
PAI_2[a]	Difficult	Faint	Melts and drips	Yellow and porous solid
PAI_3[a]	Difficult	Faint	Melts and drips	Brown and porous solid

[a] Autoextinction positive; flame characteristics: yellow and dark smoke

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Table 3 Thermogravimetric analyses of polyamides and poly(amido-imides)

	Weight loss (%) at the T temperature (°C)											
Polymer	200	250	300	350	400	450	500	550	600	650	700	750
PA_1	0	1.25	26.58	48.10	54.43	58.23	60.76	64.30	65.82	68.35	70.88	73.42
PA_2	0	0	2.20	16.18	22.94	24.70	26.47	55.88	63.24	66.18	69.12	70.59
PA_3	0	3.39	8.65	11.53	15.47	18.49	28.30	37.74	45.28	49.00	50.94	52.83
PAI_1	0	0	0	0	4.25	9.12	11.15	22.00	29.17	34.10	40.00	43.10
PAI_2	0	0	0	0	0	3.42	6.94	8.22	16.48	17.81	34.26	41.00
PAI_3	0	0	0	0	0	2.09	10.91	18.18	27.27	34.54	40.00	43.63

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