

polymer communications

Synthesis of substituted aromatic polyamides containing p-terphenyl units in the main chain

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Soluble aromatic polyamides containing alkyl or alkoxy substituted p-terphenyls were prepared. These polyamides were obtained from solution polymerization of 4,4''-diamino-2',5'-dialkyl or dialkoxy p-terphenyls with terephthaloyl dichloride. The new dialkoxy substituted terphenyl diamines were synthesized by the palladium mediated coupling of the 2,5-disubstituted benzene diboronic acid with 4-nitrophenyl bromide and subsequent reduction of nitro groups. The synthesized polyamides were characterized by viscosimetry, thermal analysis and dynamic mechanical analysis. The dialkoxy substituted polyamide has high modulus at room temperature and despite the presence of aliphatic side chains the modulus remains constant up to 250°C. © 1997 Elsevier Science Ltd. All rights reserved.

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Introduction

The synthesis of wholly aromatic polyamides still attracts much effort mainly because of the outstanding mechanical properties of these materials¹. On the other hand, the limited solubility and the high melting temperatures of unsubstituted aromatic polyamides restrict their wider application. Aggressive solvents like concentrated sulfuric acid are used to form lyotropic solutions from which ultra high modulus fibers are produced. It is apparent that solubility is an important factor in making anisotropic solutions of appropriate concentrations to achieve good fiber properties.

The strategies which have been employed for solubility increase in aromatic polyamides, are lateral substitution^{2–7} and the distortion of the rigid character introducing non-planar, kinked or flexible parts in the main chain^{8–12}. As a consequence, the solubility is increased but in some cases the mechanical properties of the derived polymers are also influenced.

To develop high performance materials, modifications which increase solubility while maintaining the rod-like character are of particular interest. In this respect, the introduction of p-terphenyl moiety in the main chain is expected to increase the rigidity as well as the mechanical properties in the case of aromatic polyamides. Former attempts have shown that the mechanical properties of substituted aromatic polyesters have been improved by the introduction of oligophenyl moieties in the main chain^{13–15}.

We report here on the synthesis and characterization of soluble aromatic polyamides bearing alkyl or alkoxy substituents, which also contain p-terphenyl units in the main chain. New p-terphenyl diamines were synthesized and the derived polyamides were characterized by viscosimetry, thermal analysis, optical microscopy and dynamic mechanical analysis.

Experimental section

Materials. Chemicals were purchased from Aldrich and used as received. 2,5-Dialkoxy-1,4-benzene-diboronic

acids¹⁶, 4,4''-diamino-2',5'-dihexyl-p-terphenyl¹⁷ and the catalyst dichloro[1,1'-bis(diphenylphosphino) ferrocene] palladium¹⁸ [PdCl₂(dppf)] were synthesized according to known procedures. Terephthaloyl dichloride was recrystallized from n-hexane. Tetrahydrofuran was distilled from sodium in the presence of benzophenone directly into the reaction flask and 1,1,2,2-tetrachlorethane was fractionally distilled.

Monomer synthesis

4,4''-Diamino-2',5'-dihexyloxy-p-terphenyl (4b). 6.55 mmol 2,5-Dihexyloxy-1,4-benzene diboronic acid (**1b**), 16.37 mmol 4-bromonitrobenzene and 100 mg PdCl₂(dppf) were added in a flask. The flask was degassed and flushed with Ar (3 times). 50 ml THF and 13 ml NaOH 3N were added and the mixture was heated with vigorous stirring at 70°C for 48 h. After cooling at room temperature, the mixture was treated with acetone and the 4,4''-dinitro-2',5'-dihexyloxy-p-terphenyl (**3b**) was isolated by filtration and dried in vacuo. Recrystallization from toluene gave 3.3 g (yield 73%) of pure compound **3b**. Catalytic reduction of **3b** with hydrogen in DMA with Pd on activated carbon at 40°C and recrystallization from toluene gave 2.4 g (yield 91%) of the desired product **4b**, m.p.: 125–127°C.

FTi.r. (KBr, cm⁻¹): 3446, 3368, 2932, 2852, 1622, 1528, 1490, 1474, 1382, 1294, 1250, 1184, 1126, 1046, 1020, 992, 880, 834, 724, 598, 532.

¹H-n.m.r. (CDCl₃): δ = 0.89(t; 6H, CH₃), 1.30(m; 12H, CH₂), 1.70(m; 4H, CH₂), 3.92(t; 4H, OCH₂), 6.75(d; 4H, CH), 6.94(s; 2H, CH), 7.44(d; 4H, CH).

¹³C-n.m.r. (CDCl₃): δ = 14.02, 22.60, 25.76, 29.37, 31.50, 69.55, 114.65, 116.01, 128.01, 128.81, 129.95, 130.38, 145.20, 150.20.

4,4''-diamino-2',5'-didodecyloxy-p-terphenyl (4c). The same procedure, as above, was adopted using **1c** instead of **1b** to synthesize **3c**. The product **3c** was recrystallized from toluene. The yield was 75%, m.p.: 151–152°C. The dinitro compound **3c** was reduced by hydrogen in DMA in the

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presence of Pd/C as the catalyst, **4c** was purified by recrystallization from toluene, (yield 89%), m.p.: 83–84°C.

FTi.r. (KBr, cm^{-1}): 3446, 3366, 2916, 2850, 1622, 1528, 1490, 1474, 1384, 1294, 1254, 1188, 1046, 1018, 992, 834, 718, 602, 534.

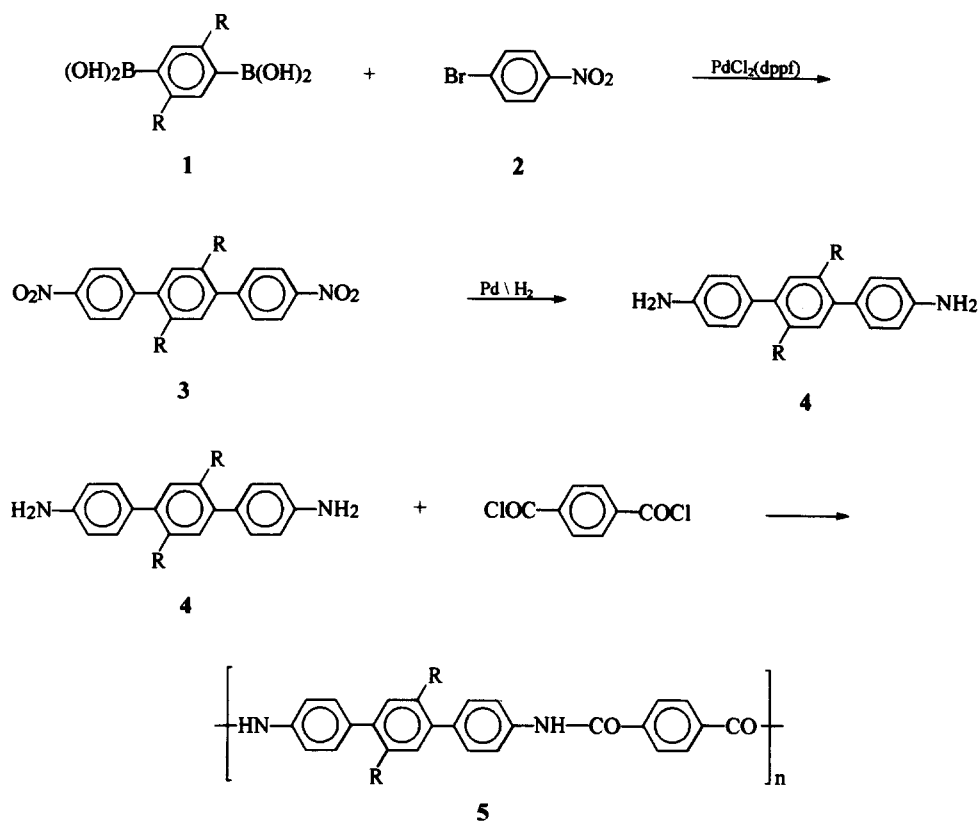
$^1\text{H-n.m.r.}$ (CDCl_3): $\delta = 0.88(\text{t}; 6\text{H}, \text{CH}_3)$, $1.34(\text{m}; 36\text{H}, \text{CH}_2)$, $1.67(\text{m}; 4\text{H}, \text{CH}_2)$, $3.69(\text{s}; 4\text{H}, \text{NH}_2)$, $3.87(\text{t}; 4\text{H}, \text{OCH}_2)$, $6.72(\text{d}; 4\text{H}, \text{CH})$, $6.92(\text{s}; 2\text{H}, \text{CH})$, $7.42(\text{d}; 4\text{H}, \text{CH})$.

Polymer synthesis. 1.00 mmol terephthaloyl dichloride was added under inert atmosphere to a solution of 1.01 mmol of the diamine **4** in 3 ml 1,1,2-tetrachloroethane (TCE) in a round flask of 50 ml, followed by step addition of 4 mmol triethylamine. The solution was stirred

for 15 min at room temperature (R.T.), 4 h at 80°C and after cooling at R.T., was diluted with 5 ml of TCE. The polymer was precipitated by addition of the solution to methanol, filtering and washing by methanol and drying at 80°C in high vacuo.

Results and discussion

In our attempt to study the influence of various substituents, as well as the introduction of oligophenyl moieties in the main chain, on the properties of aromatic polymers^{13–15}, aromatic polyamides have been selected. New *p*-terphenyl diamines **4b** and **4c** were synthesized by reduction of 4,4'-dinitro-2',5'-dialkoxy-*p*-terphenyl (**3**) which derived from 2,5-dialkoxy-1,4-benzene diboronic acids (**1**) and 4-bromonitrobenzene, as shown in *Scheme 1*.



1, 2, 3, 4, 5	a	b	c
R	C ₆ H ₁₃	OC ₆ H ₁₃	OC ₁₂ H ₂₅

Scheme 1

Table 1 Viscosity, thermal stability and solubility of polyamides **5**

Polymer	[η] (dl/g)	T_d^d (°C)	T_{max} (°C)	Solubility ^e				
				TCE	DMAc	DMSO	CHCl ₃ /TFA (9/1)	H ₂ SO ₄
5a	1.10 ^a	420	480	–	+	+	+	+
5b	1.12 ^b (1.05 ^c)	410	457	–	±	±	±	+
5c	0.45 ^c	380	447,475	–	–	±	±	+

^a in DMAc at 30°C

^b in DMAc at 70°C^c in conc. H₂SO₄ at 30°C

^d 5% weight loss under nitrogen

^e (+) soluble at room temperature, (±) soluble at 70°C, (–) insoluble

Polymerization of the diamines **4** with terephthaloyl dichloride was performed in 1,1,2,2-tetrachloroethane in the presence of triethylamine. The synthesized polyamides were characterized by viscosimetry, as shown in *Table 1*. Moderate viscosities for aromatic polyamides were obtained, however polymers **5a** and **5b** form self supporting films after solution casting from dimethylacetamide. For polymer **5b** intrinsic viscosity was estimated in concentrated sulfuric acid and dimethylacetamide. The obtained values are comparable, as expected for rigid polymers.

Polyamides **5a** and **5b** were soluble in organic solvents like DMAc, DMSO, DMF without the addition of inorganic salts as also shown in *Table 1*. The significant improvement in solubility compared to poly(*p*-phenylene terephthalamide) despite the presence of the *p*-terphenyl unit in the main chain, is evidently attributed to the side chains which prevent the polymer chains from close packing or strong interchain interactions.

Structural characterization of polyamide **5b** is shown in *Figure 1* by means of ^1H and ^{13}C n.m.r. The assignment of

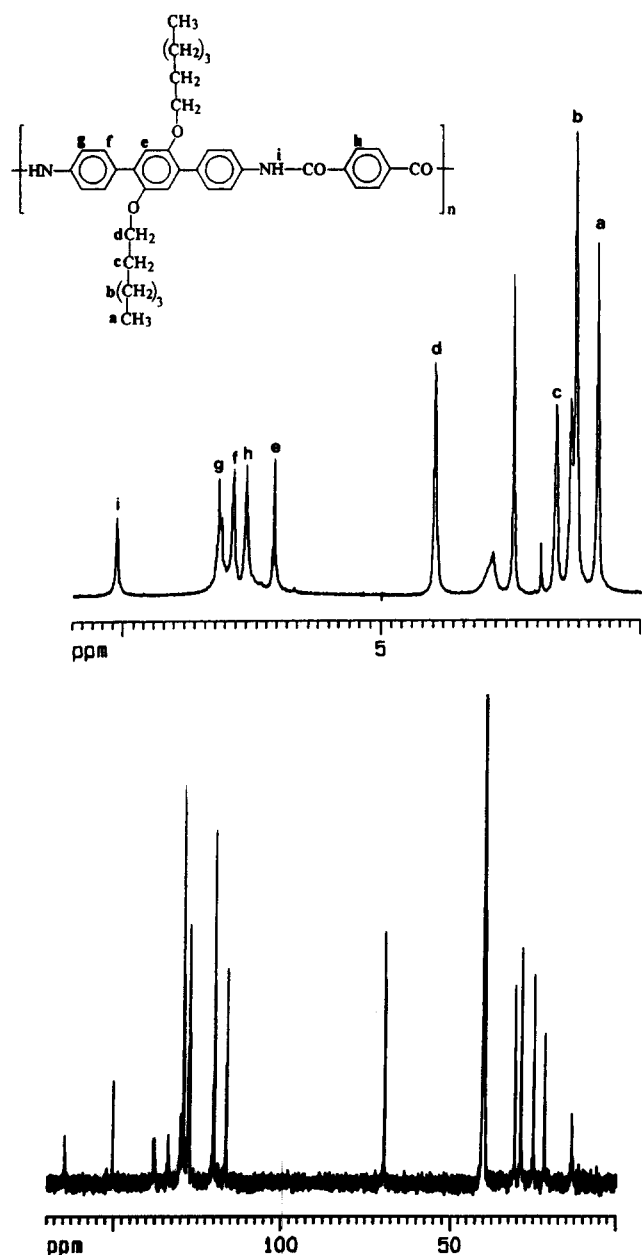


Figure 1 ^1H (at 400 MHz) and ^{13}C (at 100 MHz) n.m.r. spectra of polyamide **5b** in DMSO- d_6 .

the different protons is also shown in this figure. The aromatic protons adjacent to the amine groups in the monomer **4b** appeared at 6.75 ppm. This signal is drastically reduced in the spectrum of polymer **5b**. The degree of polymerization can be calculated based on the above signal due to the presence of amino end groups in the polymer and the aromatic protons in ortho position to the side chains. Thus a degree of polymerization equal to 18 was derived for polymer **5b**.

The lyotropic liquid crystalline behavior of polyamides **5a**, **5b** and **5c** was examined in DMAc. All polymers show lyotropic phases in solutions of 10 wt% directly after sample preparation. Upon standing at room temperature, polymers **5b** and **5c** form gels.

Thermal properties of the polyamides were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) under nitrogen. The polyamides studied showed neither a distinct glass transition nor a melting endotherm up to 350°C. The absence of a glass transition is in agreement with aromatic polyesters bearing aliphatic side chains¹³.

Table 1 shows the results for the thermal stability of polyamides **5** in terms of the 5% weight loss (T_d) and the temperature of the maximum weight loss rate (T_{max}). As expected, polyamides **5a** and **5b** show relatively improved thermal stability compared to **5c** but their thermal stability is considerably lower than the unsubstituted aromatic polyamides. The maximum of the single step of weight loss for polymer **5b** appeared at 460°C, compared to 540°C for poly(*p*-phenylene terephthalamide).

The dynamic mechanical properties of the polyamide **5b** were examined and the results for the temperature dependence of the tensile storage (E') and loss modulus (E'') are shown in *Figure 2*. The high values of E' at room temperature obtained for the untreated film (8×10^9 Pa) as well as the very weak dependence of E' on temperature up to 250°C show the excellent heat resistance of this material. It is interesting to note that the presence of the hexyloxy side chains did not affect the modulus up to 250°C, although a secondary transition attributed mainly to the side chains was obtained in all alkyl or alkoxy substituted aromatic polyesters. A more straightforward comparison of the

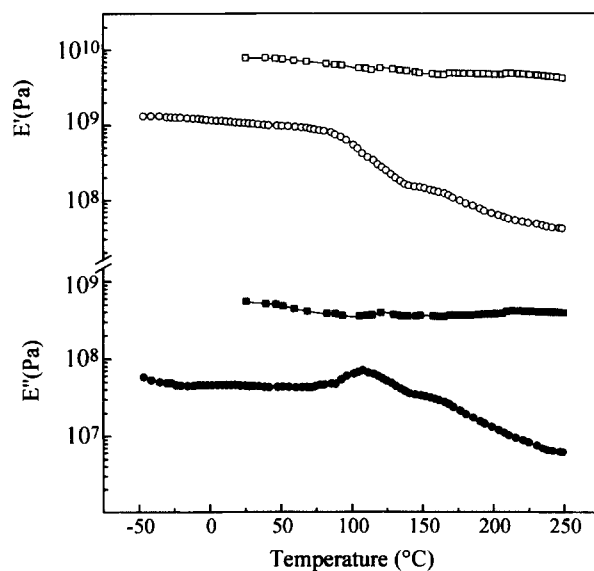


Figure 2 Dynamic-mechanical spectra of polymer **5b** (□, ■) and the respective polyester (○, ●)

influence of the polymer backbone on the mechanical properties may be made using the aromatic polyester which possesses the same structural characteristics, e.g. the same kind of substituents as well as the terphenyl moiety in the main chain. Figure 2 displays also the mechanical properties of the above-mentioned polyester¹⁵ showing a considerably lower storage modulus at room temperature ($E' \cong 1 \times 10^9$ Pa) and also a decrease of one order of magnitude above 100°C. This comparison clearly shows that in the case of aromatic polyamides the nature of the backbone determines their mechanical properties notwithstanding the presence of aliphatic side chains.

In conclusion, the combination of aliphatic side chains with the introduction of terphenyl moieties in the main chain is an effective way to obtain soluble aromatic polyamides with high modulus up to 250°C.

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