Solid-state polymerization of 4-amino-4″-carboxy-*p*-terphenyl

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The synthesis of 4-amino-4″-carboxy-*p*-terphenyl is reported and a solid-state polycondensation reaction of the synthesized product is studied by thermogravimetry. From the isothermal weightloss–time curves the rates of volatilization of water evolved during the polyamidation reaction were calculated and, by applying the Arrhenius relationship, the activation energy (46 kcal mol^{-1}) of the process was obtained. Infrared spectra of the poly[4,4″(*p*-terphenylene)amide] formed at various temperatures, electrical conductivity data and activation energy values, for both the monomer and polymer, are given.

INTRODUCTION

An investigation on the behaviour of electrical conductivity of *p*-terphenyl derivatives[1] as a function of temperature gave the starting point for a preliminary study on the thermal characteristics of 4-amino-4″-carboxy-*p*-terphenyl.

At high temperature ($\simeq$260°C) a solid-state polycondensation of this derivative takes place and the product obtained is of fully aromatic polyamide type, which in recent years have assumed great importance in the field of synthetic fibres, characterized by high thermal stability and outstanding mechanical properties[2–4].

Aromatic polyamides (aramides) whose structure is characterized mainly by a benzenic back-bone are already well known[4,5]. However, to the authors' knowledge, polyamides having the *p*-terphenyl as recurring aromatic unit have not yet been reported.

This led us to examine the polyamidation reaction of the 4-amino-4″-carboxy-*p*-terphenyl, before studying its electrical conductivity behaviour.

EXPERIMENTAL

Materials

The meltings points of the materials were uncorrected. Elemental analyses were obtained on a F & M Scientific Corporation Carbon, Hydrogen, Nitrogen Analyzer, Model 185.

(a) 4-Nitro-*p*-terphenyl (I) was prepared by the method of Splies[6].

(b) 4-Nitro-4″-acetyl-*p*-terphenyl (II) — a solution of anhydrous aluminium chloride (1.6 g, 11.9 mmol) in nitrobenzene (7 ml) was added dropwise, over a period of 2 h, to a stirred solution of 4-nitro-*p*-terphenyl (I) (1 g, 3.7 mmol) and acetyl chloride (0.8 ml, 11.1 mmol) in nitrobenzene (22 ml), at 18–22°C. The mixture was stirred for another hour at room temperature and was then added slowly to vigorously stirred ice water. After steam distillation of nitrobenzene, the residual suspension was filtered to give an orange, crystalline material which was washed with water and dried. The yield was 1.2 g (98%); m.p. 182–185°C (K–N)*, 229°C (N–I). The product was recrystallized from toluene to give pale yellow crystals, pure according to t.l.c. analysis; m.p. 186.5–188°C (K–N)*, 231°C (N–I)*. Composition found: C, 75.55%; H, 4.74%; N, 4.46%. $C_{20}H_{15}NO_3$ requires C, 75.69%; H, 4.76%; N, 4.41%; i.r. (KBr): ν_{max} 1670 cm^{-1} (C=O); 1505, 1335 cm^{-1} (NO_2).

(c) 4-Nitro-4″-carboxy-*p*-terphenyl (III) — a slight excess of a commercial hypochlorite solution was added dropwise to a stirred solution of (II) (1 g, 3.2 mmol) in dimethylformamide (30 ml) at 70°C. The mixture was stirred at this temperature for 1 h and then diluted with boiling water and acidified by addition of aqueous hydrochloric acid. The resultant suspension was filtered, while hot, to give a yellow solid which was washed with water. The yield was 0.99 g (99%). The product, recrystallized from glacial acetic acid, appeared to be pure by t.l.c.; m.p. 334–336°C. Composition found: C, 71.10%; H, 4.23%; N, 4.29%. $C_{19}H_{13}NO_4$ requires C, 71.47%; H, 4.10%; N, 4.39%; i.r. (KBr): ν_{max} 1720, 1670 cm^{-1} (C=O); 1510, 1340 cm^{-1} (NO_2).

(d) 4-Amino-4″-carboxy-*p*-terphenyl (IV) — a solution of dihydrated stannous chloride (2.34 g, 10.4 mmol) in aqueous 37% hydrochloric acid (2.7 ml, 32.4 mmol) was added dropwise to a stirred suspension of (III) (1 g, 3.1 mmol) in glacial acetic acid (105 ml). The mixture was refluxed for 1 h with stirring, then allowed to cool and filtered. The solid residue, washed with water, was decomposed with aqueous 5% sodium hydroxide (56 ml), by stirring for 10 min. After filtration, the residue was suspended in stirred water and the suspension was acidified by the addition of acetic acid to pH 4 and then filtered to give a yellow solid.

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

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The yield was 0.86 g (93%). The product was recrystallized from dimethylformamide/anisole (1:5) to give a pale yellow solid, pure by t.l.c.; m.p. not determinable. Composition found: C, 78.80%; H, 5.39%; N, 4.89%. $C_{19}H_{15}NO_2$ requires C, 78.87%; H, 5.23%; N, 4.84%; i.r. (KBr): v_{max} 3370, 3290 cm^{-1} (NH_2); 1680 cm^{-1} (C=O).

(e) Deamination of (IV) — aqueous 5N hydrochloric acid (40 ml) was added to a stirred suspension of (IV) (1 g, 3.1 mmol) in glacial acetic acid (120 ml). After quick cooling (0°C) aqueous sodium nitrite was added (6.6 mmol), with stirring for 2 h at 0–5°C. The filtered brilliant yellow solution of diazotized amine was used immediately for the next step. Aqueous 50% hypophosphorus acid (3.6 ml) was added and the mixture was let to stand at room temperature for a week. The white solid was collected and washed with water. The sample, purified by vacuum sublimation (37% yield; m.p. 306–307°C), was identical with an authentic sample[7], as shown by mixed melting point, t.l.c. analysis and i.r. spectra.

(f) Polycondensation of (IV) — the aminoacid (IV) was heated for 2 h at 282°C under an argon stream (these conditions ensured, according to the thermogravimetric experiments, that complete conversion of the monomer occurred). A yellow-brown powder, insoluble in the usual amide solvents and infusible up to 500°C was obtained.

Elemental analysis showed sometimes irregularities between observed and calculated data, probably due to the polymer combustion difficulties; however all the analyses confirmed that polycondensation took place. A typical result of one of those is reported here. Composition found: C, 83.82%; H, 5.32%; N, 5.16%. $(C_{19}H_{13}NO)_n$ requires C, 84.11%; H, 4.83%; N, 5.16%.

Thermogravimetry

The thermogravimetric experiments were carried out in air and argon with a Cahn RG electrobalance, with an ultimate precision of 2×10^{-7} g, connected to an L & N recorder. For the furnace temperature control a Pt–Rh/Pt thermocouple was used in conjunction with an electronic thermoregulator and heating rate programmer. Temperature fluctuation as sensed by a cromel–alumel thermocouple positioned immediately under the sample was less than ±1°C. In all the experiments thermal equilibrium was usually reached within 7 min from the time the preheated furnace was raised into position. During this period, volatilization of the sample was negligible at the experimental temperatures chosen; weight losses due to spattering could be reduced by the use of small samples (2–3 mg) and by means of special cylindrical capsule (dimensions 12 × 5 mm). However, some volatilization of the sample occurred during the heating treatment at the temperatures 272 and 282°C.

Infrared spectra

The i.r. absorption spectra were obtained on a Perkin–Elmer 577 grating spectrophotometer, by samples incorporated in a potassium bromide disc.

Electrical conductivity measurements

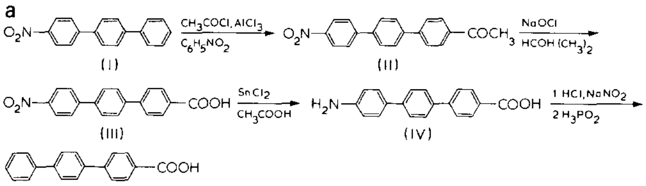
Powdered samples of the compounds were pellet shaped (9–13 mm in diameter and 0.5–0.7 mm thick) at the pressure of 10000 kg cm^{-2}. The pellets were heated for a day at 100°C in vacuo over phosphorus pentoxide and provided with silver paint contacts.

The DC conductivity was measured in an inert atmosphere of flowing anhydrous nitrogen at equilibrium temperature in the range 25–80°C. A DC voltage of 10–100 volt between the electrodes was applied by means of a Keithley 240 power supply and the steady-state current was measured through the sample with a Keithley 610 C electrometer.

RESULTS AND DISCUSSION

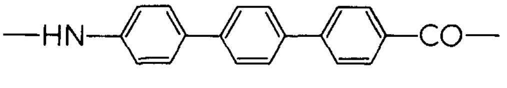
Synthesis

The 4-amino-4''-carboxy-*p*-terphenyl (IV) was prepared according to the following scheme:



The single reactions had been optimized accurately in order to give high product yield.

The compound (IV) structure was determined by elemental and infrared analysis. The carboxyl 4'' position had been confirmed unambiguously in a chemical way by deamination reaction which gave the acid (V) already known[7]. The subsequent polyamidation of (IV) gave the poly[4,4''(*p*-terphenylene)amide] with the repeat unit:



Thermogravimetry

The thermogravimetric experiments carried out under atmospheric conditions in the presence of air (to note that the experiments conducted in argon atmosphere did not show sensible difference) are summarized in *Figure* 1, where the curves of weight loss as function of time, for the sample treated at various temperatures between 253 and 282°C are shown. In the temperature range 267–282°C volatilization of the reaction product approached within 3–4 h, the stoichiometric weight loss (6.2% of the original sample weight) for the formation of a polyamide, except for some volatilization of the sample that took place at 272 and 282°C.

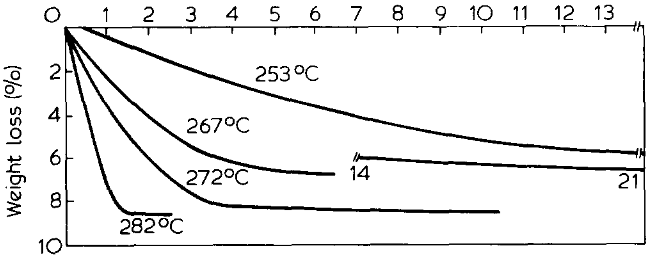


Figure 1 Isothermal weight loss curves for the volatilization of water in the polyamidation process in air

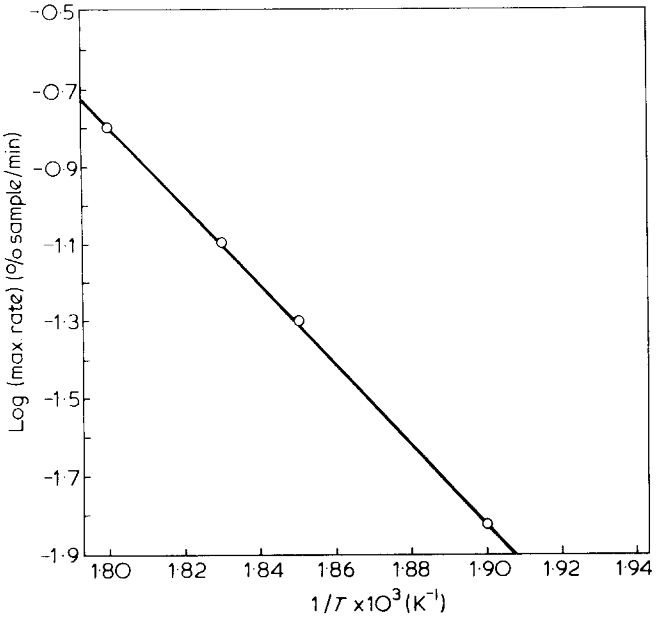


Figure 2 Arrhenius plot for the polyamidation reaction in air

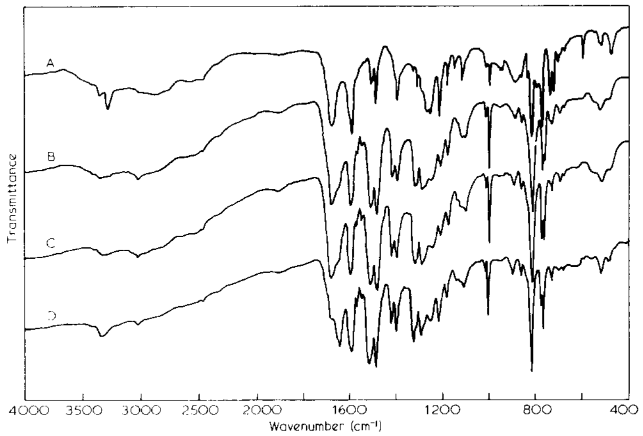


Figure 3 Infrared spectra of A, aminoacid (IV); B, polyamide obtained at 253°C; C, polyamide obtained at 267°C; D, polyamide obtained at 282°C

After, the condensated product became stable with respect to prolonged heating.

Below 253°C the samples did not suffer any weight loss, and at this temperature the reaction product volatilization was much slower — ~18 h.

From the weight loss profiles the rates of volatilization of water were determined and, by plotting the logarithm of maximum rates (expressed in % of sample volatilized per min) versus the inverse of the absolute temperature, according to the Arrhenius relationship $K = S\exp(-E/RT)$ an activation energy of 46 Kcal mol^{-1} was calculated (*Figure* 2).

Infrared analysis

The i.r. spectra of polymerized samples from the thermogravimetric experiments in air (those of polymerized samples in argon atmosphere did not show a substantial difference) present (*Figure* 3) the characteristic absorption bands of secondary polyamides[8]:

3420 cm^{-1}	free N–H stretching
3340 cm^{-1}	associated N–H stretching
1680 cm^{-1}	free C=O stretching (amide I)
1645 cm^{-1}	associated C=O stretching (amide I)
1510 cm^{-1}	N–H bending and/or C–N stretching (amide II)
1320 cm^{-1}	C–N stretching (amide III)

The bands at 3340 cm^{-1} are always broad and have low intensity varying with the extent of humidity, in agreement with Gan *et al.*[9]. The band at 3420 cm^{-1}, usually exhibiting very low intensity, became well pronounced if the samples had been dried accurately (*Figure* 4).

The amide I, II, III band intensities varied according to the temperature at which the samples were obtained; in details, as shown in *Figure* 3:

(a) amide I — at lower temperature, the band intensity at 1680 cm^{-1} is higher than that at 1645 cm^{-1}, signifying that the amide free form is prevailing over the associated one. The situation is reversed as the temperature is increased.

(b) amide II — at lower temperature the band intensity can be compared with that at 1680 cm^{-1}. At higher temperatures it prevails over both band intensities of amide I.

(c) amide III — the band intensity increases with the temperature.

It was noted also that the band intensities of amides I and II depend on moisture content of the samples.

Other polymer bands of special interest are at 770 and 760 cm^{-1}, their intensities being affected by the polymerization temperature. At lower temperature the band intensity at 770 cm^{-1} is higher than the other,

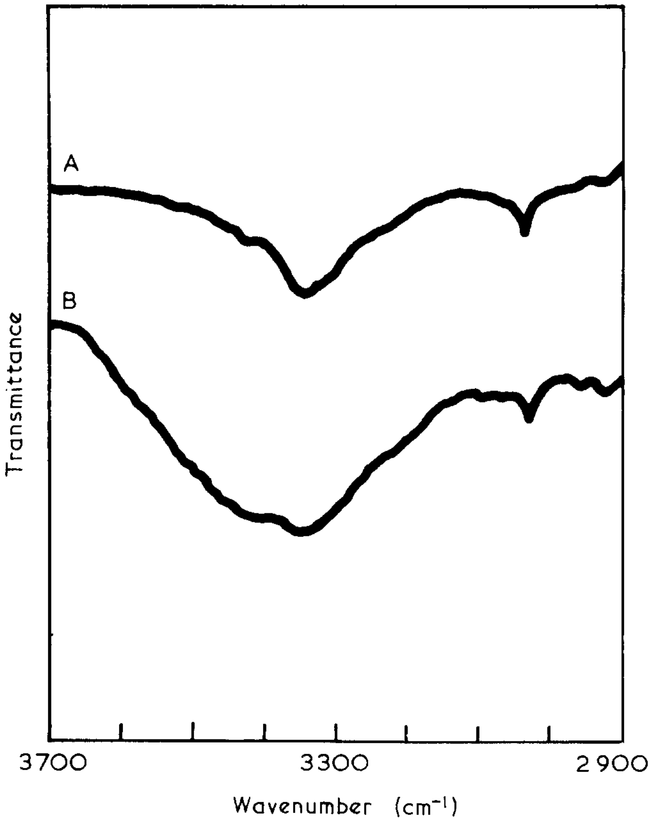


Figure 4 Infrared bands of N-H: A, sample not dried; B, sample dried

Table 1 Conductivity data under an applied field of 1000 V cm^{-1}

Material	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
4-Amino-4''-carboxy-*p*-terphenyl	30–45	0.53	1.0×10^{-3}	1.3×10^{-12}	3.9×10^{-11}
	45–80	0.76	3.8		
Poly[4,4''(*p*-terphenylene)amide]	25–45	0.71	4.1×10^{-4}	7.0×10^{-16}	4.0×10^{-13}
	45–75	1.67	6.6×10^{-11}		

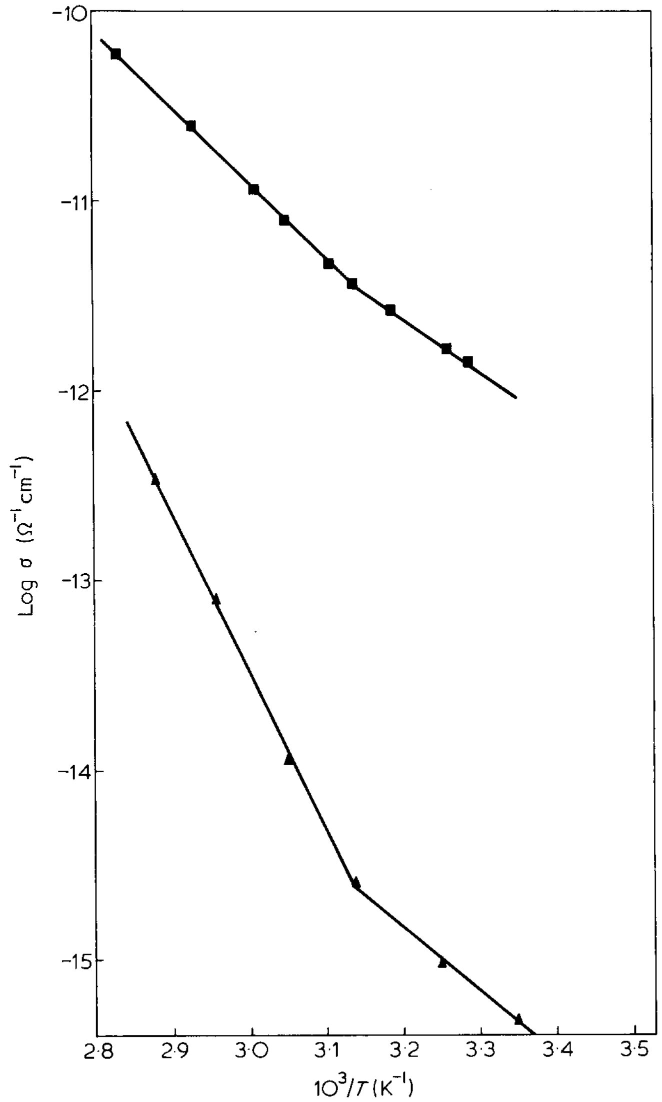


Figure 5 Temperature dependence of conductivity for: ■, amino-acid (IV); ▲, polyamide obtained at 282°C in argon for 2 h

whereas, as the temperature increases the situation is gradually reversed.

These bands may be attributed to the out of plane C–H bending of the terphenyl system outer rings. This is confirmed by comparing the *p*-terphenyl spectrum with those of more than twenty derivatives, with different substituents in 4 and 4'' position, in which two bands have been revealed in the range 750±30 cm^{-1} that may be ascribed to the out of plane C–H bending of the outer rings, on the analogous assignment of the *p*-terpehnyl bands[10].

Electrical conductivity

In *Table* 1 the activation energy, E_a, and σ_0 values of the monomer and of the polymer (from the polycondensation in argon at 282°C for 2 h) are reported — calculated by using the Arrhenius relationship $\sigma = \sigma_0 \times \exp(-E_a/RT)$ together with the experimental values of the conductivity, σ, determined at two different temperatures.

The monomer conductivity at 30°C is about four orders of magnitude greater than that of the polymer. In the temperature range 25–80°C the polymer conductivity varies to a greater extent as compared with that of the monomer. The polymer conductivity also varies with the applied electric field.

Both the conductivity characteristics (*Figure* 5) exhibit a kink at the temperature of 45°C. The higher E_a value, as regards the polymer, may be referred to its intrinsic conductivity. The respective energy gap value, $\Delta E = 2E_a$ is in agreement with that reported by Eley and Pacini[11] for a terphenyl type polymer.

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