

Tetracarboxylic bisimide–lactam ring contraction: a route to lactamimide-containing polymers

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First lactamimide monomers were synthesised by the bisimide–lactam ring contraction and polymerised by the high-temperature transesterification in the melt to give lactamimide-containing polymers. The polymers were amorphous with good film-forming properties, soluble in common organic solvents, and showed from low to medium molecular weight. Lactamimide-containing polymers bearing aliphatic spacers showed strong fluorescence with large Stokes shift (140–150 nm) peaking at 580–585 nm while those with phenyl groups on nitrogen atoms presented very weak fluorescence probably resulting from loose-bolt quenching, peaking at 610–615 nm. The polymers showed third-order non-linear optical susceptibility in the range of 10^{-10} – 10^{-11} e.s.u.
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INTRODUCTION

Six-membered ring dicarboximides are commonly viewed as chemically very inert. Strong hydrolysing reagents such as hot, concentrated sulphuric acid or KOH *tert*-butyl alcohol are required for their saponification¹. A completely different reaction pathway is observed, however, if under much milder conditions, alkali metal hydroxides in alcohol react with six-membered ring bisimides such as naphthalene-1,8:4,5-tetracarboxylic bisimides to produce lactamimides² with loss of a C1 fragment from one carboximide. In all cases only one of the imide ring systems is transformed in lactam leaving the second one unchanged. In agreement with this conclusion is the finding that monoimide does not undergo ring contraction.

Recently the mechanism of this rearrangement has been proposed³, which includes the addition of one equivalent of OH⁻ to one of the imide carbonyl. Subsequent ring contraction leads to the formation of a lactam followed by decarboxylation. This is a novel type of rearrangement and appears to be a general reaction for other six-membered ring bisimides.

Several naphthalene–lactamimides, starting from naphthalene–bisimides, have been prepared and characterised. They show absorption in the visible region due to intramolecular charge transfer from donor lactam to acceptor imide fragments and exhibit strong fluorescence (quantum yields >80%)³. Their large Stokes shifts are remarkable, rendering them promising compounds for dye lasers. Yet, strong intramolecular charge transfer and conjugation make them candidates for third-order non-linear optics materials.

The goal of this work is to apply bisimide–lactam ring contraction for the synthesis of novel polymers containing lactamimide fragments in the main chain. These polymers should possess luminescent and non-linear optical proper-

ties due to their electronic structure and show good environmental stability. Yet, the reduction in symmetry of lactamimide (C_{1h}) compared to bisimide (D_{2h}) is favourable for the tractability of polymers and transparency of polymer films which are of importance for optical applications. This paper reports the first synthesis of lactamimide monomers, their polymerisation, and the characterisation of the obtained polymers.

EXPERIMENTAL

Materials

All reagents were used as received from Aldrich.

Model compound and monomer synthesis

N,N'-Bis(*n*-nonyl)-1,8,4,5-naphthalenetetracarboxylic bisimide (2). 1,4:5,8-Naphthalenetetracarboxylic acid dianhydride (1) (5.0 g, 18.6 mmol) and *n*-nonylamine (5.4 g, 37.3 mmol) and *o*-dichlorobenzene (80 ml) were refluxed until the reaction mixture became clear (3 h). The hot solution was filtered and cooled. The solid formed was filtered off and dried in vacuum. Yield 86%, mp = 173–175°C. ¹H n.m.r. (CDCl₃) 8.73 (s, 4H, arom), 4.17 (t, 4H, $J = 7.5$ Hz NCH₂-), 1.77–1.67 (m, 4H, NCH₂CH₂), 1.40–1.2 (m, 24H, (CH₂)₆), 0.85 (t, 6H, $J = 6.9$ Hz CH₃), ¹³C n.m.r., 162.8 (C=O, imide), 130.9 (C_{ar}-H, C_{ar}), 126.7 (C_{ar}-C=O), 41.0 (NCH₂), 31.8 (NCH₂CH₂), 29.5 (NCH₂CH₂CH₂), 29.3 (NCH₂CH₂CH₂CH₂), 29.2 (NCH₂CH₂CH₂CH₂CH₂), 28.1 (CH₃CH₂CH₂CH₂), 27.1 (CH₃CH₂CH₂), 22.6 (CH₃CH₂), 14.0 (CH₃).

N,N'-Bis(*n*-nonyl)-1-amino-4,5,8-naphthalenetetracarboxylic acid-1,8-lactam-4,5-imide (3). A solution of KOH (6.0 g, 107 mmol), compound 2 (2.0 g, 3.86 mmol) in mixture of DMSO (25 ml) and MeOH (30 ml) was heated at 70°C overnight. The reaction mixture was poured into

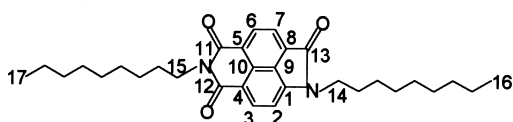
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diluted HCl and the precipitate formed was filtered off and refluxed with ethanol (100 ml) and conc. HCl (15 ml) for 3 h. The solution was filtered and the precipitate was crystallised from ethanol. Yield 42%, mp = 105–106°C ^1H n.m.r., (CDCl_3), 8.55 (d, ^1H , $J = 7.5$ Hz, H^6), 8.40 (^1H , $J = 7.5$ Hz, H^3), 8.15 (d, ^1H , $J = 7.5$ Hz, H^7), 7.05 (d, ^1H , $J = 7.5$ Hz, H^2), 4.14 (t, 2H, $J = 7.5$ Hz, H^{15}), 3.92 (t, 2H, $J = 7.2$ Hz, H^{14}), 1.90–1.1 (m, 28H (CH_2) aliph.) 0.90–0.80 (m, 6H, H^{16} , H^{17}) ^{13}C n.m.r., 167.5 (C^{13}), 163.4, 162.8 (C^{11} , C^{12}), 144.8 (C^1), 134.3, 131.4, 125.1 (C^6 , C^7 , C^3), 130.0, (C^{10}), 126.6, (C^8), 124.6, 124.1 (C^4 , C^5), 116.6 (C^9), 105.8 (C^2), 40.9, 40.5 (C^{15} , C^{14}), 31.8, 29.5, 29.4, 29.3, 28.6, 28.4, 28.1, 27.1, 26.9, 22.6 (CH_2 aliph.), 14.1 (C^{16} , C^{17}).

Formula 1

N,N'-Bis(6-hydroxyhexyl)-1,8,4,5-naphthalenetetracarboxylic bisimide (**4**). Compound **4** was prepared similar to compound **2** from anhydride **1** (2.0 g, 7.46 mmol) and 6-aminohexanol (1.75 g, 15.0 mmol) Yield 85%, mp = 205–

Formula 1



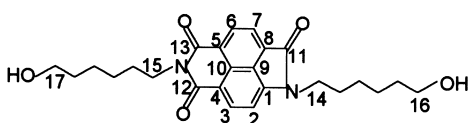
207°C, ^1H n.m.r. (DMSO-d_6) 8.47 (s, 4H, arom.), 4.20 (t, 2H, $J = 5.1$ Hz, $-\text{OH}$), 3.92 (t, 4H, $J = 6.9$ Hz, $\text{N}-\text{CH}_2$), 3.40–3.20 (m, 4H, CH_2-O), 1.60–1.00 (m, 16H, (CH_2)₄). ^{13}C n.m.r., 162.3 ($\text{C}=\text{O}$), 130.7 ($\text{C}_{\text{ar}}-\text{H}$, C_{ar}), 126.0 ($\text{C}_{\text{ar}}-\text{C}=\text{O}$), 60.5 (CH_2-OH), 32.3, 27.3, 26.3, 25.1 (CH_2 aliph).

N,N'-Bis(6-hydroxyhexyl)-1-amino-4,5,8-naphthalenetetracarboxylic acid-1,8-lactam-4,5-imide (**5**). A solution of compound **4** (2.0 g, 4.62 mmol), KOH (6.7 g, 120 mmol) in the mixture of MeOH (40 ml) and DMSO (30 ml) was heated at 70°C overnight. The reaction mixture was poured into diluted HCl, the precipitate formed was filtered off and refluxed for 3 h with 100 ml ethanol containing 15 ml conc. HCl. The hot solution was filtered and poured into water (500 ml). The precipitate formed was filtered off, dried in vacuum and crystallised from ethyl acetate. Yield 57%, mp = 118–120°C. ^1H n.m.r. (DMSO-d_6), 8.24 (d, ^1H , $J = 7.2$ Hz, H^6), 8.14 (d, ^1H , $J = 7.5$ Hz, H^3), 8.03 (d, ^1H , $J = 7.2$ Hz, H^7), 7.25 (d, ^1H , $J = 7.5$ Hz, H^2), 3.90 (t, 2H, $J = 7.5$ Hz, H^{14}), 4.20 (s, 2H, OH), 3.80 (t, 2H, $J = 6.6$ Hz, H^{15}), 1.70–1.10 (m, 20H, CH_2). ^{13}C n.m.r., 166.7 (C^{11}), 162.5, 162.4 (C^{12} , C^{13}), 144.0 (C^1), 134.1, 130.1, 125.0 (C^3 , C^6 , C^7), 129.0 (C^{10}), 125.9 (C^8), 123.5, 122.9 (C^4 , C^5), 115.4 (C^9), 106.7 (C^2), 60.6, 60.5 (C^{16} , C^{17}), 32.4, 28.1, 27.8, 26.5, 26.1, 25.3, 25.1 (CH_2 aliph.).

Formula 2

1-(5-Bromopentyloxy)-4-nitro-benzene (**7**). A solution of 4-nitrophenol (10 g, 72 mmol), and 1,5-dibromopentane (50 g, 217 mmol) in *N*-methylpyrrolidone (NMP) was heated at 80°C in the presence of potassium carbonate (10 g,

Formula 2



72 mmol) with stirring for 48 h. The solid was filtered off and the liquid was diluted with CH_2Cl_2 (300 ml) and washed

successively with 5% NaOH, water, dried over MgSO_4 , and distilled in vacuum to remove the excess of 1,5-dibromopentane and NMP. The residue was extracted with hot hexane to give white crystals on cooling. Yield 60%, mp = 30°C. ^1H n.m.r. (CDCl_3), ^1H n.m.r. (CDCl_3) 8.21 (d, 2H, $J = 9.3$ Hz, *ortho* to NO_2), 6.96 (d, 2H, $J = 9.3$ Hz, *meta* to NO_2), 4.09 (t, 2H, $J = 6.3$ Hz, $\text{C}_{\text{ar}}-\text{O}-\text{CH}_2-$), 3.44 (t, 2H, $J = 6.6$ Hz, CH_2Br), 2.00–1.80 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$), 1.70–1.60 (m, 2H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2-$). ^{13}C n.m.r., 164.0 ($\text{C}_{\text{ar}}-\text{O}$), 141.3 ($\text{C}_{\text{ar}}-\text{NO}_2$), 125.9 (C_{ar} *ortho* to NO_2), 114.4 (C_{ar} *meta* to NO_2), 68.5 ($\text{O}-\text{CH}_2$), 33.4 (CH_2Br) 32.2, 28.7, 22.2 ($(\text{CH}_2)_3$).

1-(5-Hydroxypentyloxy)-4-nitrobenzene (**8**). A solution of compound **7** (10.5 g, 36 mmol) was stirred overnight in hexamethylenephosphotriamide (HMTA) (20 ml) at 100°C containing 10 ml of water and 3.6 g, 43 mmol sodium hydrocarbonate. The reaction mixture poured into diluted HCl, The solid formed on cooling was filtered off, dried in vacuum and crystallised from carbon tetrachloride, Yield 87%, mp = 25°C. ^1H n.m.r. (CDCl_3) 8.21 (d, 2H, $J = 9.0$ Hz, *ortho* to NO_2), 6.94 (d, 2H, $J = 9.0$ Hz, *meta* to NO_2), 4.07 (t, 2H, $J = 6.3$ Hz, $\text{C}_{\text{ar}}-\text{O}-\text{CH}_2-$), 3.70 (t, 2H, $J = 6.3$ Hz, CH_2OH), 2.00–1.80 (m, 2H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2-$), 1.70–1.50 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$). ^{13}C n.m.r., 164.1 ($\text{C}_{\text{ar}}-\text{O}$), 141.3 ($\text{C}_{\text{ar}}-\text{NO}_2$), 125.8 (C_{ar} *ortho* to NO_2), 114.3 (C_{ar} *meta* to NO_2), 68.7 ($\text{O}-\text{CH}_2$), 62.6 (CH_2OH), 32.2, 28.7, 22.2 ($(\text{CH}_2)_3$).

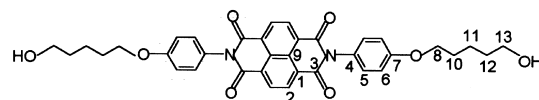
4-(5-Hydroxypentyloxy)aniline (**9**). A solution containing compound **8** (6.2 g, 27.5 mmol), hydrazine hydrate (3 ml) and Raney-Ni catalyst 1.5 g was refluxed for 8 h. The catalyst was filtered off and the solvent was evaporated in vacuum to give yellowish crystals. Yield 88%. ^1H n.m.r. (CD_3OD), 6.80–6.60 (m, 4H, arom.), 4.82 (s, 2H, NH_2), 3.89 (t, 2H, $J = 6.3$ Hz, $\text{C}_{\text{ar}}-\text{O}-\text{CH}_2-$), 3.56 (t, 2H, $J = 6.3$ Hz, CH_2OH), 1.80–1.60 (m, 2H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2-$), 1.65–1.40 (m, 4H, $\text{Ar}-\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$). ^{13}C n.m.r., 154.3 ($\text{C}_{\text{ar}}-\text{O}$), 142.0 ($\text{C}_{\text{ar}}-\text{NH}_2$), 118.7, 117.1 (C_{ar}), 70.1 ($\text{O}-\text{CH}_2$), 63.4 (CH_2OH), 33.9, 30.9, 24.0 ($(\text{CH}_2)_3$).

N,N'-Bis(4-(5-hydroxypentyl)phenyl)-1,8,4,5-naphthalenetetracarboxylic bisimide (**10**). Compound **10** was prepared similar to bisimide **2** from **1** (2.8 g, 10.4 mmol) and amine **9** (4.5 g, 23 mmol) and 100 ml *o*-dichlorobenzene. Yield 85%, mp > 300°C. ^1H n.m.r. (DMSO-d_6), 8.69 (s, 4H, H^2), 7.33 (d, 4H, $J = 8.7$ Hz, H^5), 7.08 (d, 4H, $J = 8.7$ Hz, H^6), 4.13 (s, 2H, OH), 4.05 (t, 4H, $J = 6.3$ Hz, H^8), 3.42 (m, 4H, H^{13}), 1.82–1.75 (m, 4H, H^{10}), 1.60–1.40 (m, 8H, H^{11} , H^{12}), ^{13}C n.m.r., 163.1 (C^3), 158.5 (C^7), 130.4 (C^2), 130.0 (C^5), 127.8, 126.9, 126.6 (C^9 , C^1 , C^4) 114 (C^6), 67.7 (C^8), 60.6 (C^{13}), 32.2, 28.8, 22.2 (C^{10} , C^{11} , C^{12}).

Formula 3

N,N'-Bis-(4-(5-hydroxypentyl)phenyl)-1-amino-4,5,8-naphthalenetetracarboxylic acid-1,8-lactam-4,5-imide (**11**). A solution of compound **10** (3.5 g, 5.6 mmol), and KOH (10 g, 178 mmol) in a mixture of 60 ml methanol and

Formula 3



60 ml DMSO was refluxed overnight. The reaction mixture was poured into diluted HCl, the precipitate

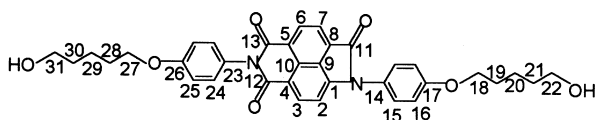
formed was filtered off, washed with water and dried in vacuum. The solid was refluxed in a mixture of EtOH (70 ml) and conc. HCl (15 ml) until the colour of the solid turned from red to yellow. The reaction mixture was poured into water washed with water, dried in vacuum and crystallised from chlorobenzene. Yield 72%, mp = 205–207°C. ^1H n.m.r. (DMSO- d_6) 8.45 (d, ^1H , $J = 7.2$ Hz, H^6), 8.27 (d, ^1H , $J = 7.2$ Hz, H^7), 8.26 (d, ^1H , $J = 7.5$ Hz, H^3), 7.50 (d, 2H, $J = 9.0$ Hz, H^{24}), 7.23 (d, 2H, $J = 8.7$ Hz, H^{15}), 7.14 (d, 2H, $J = 9.0$ Hz, H^{25}), 7.13 (d, ^1H , $J = 7.5$ Hz, H^1), 7.03 (d, 2H, $J = 9.0$ Hz, H^{16}), 4.40 (s, 2H, OH), 4.10–4.00 (m, 4H, H^{18} , H^{27}), 3.50–3.40 (m, 4H, H^{22} , H^{31}), 1.90–1.70 (m, 4H, H^{28} , H^{21}), 1.60–1.40 (m, 8H, H^{29} , H^{28} , H^{19} , H^{20}). ^{13}C n.m.r., 166.2 (C^{11}), 163.1, 163.0 (C^{12} , C^{13}), 158.3, 158.2 (C^{26} , C^{17}), 144.7 (C^1), 134.2, 131.3, 125.5 (C^3 , C^6 , C^7), 128.8, 128.3, 126.2, 126.0, 124.3, 123.1 (C^{23} , C^5 , C^4 , C^{10} , C^8 , C^{14}), 130.1 (C^{24}), 127.4 (C^{15}), 116.4 (C^9), 115.2 (C^{25}), 114.5 (C^{16}), 107.0 (C^2), 67.9, 67.7 (C^{18} , C^{27}), 60.6 (C^{31} , C^{22}), 32.2, 28.6, 22.1 (C^{19} , C^{20} , C^{21} , C^{28} , C^{29} , C^{30}).

Formula 4

Polymerisation. All polymers were prepared by high-temperature transesterification in melt.

Poly-4m. A mixture of monomer **4** (0.500 g,

Formula 4



1.15 mmol) and dimethylisophthalate (**13**) (0.223 g, 1.15 mmol) and titanium tetraisopropoxide ($\text{Ti}(\text{O}(\text{i-Pr})_4)$) (0.001 g) was heated for 1.5 h at 255°C under nitrogen flow. Then the pressure was reduced to 0.1 mmHg and the reaction mixture was heated for 1 h more. The polymer formed was dissolved in CHCl_3 on heating, purified by precipitation into methanol and dried in vacuum until constant weight.

Poly-4p. The polymerisation was carried out similarly to **Poly-4m** from monomer **4** (0.500 g, 1.15 mmol) and dimethylterephthalate (**12**) (0.223 g, 1.15 mmol). The polymer formed was not soluble in common organic solvents and was not purified by precipitation.

Polymers **Poly-5m** and **Poly-5p** were prepared similarly to **Poly-4m** from monomer **5** (0.500 g, 1.23 mmol) and dimethylisophthalate (**13**) and dimethylterephthalate (**12**) (0.239 g, 1.23 mmol), respectively.

Poly-11m and Poly-11p. These were prepared from monomer **11** (0.500 g, 0.841 mmol) and dimethylisophthalate (**13**) and dimethylterephthalate (**12**) (0.163 g, 0.841 mmol), respectively, similarly to **Poly-4m**.

Poly-10m. A mixture of monomer **10** (0.500 g, 0.803 mmol), dimethylisophthalate (**13**) (0.156 g, 0.803 mmol) and $\text{Ti}(\text{O}(\text{i-Pr})_4)$ (0.001 g) was heated at 320°C for 30 min under nitrogen flow. Then pressure was reduced to 0.1 mmHg and the reaction mixture was heated until it solidified (15 min). The polymer formed was not soluble in common organic solvents.

Measurements

The number average molecular weights of polymers were determined by ^1H n.m.r. analysis of the end groups, d.s.c., and t.g.a., performed at a heating rate of 10°C/min under nitrogen with a du Pont 2100 machine. Glass transition (T_g) temperatures were determined from d.s.c. curves. ^1H n.m.r. and ^{13}C n.m.r. spectra were taken using a Varian spectrometer at 300 and 75.5 MHz, respectively, in DMSO- d_6 , CDCl_3 or CD_3OD , with TMS as the internal standard. Emission and excitation spectra were measured with a Perkin-Elmer 630-10S fluorimeter using thin films spin-coated onto a quartz slide. All $\chi^{(3)}$ data were obtained on cast films using the picosecond laser consisting of a mode-locked Quantel Nd:YAG laser with frequency doubled to 532 nm.

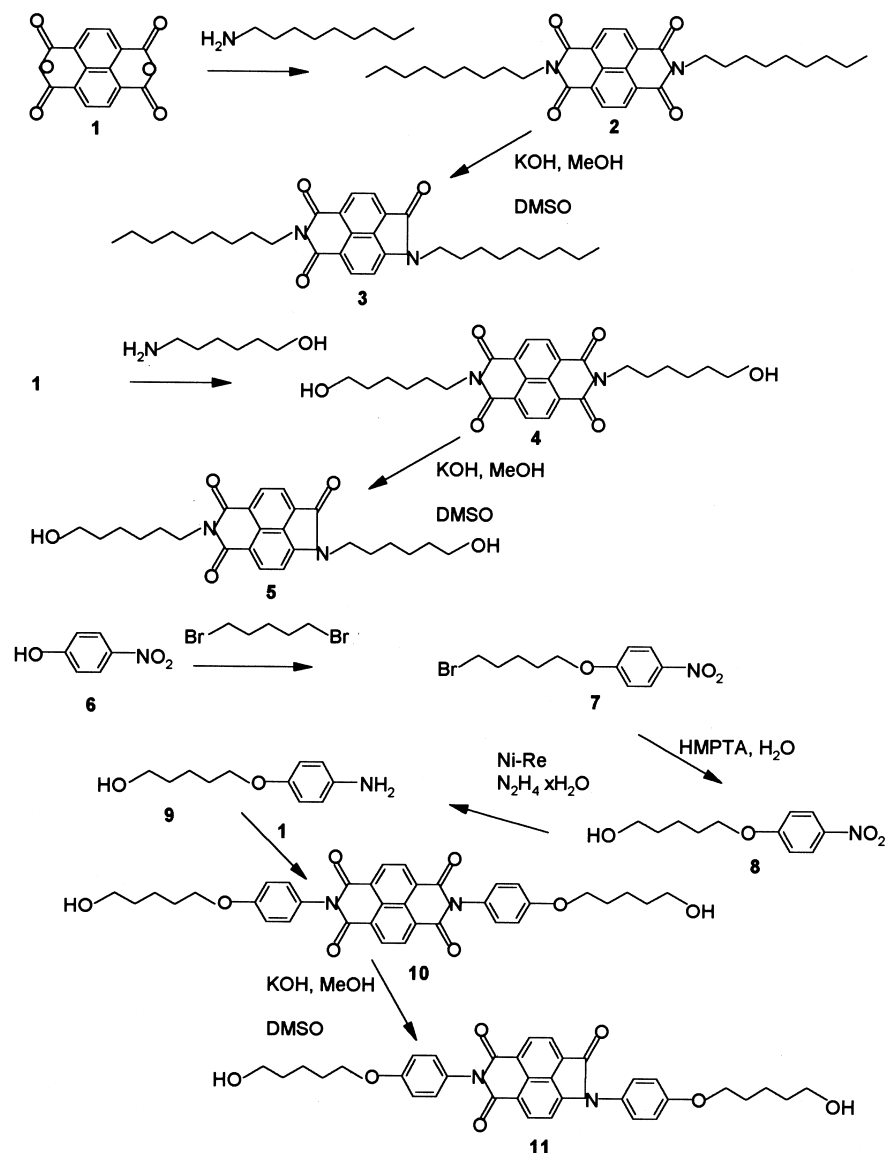
RESULTS AND DISCUSSION

Monomer and polymer synthesis

The synthetic route to model compound **3** and lactam-imide monomers **5** and **11** is shown in *Scheme 1*. Dianhydride **1** was used as starting material in all cases. The reaction at high temperature between **1** and *n*-nonylamine or 6-aminohexanol produced bisimides **2** and **4**, respectively. The obtained bisimides underwent bisimide–lactam ring contraction to give model compound **3** and monomer **5**, respectively. As seen from Section 2, significant decrease in melting points were observed for compounds **3** and **5** compared to bisimides **2** and **4** (68 and 87°C, respectively) due to symmetry reduction occurring during the ring contraction. Monomer **11** bearing phenyl substituents at nitrogen atoms was also synthesised to study the effect of aromatic substituents on polymer properties. The synthetic route includes aromatic amine **9** synthesis comprising of alkylation of 4-nitrophenol (**6**) with 1,5-dibromopentane generating monosubstituted intermediate **7** followed by the hydrolysis of bromine atom and the reduction of NO_2 group. The reaction between dianhydride **1** and amine **9** produced bisimide **10** which was isomerized to give lactamimide monomer **11**. Again, it is remarkable that a large melting point depression of **11** compared to **10** is observed. Compound **10** did not melt below 300°C while monomer **11** melted at 205°C.

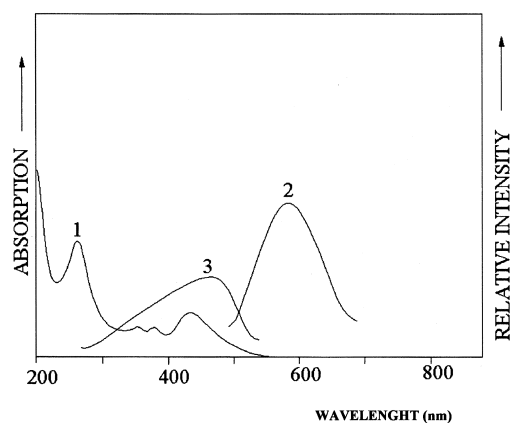
As bifunctional hydroxy-terminated monomers, compounds **5** and **11** were copolymerised with dimethyl isophthalate and dimethyl terephthalate by transesterification in melt to produce polyesters **Poly-5m**, **Poly-5p**, **Poly-11m** and **Poly-11p** (*Scheme 2*). To study the effect of bisimide–lactam ring contraction on polymer properties, model polyesters containing bisimide units were prepared from bisimides **4** and **10** and dimethyl isophthalate and dimethyl terephthalate to give bisimide-containing polyesters **Poly-4m**, **Poly-4p** and **Poly-10m**. It was impossible to prepare model polymer from **10** and dimethyl terephthalate due to extremely low tractability of both **10** and the polymer. The structure of polymers was confirmed by ^1H n.m.r. and ^{13}C n.m.r. spectroscopy. As an example, *Figure 1* presents ^1H n.m.r. spectra of **Poly-5m** and the respective model polymer **Poly-4m**. The spectra of **Poly-4m** are easy to assign. They consist of a singlet at 8.72 ppm, corresponding to naphthalene H^2 protons, and three signals of isophthaloyl protons appearing at 8.61 (s, H^{11}), 8.17 (d, H^8 , $J = 7.8$ Hz) and 7.49 (t, H^{10} , $J = 7.8$ Hz). There are two triplets at 4.33 and 4.19 ppm with $J = 6.6$ Hz corresponding to methylene protons of an aliphatic spacer connected to

Model Compound and Monomer Synthesis

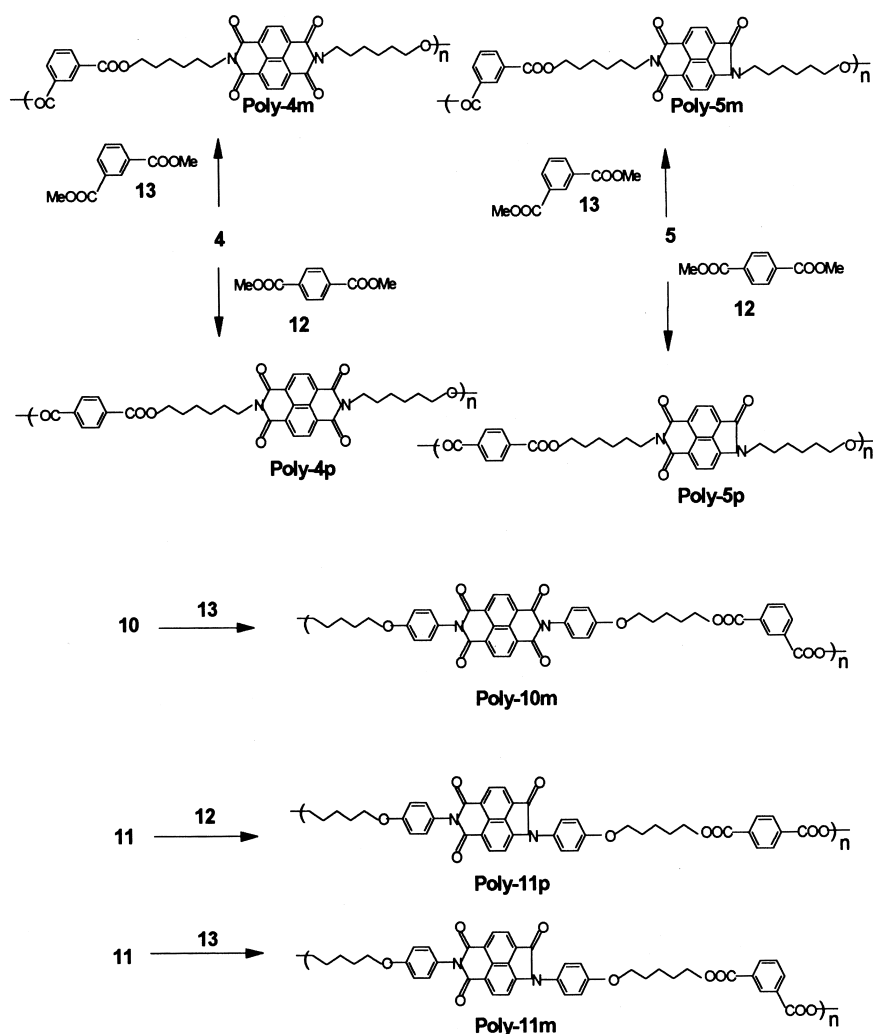


Scheme 1

oxygen and nitrogen atoms, respectively (H⁵ and H⁴). Weak signals of terminal methylene protons of –CH₂OH and COOMe groups are seen at 3.64 (t, *J* = 6.6 Hz) and 3.89 (s) ppm. In the spectra of **Poly-5m**, naphthalene protons are no longer equivalent due to symmetry reduction and are split into four doublets with *J* = 7.2–7.5 Hz at 8.51, 8.35, 8.12 and 7.02 ppm. Isophthaloyl signals do not change compared to **Poly-4m**. An additional multiplet corresponding to two protons appeared at 3.94 ppm in the spectra of **Poly-5m**. This signal is due to CH₂ connected to a nitrogen atom of the lactam ring. These protons are shielded compared to CH₂ connected to imide nitrogen due to the absence of additional carbonyl in lactam. Similarly to **Poly-4m** a weak signal of terminal methylene protons of –CH₂OH group is seen at 3.64 ppm. The ¹H n.m.r. spectrum of **Poly-5p** is similar to that of **Poly-5m** with the only difference being that four protons of terephthaloyl units appeared as singlets at 8.07 ppm. *Figure 2*. Shows assigned ¹H n.m.r. spectra of **Poly-11m** and **Poly-11p**, derived from monomer **11**. Similarly to the spectra of other polymers, the signals of

Figure 1 Absorption (1), emission (2) and excitation (3) spectra of **Poly-5p**

Polymer Synthesis



Scheme 2

Table 1 Some physico-chemical properties of synthesized polymers

Polymer	T_m (°C)	T_g (°C)	M_n ($\times 10^3$)	λ_{max} (nm) ^a	λ_{em} (nm) ^b	λ_{ex} (nm) ^c	Solubility in $CHCl_3$	$\chi^{(3)}$ (10^{11} e.s.u.) ^e
Poly-4m	180	30	4.8	377	–	–	+ (hot)	–
Poly-5m	–	60	34.1	434	581	466	+	2.2
Poly-4p	262	30	–	376 ^d	–	–	–	–
Poly-5p	–	50	33.1	435	582	467	+	4.1
Poly-10m	254	–	–	380 ^d	–	–	–	–
Poly-11m	–	50	4.3	446	615	469	+	8.2
Poly-11p	–	50	4.4	447	614	470	+	9.2

^aLong-wave absorption maximum^bEmission maximum (measured at the excitation maximum (λ_{ex}) for the respective compound)^cExcitation maximum (measured at the emission maximum (λ_{em}) of the respective compound)^dMeasured for the respective bisimide in DMSO solution^eThird-order non-linear optical susceptibility

terminal CH_2OH groups are seen at 3.64 ppm. The number average molecular weights (M_n) of polymers were calculated from 1H n.m.r. data and the results are listed in the *Table 1*. As can be seen, **Poly-5p** and **Poly-5m** show reasonably high molecular weight while other soluble

polymers are of low molecular weight. This is due to the fact that monomers **4** and **11** have high melting points ($>200^\circ C$), and dimethylisophthalate or dimethylterephthalate used as comonomers sublime noticeably before the polymerisation started. This can be confirmed by the n.m.r.

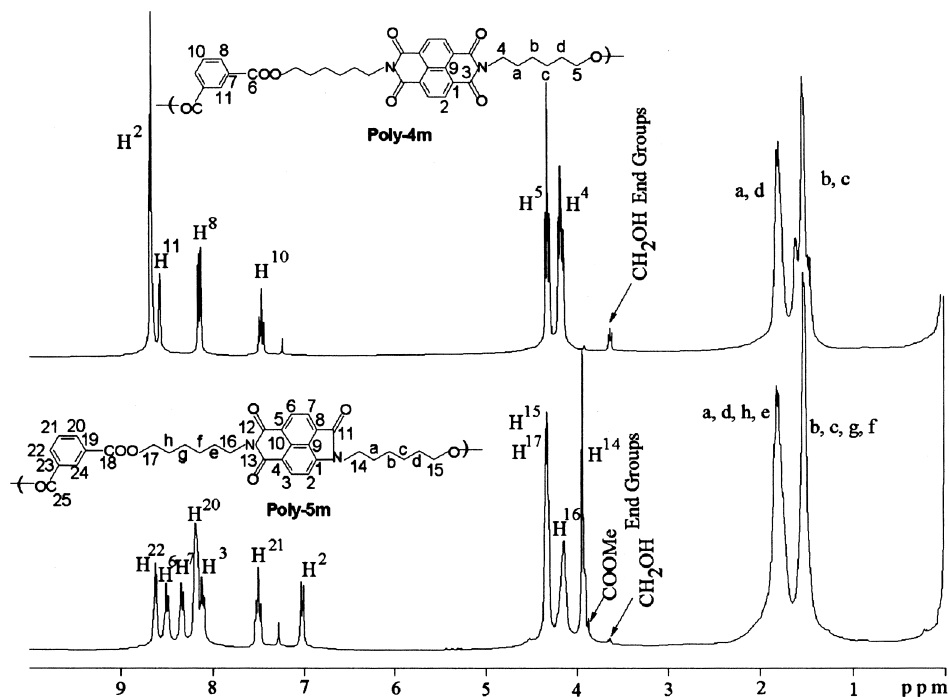


Figure 2 ^1H n.m.r. spectra of Poly-5m and Poly-4m

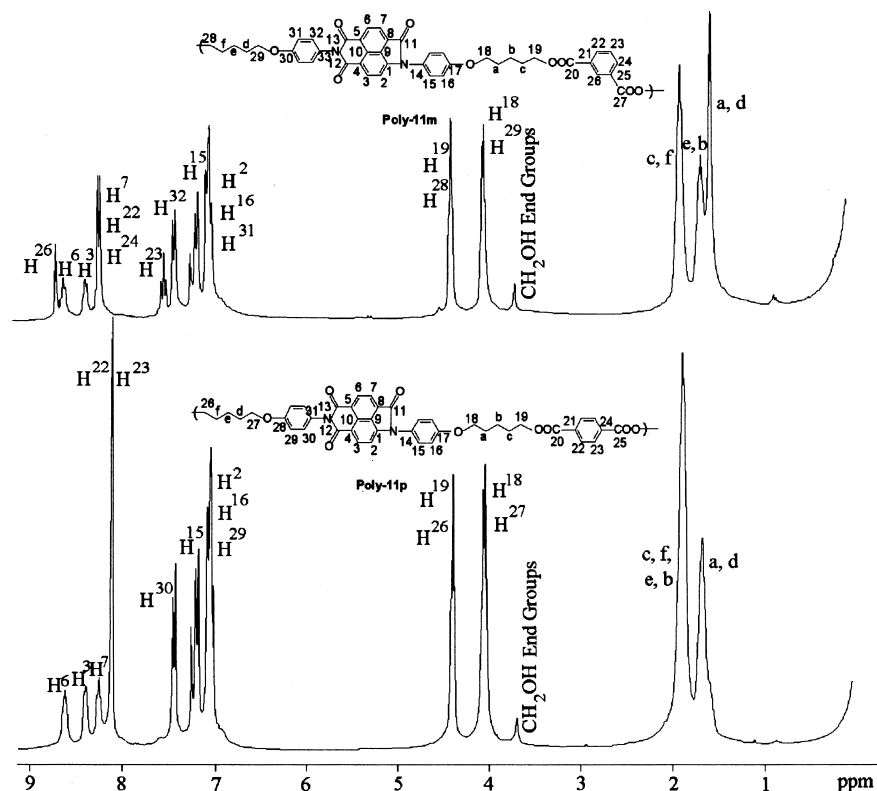


Figure 3 ^1H n.m.r. spectra of Poly-11m and Poly-11p

spectra; while the ^1H n.m.r. spectra of **Poly-5p** and **Poly-5m** show two types of terminal groups (COOMe and $-\text{CH}_2\text{OH}$), in the spectra of other polymers only $-\text{CH}_2\text{OH}$ terminal groups are observed. This means that sublimation of comonomer in the initial stage of polymerisation disturbs the stoichiometry resulting in low-molecular weight hydroxy-terminated polymers.

Polymer properties

As expected, the incorporation of lactamimide units into the polymer chain changes drastically polymer properties compared to their bisimide analogues. First of all with regard to the tractability and crystallinity of polymers. As seen from *Table 1*, all polymers containing lactonimide

units are readily soluble in common solvents like chloroform. They are amorphous, as can be seen from their d.s.c. traces (showing no melting endotherm) and give transparent films on casting. On the other hand, bisimide-containing model polymers show poor tractability. Only **Poly-4m** is soluble in hot chloroform, while the others are not soluble in common organic solvents. All bisimide-containing polymers show a crystalline phase, as indicated in the melting endotherms in their d.s.c. traces. A loss of one carbonyl group during bisimide–lactam ring contraction reduces the symmetry of monomer from D_{2h} to C_{1h} producing monomers **5** and **11**. The polymerisation of the monomers gives polymers with randomly distributed head to head, head to tail, tail to head and tail to tail sequences which contribute to the solubility and amorphous nature of the polymers. The ring contraction does not affect the thermostability of the polymers. All polymers show 10% weight loss at 400–415°C. It is noteworthy that T_g values of lactamimide-containing polymers are raised by 20–30°C compared to their bisimide analogies (*Table 1*). This phenomenon may be attributed to strong dipolar interaction between polar lactamimide fragments. Bisimide–lactam ring contraction causes a drastic change in electronic structure of aromatic moieties, reflected in the significant bathochromic shift of long-wave absorption maximum (55–70 nm) of lactamimide-containing polymers compared to the bisimide analogies (*Table 1*). This bathochromic shift is due to intramolecular charge transfer from donor lactam to acceptor imide moieties. The long-wave absorption maxima of **Poly-11p** and **Poly-11m** bearing phenyl substituents on nitrogen atoms are 10 nm red-shifted compared to those of **Poly-5p** and **Poly-5m**, where the aliphatic spacer connected directly to the nitrogen. Most likely, the phenyl ring participates in conjugation with the naphthalene moiety, thus shifting the long-wave absorption.

Poly-5m and **Poly-5p** were found to show strong fluorescence, suggesting that there was no electronic coupling between the flexible spacers and the π system of the chromophore. Their large Stokes shifts (140–150 nm) are remarkable. The long-wave electronic transition is responsible for the emission, as followed from the excitation spectra. As seen from *Table 1*, the excitation maxima of **Poly-5m** and **Poly-5p** lie close to those of their long-wave absorption. Polymers **Poly-11p** and **Poly-11m**, bearing phenyl substituents on the nitrogen atoms, present fluorescence of about two orders of magnitude less intense than that of **Poly-5m** and **Poly-5p**. The fluorescence quenching in polymers **Poly-11p** and **Poly-11m** may occur by the loose-bolt mechanism³ due to coupling of the π system of

the chromophore with that of the phenyl groups after rotation about the N–C_{ar} bond. The absorption, emission and excitation spectra of **Poly-11p** and **Poly-11m** are red shifted compared to these of **Poly-5m** and **Poly-5p** due to the electronic coupling between chromophore and phenyl rings; *Figure 3* shows the absorption, emission and excitation spectra of **Poly-5p** as an example.

The third-order non-linear optical susceptibilities ($\chi^{(3)}$) of the synthesised poly(lactamimides) were found to be in the range of 10^{-10} – 10^{-11} e.s.u. (*Table 1*), which is comparable to those of polydiacetylenes, polyanilines and polythiophenes⁴, which are known for their non-linear optical properties.

CONCLUSIONS

First, lactamimide monomers were synthesised by bisimide–lactam ring contraction and polymerised by high-temperature transesterification in the melt to give lactamimide-containing polymers. The polymers were amorphous with good film-forming properties, soluble in common organic solvents, and showed from low to medium molecular weight. Lactamimide-containing polymers bearing aliphatic spacers showed strong fluorescence with large Stokes shift (140–150 nm) peaking at 580–585 nm, while those with phenyl groups on nitrogen atoms presented very weak fluorescence, probably caused by loose-bolt quenching, peaking at 610–615 nm. The polymers showed third-order non-linear optical susceptibility in the range of 10^{-10} – 10^{-11} e.s.u.

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