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Synthesis and structural study of poly(isophthalamide)s

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Abstract: The synthesis of a series of soluble 5-alkoxy substituted isophthalamides is described. Condensation of 1,3-diaminobenzene or 2,6-diaminopyridine with alkoxy substituted isophthaloylchlorides yields the title polyaramides. The influence of the alkyl chain length on the supramolecular structure of the polymer is investigated by X-ray diffraction experiments. Initial results indicate a lamellar type solid lattice for the polymers studied here.

Introduction

The synthesis of polyamides has been an active area of research during the last three decades mainly due to their wide range of applications in textile industry and in membrane fabrication.[1-5] Polyaramides are known for their high thermal stability and flame retardance. Most of the known polyaramides are insoluble in common solvents. Poly(p-phenylene terephthalamide) and its alkyl substituted derivatives have been studied extensively due to its high mechanical strength, fiber formation and the lyotropic liquid crystalline properties.[6-8] However, simple poly(m-phenylene isophthalamide) escaped thorough investigation so far due to the lack of the above mentioned properties.

The crystal structure of poly(m-phenylene isophthalamide) shows a contracted triclinic crystal lattice[9] when compared to the fully extended monoclinic crystal lattice of poly(p-phenylene terephthalamide).[10] The poly(m-phenylene isophthalamide) chain possesses a so called *check-patterned* hydrogen bond or *jungle gym* network structure with extensive hydrogen bonding along the *a* and *b* axis (Fig. 1a).[9] The low tensile modulus of poly(m-phenylene isophthalamide) is also attributed due to this contracted structure.[11]

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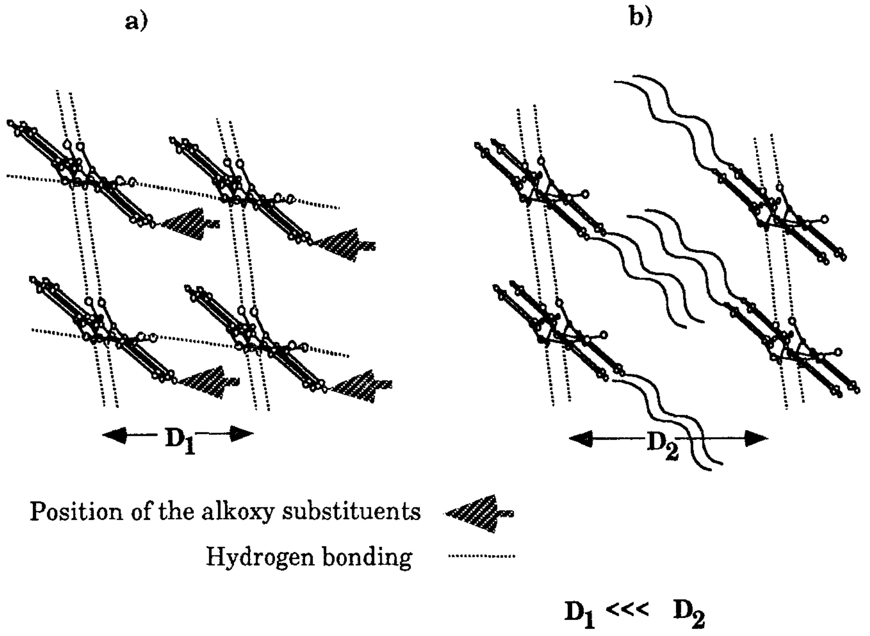


Figure 1: Schematic representation of the site of substitution and its anticipated consequences for the polymer lattice based on the crystal structure of the poly(m-phenylene isophthalamide)

From the crystal structure it is clear that substitution at C-5 of the isophthalic acid monomer may change the packing of the molecular chains and thereby the hydrogen bonding pattern (Fig. 1b). The inter-chain hydrogen bonds can be affected by using different alkyl chain lengths on the alkoxy substituted polymeric backbone. We are interested in developing a soluble poly(m-phenylene isophthalamide) whose structural and physical properties can be changed by systematically varying the structure of the monomers. Two approaches are followed:

i) modification of the hydrogen bonding pattern by introducing functional groups at C-5 of isophthalic acid monomer,
ii) incorporation of hydrophobic effects of the long alkyl chains.

Here we report on the synthesis and characterisation of soluble poly(m-phenylene isophthalamide)s and poly(2,6-pyridylene isophthalamide)s and the initial results of the structural features from X-ray diffraction measurements.

Experimental:

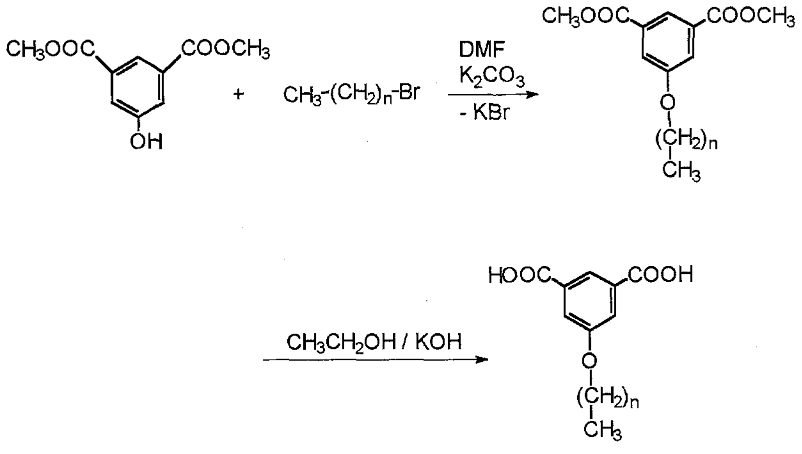
All solvents used were dried and freshly distilled. 1,3-Diaminobenzene and the 2,6-diaminopyridine were purified by sublimation. Triethylamine was dried over potassium hydroxide and distilled before use. All other reagents were used as obtained from commercial sources. The NMR measurements were done by using Brucker AM 300 and AMX 500 MHz spectrometers and the IR spectra were recorded on a Nicolet FTIR Spectrometer 320. The mass spectra were recorded on a Finnigan MAT 95, Fison Instruments ZAB 2-SE-FPD. The TGA data were obtained using a Mettler 500 Thermogravimetric Analyser and the X-ray diffractions were measured on a Vertical Goniometer PW 1820/00, Philips. GPC analyses were performed with PSS-Gel, SDV10^3, 10^5, 10^6 Å with an elution rate of 1ml/min with an UV-Vis Detectometer S 3702.

General procedure for the synthesis of 5-alkoxyisophthalic acid (C_nISA) given for C_{11}ISA: Dimethyl-5-hydroxyisophthalate (15g, 14.3mmol) and potassium carbonate (19.6g, 35.75 mmol) were stirred in 750ml of DMF for one hour at 80°C. To this mixture 1-undecylbromide (20g, 15.6 mmol) in 50 ml of DMF was added and the mixture was left stirring for six hours. The solvent was then evaporated and the residue mixed with water followed by extraction with dichloromethane (5 *150 ml). The combined organic phase was dried over magnesium sulphate and evaporated to afford a white solid which was recrystallized from methanol and identified as dimethyl-5-undecyloxyisophthalate. Hydrolysis of the ester was performed in a solution of sodium hydroxide (7 equiv.) in ethanol and water (2:1 mixture) which was stirred for six hours under reflux. The solution was concentrated and cooled to 0°C. The white precipitate obtained after the addition of conc. HCl was filtered, washed with water and dried under high vacuum. The crude acid was recrystallized from methanol. Yield: 21.6 g (90%); m.p. 182°C; ^{1}H NMR (300 MHz, DMSO-d_6, ppm): δ = 0.85 (t, 3 H, CH_3), 1.35 (m, 16 H, -CH_2), 1.70 (m, 2H, CO-CH_2-), 4.05 (t, 2H, -O-CH_2-), 7.6 (s, 2H, ArH), 8.1 (s, 1H, ArH); 13.0 (s, 2H, -OH); ^{13}C NMR (75 MHz, DMSO-d_6, ppm): 13.7, 22.0, 25.3, 28.5, 28.6, 28.9, 31.3; 68.0, 119.0, 122.1, 132.6, 158.8, 166.4; EI MS (m/e): 336.2

General procedure for the synthesis of poly(isophthalamide)s C_nPA given for C_{11}PA: 5-Undecyloxyisophthalic acid (4.0 mmols) was refluxed in freshly distilled thionyl chloride (15ml) for three hours. The mixture was cooled and the excess thionyl chloride was removed under high vacuum to obtain a solid. The resulting dichloride was dissolved in dry chloroform (100 ml). m-Phenylene diamine (4.0 mmols, or 1 equivalent of 2,6-diamino-pyridine) and triethylamine (5 ml) in dry chloroform was added dropwise to the dichloride solution and stirred under room temperature for two days. The excess solvent was removed under high vacuum and the residue was mixed with water (100 ml). The mixture was extracted with dichloromethane (3x50 ml). The organic fraction was then washed with water (2x25 ml), dried and evaporated to get a brown powder. This powder was characterised as the poly(m-phenylene isophthalamide) from GPC, NMR, and IR.; GPC: 91,570(M_w); IR (cm^{-1}): 3301 (N-H), 2924-2853 (C-H), 1655 (C=O), 1594 (C=C), 1540 (CO-NH); ^1H NMR (500MHz, $CDCl_3$, ppm): 0.9-2.5 ($-CH_2-$), 4.1-5.0 ($-CH_2-$), 7.4 (s, 1H, ArH), 8.0 (s, 2H, ArH), 8.1 (s, 2H, ArH), 8.2 (t, 1H, ArH), 9.3 (s, 1H, ArH), 11.6 (s, 2H, NH); ^{13}C NMR (125 MHz, $CDCl_3$, ppm) 13.9, 22.6, 26.0, 29.3, 29.4, 29.6, 31.9, 68.7, 113.9, 116.9, 117.9, 129.9, 136.0, 139.8, 159.6, 163.3, 165.1.

Results and discussion

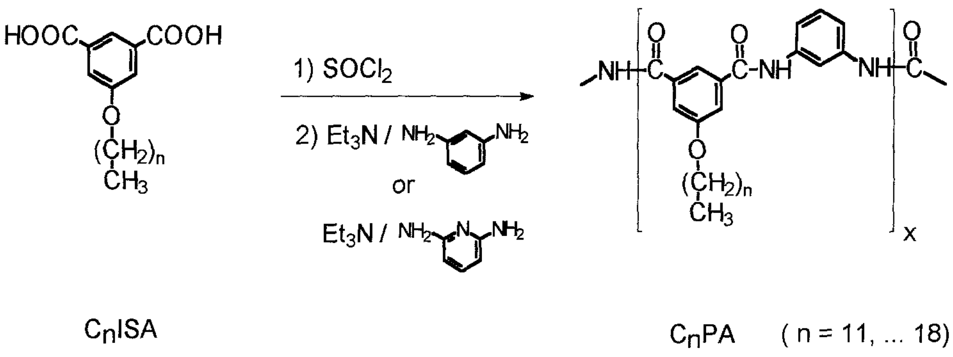
The synthesis of the polymers was achieved in good yields from 5-alkoxyisophthalic acid and the commercially available diamines such as m-phenylene diamine and 2,6-diaminopyridine. 5-alkoxyisophthalic acid was synthesised from the commercially available 5-hydroxyisophthalic acid and various alkyl bromides in the presence of potassium carbonate as base.



C_nISA

Scheme 1: Synthesis of the 5-alkoxyisophthalic acids (C_nISA)

Conversion of the diacid into the diacid chloride with thionyl chloride followed by condensation with the diamino compound in presence of triethylamine gave the required polyamide. The characterisation of these polyamides was done by GPC, ^1H and ^{13}C NMR and IR measurements.



Scheme 2: Synthesis of the poly(isophthalamide)s

The GPC results indicate a high degree of polymerisation in the case of poly(m-phenylene isophthalamide) (typically M_W = 60 000 up to 90 000) and a relatively low degree of polymerisation in the case of poly(2,6-pyridylene isophthalamide) (typically M_W = 10 000 up to 20 000). The low degree of polymerisation in the case of 2,6-diaminopyridine is attributed to the low nucleophilicity of the amino group on the pyridine ring. However, a synthetic approach to increase the degree of polymerisation of poly(2,6-pyridylene isophthalamide) is currently under way in our laboratory.

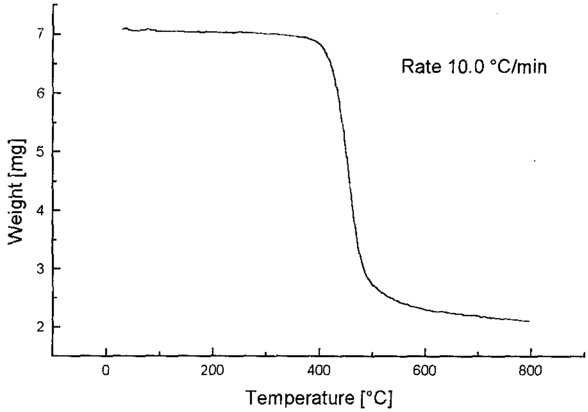


Figure 2: TGA diagram of the polymer $C_{11}PA$

The synthesised polymers have high thermal stability according to the TGA analysis. No significant decomposition was observed below 400°C. The alkyl chain length does not influence the thermal stability of the polymers.

IR spectra of the polymers indicate two strong absorptions at 1655 and 1540 cm^{-1} due to the hydrogen bonded amide groups. The X-ray diffraction measurements of the polyaramides show a sharp reflection in the small angle region and a broad peak in the wide angle region. A plot of the number of C-atoms in the side chain of the polymer versus the *d* spacings gives a straight line for the homologous series which indicates an ordered structure for the polymer chains in the lattice. Inter-chain hydrogen bonding and side-chain crystallisation induce a lamellar structure for the polymer lattice. The high crystallinity for the polyaramides with long alkyl chains observed in the powder diffraction spectrum also indicates a side-chain crystallisation which is seen clearly in case of the 5-alkoxyisophthalic acid monomers well characterised in our laboratory.[12]

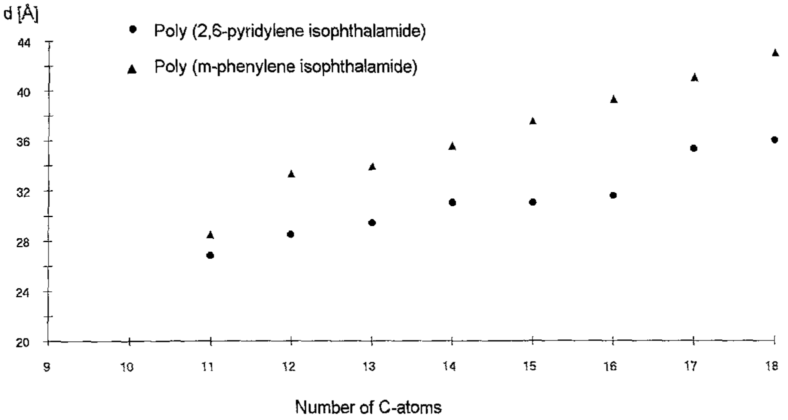


Figure 3: Plot of the *d* spacings vs the number of C-atoms in the side chain of the polymers

In conclusion, we demonstrate a synthetic approach to control the polymer chain organisation in the solid lattice by systematically varying the substitution on the polymer backbone. Initial results from X-ray diffraction studies indicate a lamellar structure for the polyaramides synthesised here. The results from IR spectra and the change in physical properties such as high solubility and thermal stability also reveal a different structure for the polyaramides studied here from the reported structure of the unsubstituted poly(m-phenylene isophthalamide) due to the influence of alkyl chains at C-5 position of the isophthalic acid monomer. The complete characterisation of the supramolecular structure of the polymers and its possible liquid crystalline behaviour are currently under investigation.

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