Thermally obtained poly[4,4″(*p*-terphenylene)-amide]

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A comparison between the poly[4,4″(*p*-terphenylene)amide] obtained from: (1) solid-state polycondensation of the 4-amino-4″-carboxy-*p*-terphenyl and (2) melt polycondensation of the 4-amino-4″-carbomethoxy-*p*-terphenyl has been made. As revealed from the thermogravimetric experiments conducted under linear programmation of temperature, i.r. and X-ray analysis, scanning electron microscopy (SEM), and electrical conductivity measurements, the melt obtained polyamide shows a good thermal stability up to 410°C, thereafter undergoes a degradation reaction. The solid-state obtained polyamide is quite stable up to the temperature of 350°C, after which it suffers a crosslinking reaction with formation of a product that is heat resistant at least up to 470°C.

INTRODUCTION

In a previous paper[1] a series of thermogravimetric experiments under isothermal conditions at various temperatures in the range 253°–282°C in air and in argon atmosphere were performed, and curves of weight loss as function of time of 4-amino-4″-carboxy-*p*-terphenyl have been reported.

The temperatures chosen (intentionally low) allowed weight losses due to spattering of substance to be satisfactorily reduced during the heating up period (7 min) of the samples. Formation of a polyamide (with elimination of water) stable to prolonged heating was found and the activation energy (46 kcal mol^{-1}) for the polycondensation process was obtained.

In an attempt to study the thermal behaviour of the polycondensated product at temperatures higher than previously examined, a second series of experiments was carried out by thermogravimetry with linear programmation of temperature, heating the samples up to 470°C. The high thermal stability of fully aromatic polyamides is well known, however, only recently was an adequate study of thermal analysis initiated[2]. Also, another way to obtain the poly[4,4″(*p*-terphenylene) amide] from the melt polycondensation of 4-amino-4″-carbomethoxy-*p*-terphenyl is suggested, and the thermal stability and electrical conductivity characteristics of the polyamide, obtained in two different ways, has been studied. Later the polyamide will be indicated: PAA and PAE, depending on whether it was obtained from the solid-state polycondensation of the 4-amino-4″-carboxy-*p*-terphenyl (named AA) or from the melt polycondensation of the 4-amino-4″-carbomethoxy-*p*-terphenyl (named AE), respectively.

EXPERIMENTAL

Materials

All melting points were uncorrected. Elemental analyses were obtained on the instrument previously described[1].

*4-Nitro-4″-carbomethoxy-*p*-terphenyl.* A slight excess of an ethereal solution of diazomethane was added dropwise to a stirred suspension of 4-nitro-4″-carboxy-*p*-terphenyl[1] (1 g, 3.1 mmol) in tetrahydrofuran (500 ml) at room temperature. The resultant solution was evaporated under reduced pressure, to give a yellow solid; yield: 0.99 g (96%). Recrystallization from toluene gave the product, pure by t.l.c.; m.0. 239°–240°C (K–N)*, 289°C (N–I)*.

Composition found: C, 71.84%; H, 4.47%; N, 4.19%. $C_{20}H_{15}NO_4$ requires C, 72.06%; H, 4.54%; N, 4.19%; i.r. (KBr): ν_{max} 1710 cm^{-1} (C=O); 1505, 1330 cm^{-1} NO_2).

*4-Amino-4″-carbometoxy-*p*-terphenyl.* A solution of dihydrated stannous chloride (2.27 g, 10.1 mmol) in aqueous 37% HCl (2.6 ml, 31.5 mmol) was added dropwise to a stirred suspension of 4-nitro-4″-carbomethoxy-*p*-terphenyl (1 g, 3.0 mmol) in glacial acetic acid (55 ml). The mixture was refluxed for 1 h, allowed to cool and filtered. The washed solid residue was decomposed by stirring with aqueous 5% NaOH added up to obtain a strong basified suspension. Filtration gave a yellow solid which was washed with water; yield: 0.90 g (99%). The product, recrystallized from toluene, appeared to be pure by t.l.c.; m.p. 255°–256°C. Composition found: C, 79.08%; H, 5.71% N, 4.59%. $C_{20}H_{17}NO_2$ requires C, 79.18%; H, 5.65%; N, 4.62%; i.r. (KBr): ν_{max} 3440, 3370 cm^{-1} (NH_2); 1700 cm^{-1} (C=O). This compound was also prepared by methylation of 4-amino-4″-carboxy-*p*-terphenyl[1] with diazomethane, but the former method was preferable because the latter did not give good yields.

*Polymerization of 4-amino-4″-carbomethoxy-*p*-terphenyl.* The amino-ester was placed in a small tube equipped with a side arm and an inlet capillary for argon. The tube was quickly heated up to 282°C and then kept at this temperature for 2 h, while a slow flow of argon was passed through (some monomer sublimed). At ~280°C methanol bubbles (detected by g.l.c.) began to evolve from

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* K = crystal; N = nematic; I = isotropic liquid

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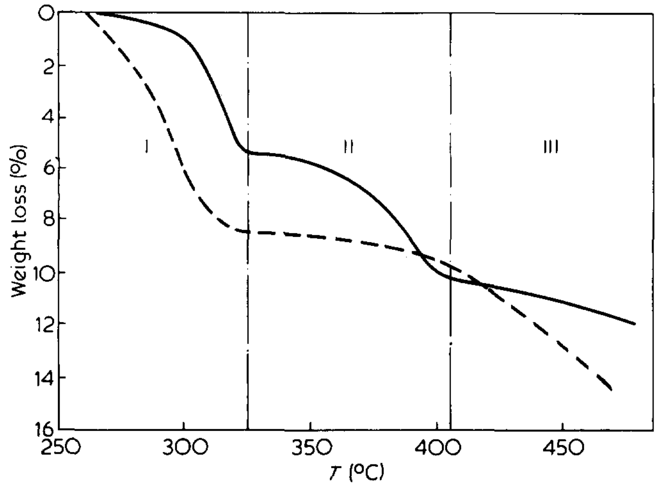

Figure 1 Thermogravimetric curves under linear programmation of temperature for the monomers: AA (——), AE (– – – –)

the melt that became cloudy and then gradually solidified. The yellow solid was finely powdered and washed with hot dichloromethane to remove traces of unreacted material. The insolubility, infusibility and microanalysis difficulties of the polymer were in complete agreement with those described in the previous work[1].

Measurements

The instrumentation used, the preparation of samples and electrical conductivity measurements were described in the previous paper[1].

The morphological analyses were performed by a Jeol P 15 table-top scanning electron microscope. The X-ray diffraction patterns were obtained by a powder diffractometer using a flat camera and Ni filtered CuK_α radiation.

RESULTS

Thermogravimetry and infra-red spectra

The behaviour of two monomer samples: 4-amino-4″-carboxy-*p*-terphenyl (AA) and 4-amino-4″-carbomethoxy-*p*-terphenyl (AE), thermally treated at a constant heating rate of 4.7°C $\min^{-1}$ under atmospheric conditions in air, is shown in *Figure 1*.

There was no appreciable weight loss of both the samples until ~260°C, thereafter in a first region of temperatures ranging 260–325°C ca. complete elimination of volatile products (respectively water or methanol, as confirmed by gas-chromatographic analysis) occurs, suggesting polyamidation reactions of the two monomers having taken place.

In a second region of temperatures, above 325°C, the weight loss–temperature curve of the polycondensated PAA exhibits a plateau which extends up to 350°C; at higher temperatures a new weight loss (5% ca.) of the polyamide occurring.

The polycondensated PAE shows quite good thermal stability up to 410°C ca. Accordingly, the i.r. analysis (*Figure 2*) of the PAE, after thermal treating up to 340 and 410°C gives spectra which are analogous, revealing that there was preservation of the polymer structure, in agreement with the extended plateau in region II of *Figure 1* (N.B. the region 4000–2000 cm^{-1} has been neglected because it is relatively uninformative as to structure).

The i.r. spectra of the polyamide formed from AA, after thermal treating up to 410°C, differs from that at 340°C. In particular this refers to the bands of amide I and to those assigned to the out of plane C–H bending of the terphenyl system outer rings[1]. However, these spectra suggest that the weight loss of the PAA at temperatures above 350°C is not due to structure degradation, but may be better attributed to cross-linking reactions with formation of a product that shows good stability at least up to 470°C (see region III of *Figure 1*). This is confirmed by i.r. analysis (*Figures 2C* and *E*) of a sample thermally treated up to this temperature.

The PAE, however, though exhibiting good stability up to ~410°C, beyond this temperature suffers a sensible weight loss (see region III of *Figure 1*) which can be properly related to a degradation reaction. In fact, as evidenced by the i.r. spectra of *Figure 2F*, substantial modification and partial disappearing of the amide bands can be observed. The product obtained after thermal treatment up to 470°C appeared dark in colour and nearly carbonized.

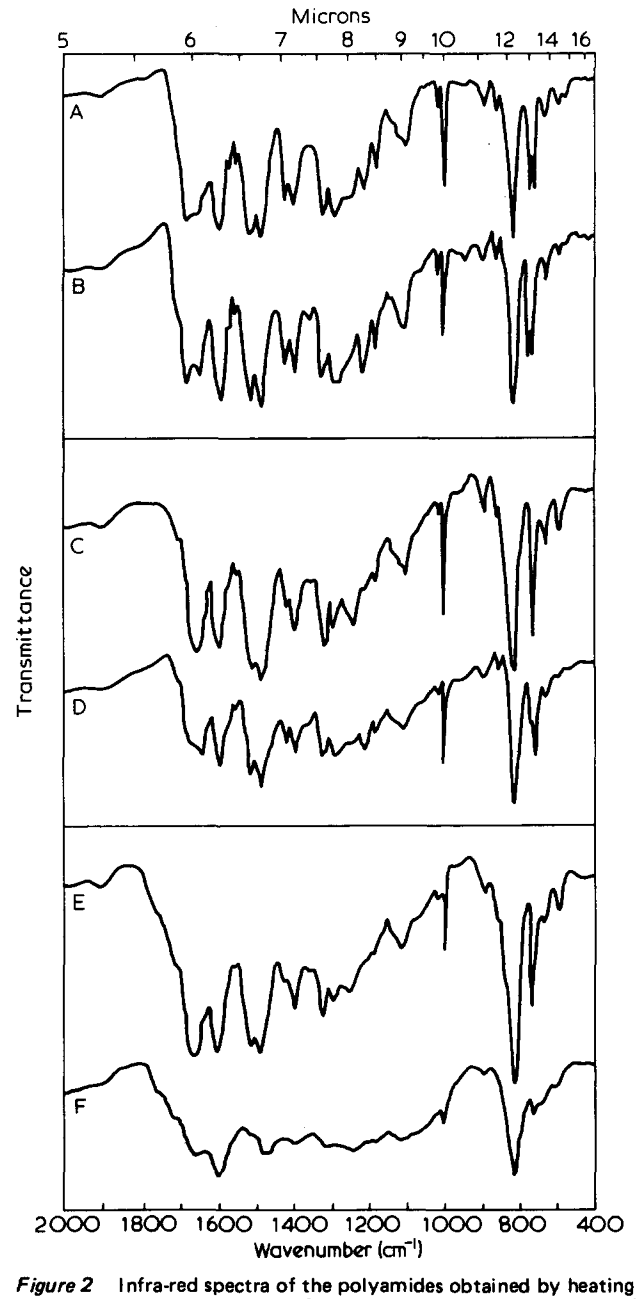

Figure 2 Infra-red spectra of the polyamides obtained by heating: (A), AA and (B), AE up to 340°C; (C), AA and (D), AE up to 410°C (E), AA and (F), AE up 470°C

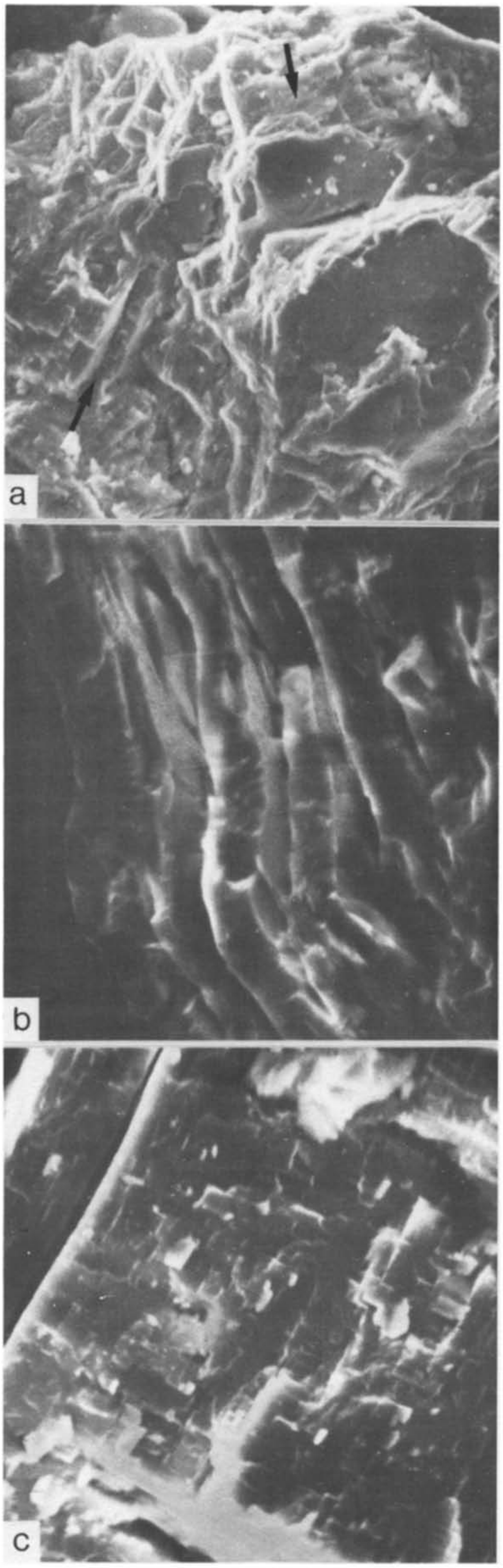

Figure 3 Scanning electron micrographs of a PAE sample thermally obtained at 282°C showing: (a) crystalline regions where parallel layers with various orientations can be observed, 800X; (b), parallel layers with regions of separation between them, 2000X; (c), microsteps of growing crystals along one of the layers together with region of separation (on the left) between the layers, 2000X

Scanning electron microscopy and X-ray analysis

The morphological analysis by scanning electron microscopy (*SEM*) of AE samples, polymerized thermally at 282°C, suggests an organized crystalline structure, where the polymer chains are arranged in a planar way (*Figure 3a*). Regions of separation between planar layers can be observed in the micrographs of *Figure 3b* and *c*, together with the growing steps of the crystals (*Figure 3c*). This ordered structure may depend on the liquid-phase polyamidation reaction which allowed the chains to be properly oriented.

The PAA did not reveal an analogously resolved structure, because of the extremely fine polymer powder. However, X-ray analysis, in both cases, showed an identical crystalline structure (*Figures 4a* and *b*) with diffraction patterns exhibiting three well defined isotropic rings corresponding to *d* values: 9.2, 8.00 and 6.52 (Å).

Electrical conductivity

Data of electrical conductivity, σ, and activation enerby, E_a, of the poly[4,4''(*p*-terphenylene)amide] from the monomer AA[1], kept at 282°C for 2 h, in argon together with these values for the poly [4,4''(*p*-terphenylene)amide], thermally obtained from the monomer AE in analogous experimental conditions, have been reported in *Table 1*. As shown, the conductivity (electric field independent) of PAE, in the temperature range 25°–75°C, is higher than the conductivity of PAA, their difference being about two orders of magnitude at the temperature of 30°C, while decreasing as the temperature increases. The activation energy, E_a, of PAE, determined by using the Arrhenius relationship, in all the temperature range 25°–75°C is lower than both the E_a values of PAA.

DISCUSSION AND CONCLUSIONS

From a comparative study of the poly[4,4''(*p*-terphenylene)amide], thermally obtained in two different

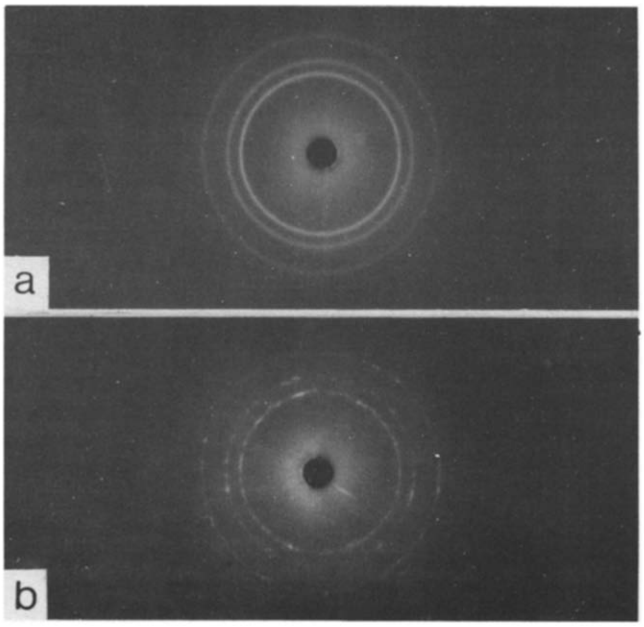

Figure 4 X-ray diffraction patterns of the polyamide formed at 282°C: (a), solid-state and (b), melt obtained

Table 1 Conductivity data

Polyamide	Temperature range (°C)	E_a (eV)	σ_0 (Ω^{-1} cm^{-1})	σ (Ω^{-1} cm^{-1}) 30°C	σ (Ω^{-1} cm^{-1}) 75°C
PAA	25–45	0.71	4.1×10^{-4}	7.0×10^{-16}	4.0×10^{-13}
	45–75	1.67	6.6×10^{-11}		
PAE	25–75	0.65	3.2×10^{-3}	5.6×10^{-14}	1.3×10^{-12}

ways, it has been revealed that in a region of temperatures up to 410°C the PAE is characterized by a higher thermal stability than PAA: the i.r. spectra of PAE, after treatment up to 340°C and 410°C, do not reveal any sensible chemical modifications. However, the spectra of the PAA treated up to 410°C definitely differ from that at 340°C, which may signify that a further chemical transformation (presumably a crosslinking reaction) for this polyamide occurred.

Actually, this different thermal behaviour of the two polyamide forms in the second region of temperatures cannot be explained easily, on account of their identical crystalline structure as revealed by X-ray diffraction patterns of the polyamide obtained at 282°C in the two different ways. At present, what may be suggested is that some other causes (unlike structure variations), for example the different extent of crystallinity or the different crystallite sizes, may give rise to the diversity, either in thermal stability or electrical conductivity, of the above mentioned polyamide forms.

Note also that the polyamidation of AE, other than AA, occurs after the monomer is melted and while it is progressing it gives a product which gradually solidifies, so the polyamide chains may orient themselves properly in the liquid phase before solidification, with the result of larger crystal growth.

The *SEM* shows crystalline regions where it may be supposed that the PAE chains are arranged in a planar way, according to a model proposed by other authors[3,4], with secondary bonds acting between the chains.

At temperatures higher than 410°C, however, the PAE undergoes a degradation reaction, with partial disappearing of the amide bands, as shown by the i.r. spectra of the samples thermally treated up to 470°C (*Figure 2F*). As a consequence of the previously occurred crosslinking reaction, the PAA suffers no further structure modifications, and the product obtained after thermal treatment up to 410°C shows quite good stability beyond this temperature, without undergoing any degradation reactions, even up to 470°C.

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