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Bisimide-lactamimide ring contraction in six-membered polyimides

Serguei Fomine*, Lioudmila Fomina, Rogelio Arreola, Juan Carlos Alonso

Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Apartado Postal 70-360, CU, Coyoacán, México DF 04510, Mexico

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Abstract

Novel lactamimide-containing polymers were first synthesized by the bisimide-lactamimide ring contraction of 1,8:4,5-tetracarboxylic bisimide-containing polymers. The conversion of bisimide moieties was in the range 60–100% depending on polymer chain flexibility. The yields of lactamimide units were between 75 and 100% with respect to bisimide group conversion owing to the insolubility of polymers during lactam ring closure. No appreciable hydrolytic degradation of polymers was observed as followed from GPC data. Both u.v. long-wave absorption and emission maxims in polylactamimides were 20–50 nm red shifted compared with those of polyimides due to intramolecular charge transfer. It was found that the thermostability of lactamimide units was close to that of bisimide as proved by TGA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Imides; Lactames; Ring contraction

1. 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 saponification [1]. 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 lactamimides [2] with loss of a Cl fragment from one carboximide. In all cases only one of the imide ring system is transformed to the lactam, leaving the second one unchanged.

Recently a mechanism of this rearrangement has been proposed [3] which includes the addition of one equivalent of OH^- to one of the imide carbonyls. Subsequent ring contraction leads to the formation of a lactam followed by decarboxylation. This is a novel type of rearrangement and appeared to be a general reaction for other six-membered ring bisimides. The second imide ring facilitates the stabilization of negative charge in the intermediate, thus promoting the ring contraction. In agreement with this conclusion is the finding that monoimides do not undergo ring contraction.

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

The authors have reported the first synthesis of lactamimide-containing monomers and polymers. Bifunctional lactamimides were prepared by the ring contraction of the respective six-membered bisimides followed by polycondensation to produce lactamimide-containing polyesters [4]. The polylactamimides were found to be much more tractable than the respective polyimides. They possessed good film-forming properties, were soluble in chloroform and some showed strong photoemission in the visible region. Polylactamimides showed third-order non-linear optical susceptibility (χ^3) of 10^{-10}–10^{-11} esu.

However, the synthesis of polylactamimides starting from lactamimide-containing monomers includes rather laborious steps. Another approach to polylactamimides is the direct ring-contaction in six membered ring polyimides. Six-membered ring polyimides prepared in one step from commercially available materials can be converted into polylactamimide by polymeric reaction. The aim of this paper is to study such a possibility and to characterize the resulting polymers. In order to be successfully converted

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* Corresponding author.

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into polylactamimides six-membered rings containing polyimides should meet such requirements as reasonable solubility in DMSO–methanol mixture and resistance of the polymer backbone to the base hydrolysis. In addition, aromatic substituents on imide nitrogens promote the ring contraction rather than aliphatic ones [3]. All these factors were taken into account when designing polymer structure. This paper reports the synthesis and ring contraction reaction in various six-membered polyimides bearing 1,8:4,5-tetracarboxylic bisimide moieties.

2. Experimental

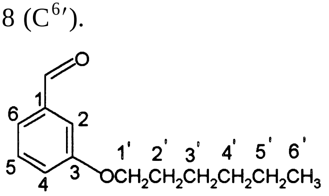
2.1. Materials

All reagents were used as received from Aldrich.

2.2. Monomer and model compound synthesis

2.2.1. 3-Hexyloxybenzaldehyde (2)

3-Hydroxybenzaldehyde (5.0 g, 41.0 mmol), *n*-hexylbromide (6.75 g, 40.9 mmol), and K_2C0_3 (11.3 g, 82.0 mmol) were stirred at 70°C overnight in 50 ml *N*-methylpyrrolidone (NMP). The reaction mixture was poured in water. The product was extracted with chloroform, the solvent was evaporated and the residue was distilled in vacuum b.p. = 125°C/0.1 mm Hg. Yield = 40%. ^{1}H-n.m.r. ($CDCl_3$) 9.78 (s, 1H, CHO), 7.26–7.24 (m, 2H, H^5, H^2), 7.18 (m, 1H, H^6), 6.99–6.96 (m, 1H, H^4), 3.85 (t, 2H, J = 6.6 Hz, $H^{1\prime}$), 2.00–1.90 (m, 2H, $H^{2\prime}$), 1.70–1.62 (m, 2H, $H^{3\prime}$), 1.38–1.30 (m, 2H, $H^{4\prime}$), 1.26–1.15 (m, 2H, $H^{5\prime}$), 0.77 (t, 3H, J = 6.6 Hz, $H^{6\prime}$), ^{13}C-n.m.r. ($CDCl_3$), 190.7 (CHO), 159.5 (C^3), 137.7 (C^1), 129.6 (C^5), 122.7 (C^6), 121.3 (C^4), 112.5 (C^2), 67.7 ($C^{1\prime}$), 31.3 ($C^{2\prime}$), 28.9 ($C^{3\prime}$), 25.5 ($C^{4\prime}$), 22.4 ($C^{5\prime}$), 13.8 ($C^{6\prime}$).



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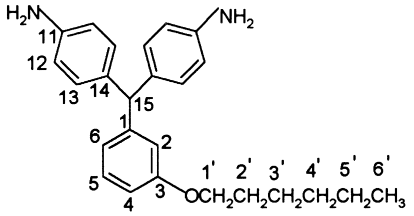
2.2.2. 4,4′-diamino-3″-hexyloxytriphenylmethane (3)

Compound **2**, (4.6 g, 22.3 mmol) aniline (12 g, 129 mmol) and aniline hydrochloride (0.4 g) were stirred under nitrogen at 120°C for 5 h. The excess of aniline was distilled in vacuum and the crude product was chromotagraphed on SiO_2 to give a colourless oil (48% yield). ^{1}H-n.m.r. (DMSO-d_6 + acetone-d_6) 7.60–7.30 (m, 5H, H^{13}, H^5), 7.20–6.80 (m, 7H, H^{12}, H^4, H^6, H^2), 5.85 (s, 1H, H^{15}), 4.42 (s, 4H, NH_2,4.40 (t, 2H, J = 6.6 Hz, H $^{<\,\prime}$), 2.42–2.40 (m, 2H, $H^{2\prime}$), 2.10–2.00 (m, 2H, $H^{3\prime}$), 1.80–1.70 (m, 2H, $H^{4\prime}$), 1.70–1.60 (m, 2H, $H^{5\prime}$), 1.20 (t, 3H, J = 6.6 Hz, CH_3) ^{13}C-n.m.r. (DMSO-d_6 + acetone-d_6), 160.3 (C^3), 150.0 (C^{11}), 140.3 (C^1), 131.0 (C^5), 130.7, (C^{13}), 128.0 (C^{14}), 120.7 (C^{12}), 116.7, 115.5, 112.8 (C^4, C^6, C^2), 68.5 ($C^{1\prime}$), 56.6 (C^{15}), 32.4 ($C^{2\prime}$), 29.0 ($C^{3\prime}$), 26.5 ($C^{4\prime}$), 23.3 ($C^{5\prime}$), 14.2 ($C^{6\prime}$).



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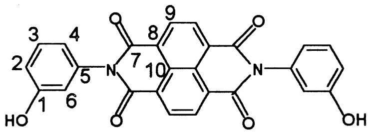
2.2.3. N,N′-Bis(3-hydroxyphenyl)-1,8:4,5-naphthalenetetracarboxylic bisimide (5)

Dianhydride 4 (2 g, 7.5 mmol) and 3-aminophenol (5.7 g 52.3 mmol) were stirred under reflux in 50 ml dioxane for 24 h. The reaction mixture was poured into diluted HCl, the product was filtered off, washed with plenty of water dried in vacuum and crystallized from ethyleneglycol. m.p. > 300°C. Yield = 67%. ^{1}H-n.m.r. (DMSO-d_6) 9.70 (s, 2H, OH), 8.70 (s, 4H, H^9), 7.33 (t, 2H, H^3, J = 8.4 Hz), 6.95–6.80 (m, 6H, H^2, H^6, H^4), ^{13}C-n.m.r. (DMSO-d_6), 162.8 (C^7), 158.0 (C^1), 136.2 (C^5), 130.4 (C^9), 129.9 (C^3), 126.4, 126.3 (C^8, C^{10}), 119.5 (C^4), 116.1, 115.8 (C^6, C^2).



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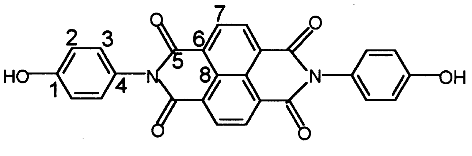
2.2.4. N,N′-Bis(4-hydroxyphenyl)-1,8:4,5-naphthalenetetracarboxylic bisimide (6)

Monomer **6** was prepared similar to **5** from dianhydride (4 (2.0 g 7.5 mmol), and 4-aminophenol (2.0 g 18.3 mmol). Yield = 78%, m.p. > 300°C, ^{1}H-n.m.r. (DMSO-d_6) 9.70 (s, 2H, OH), 8.65 (s, 4H, H^7), 7.25 (d, 4H, J = 8.7 Hz, H^3), 7.06 (d, 4H, J = 8.7 Hz, H^2). ^{13}C-n.m.r. (DMSO-d_6), 163.8 (C^5), 157.9 (C^1), 131.5 (C^7, C^4), 129.4 (C^3), 127.2 126.7 (C^8, C^6), 115.9 (C^2).



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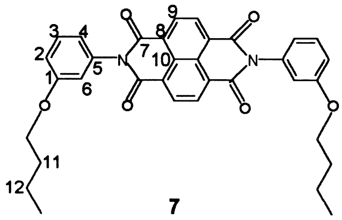
2.2.5. N,N′-Bis(3-n-butoxyphenyl)-1,8:4,5-naphthalenetetracarboxylic bisimide (7)

Compound 5 (0.15 g, 0.3 mmol), *n*-butylbromide (0.2 g, 1.5 mmol) and K_2CO_3 (0.2 g 1.5 mmol) were stirred in NMP (20 ml) at 70°C for 6 h. The reaction mixture was poured into diluted HCl, the precipitate was filtered off, dried in vacuum and chromatographed on SiO_2 with toluene. Yield = 78%, m.p. = 284–286°C. ^{1}H-n.m.r. ($CDCl_3$) 8.80 (s, 4H, H^9), 7.43 (t, 2H, J = 8.4 Hz, H^3), 7.03 (d, 2H, $J = 8.4$ Hz, H^2), 6.90–6.80 (m, 4H, H^6, H^4), 3.95 (t, 6H, $J = 6.6$ Hz, OCH_2), 1.85–1.70 (m, 4H, H^{11}), 1.60–1.40 (m, 4H, H^{12}), 1.00 (t, 6H, $J = 6.6$ Hz, CH_3). ^{13}C-n.m.r. ($CDCl_3$), 162.8 (C^7), 160.1 (C^1), 135.5 (C^5), 131.3 (C^9), 130.1 (C^3), 127.1, 127.0 (C^8, C^{10}), 120.3, (C^4), 115.6, 114.7 (C^2,C^6), 67.9 (OCH_2), 31.3 (C^{11}), 19.2 (C^{12}), 13.8 (CH_3).



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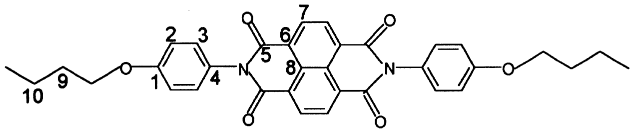
2.2.6. N,N′-Bis(4-n-butoxyphenyl)-1,8:4,5-naphthalenetetracarboxylic bisimide (8)

Model compound **8** was prepared similar to **7** from bisphenol **6** (0.5 g 1.1 mmol), butylbromide (3 g, 22 mmol) and K_2CO_3 (1.2 g, 8.7 mmol) in NMP (20 ml) and crystallized from chlorobenzene. Yield = 75%, m.p. > 300°C. ^1H-n.m.r. ($CDCl_3$) 8.82 (s, 4H, H^7), 7.23 (d, 4H, $J = 8.7$ Hz, H^3), 7.07 (d, 4H, $J = 8.7$ Hz, H^2), 4.04 (t, 4H, $J = 6.3$ Hz, OCH_2), 1.85–1.75 (m, 4H, H^9), 1.60–1.45 (m, 4H, H^{10}), 1.00 (t, 6H, $J = 7.3$ Hz CH_3). ^{13}C-n.m.r. ($CDCl_3$), 163.2 (C^5), 159.6 (C^1), 131.5 (C^7, C^4)), 129.3 (C^3), 127.2, 126.7 (C^6, C^8), 115.4 (C^2), 68.0 (OCH_2), 31.3 (C^9), 19.3 (C^{10}), 13.4 (CH_3).



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2.3. Polymer synthesis

Polymers **Poly-5** and **Poly-6** were prepared similar to model compounds as follows; monomer **5** or **6** (10 mmol), decamethylenedibromide (10 mmol) and powdered K_2CO_3 were stirred for 24 h in 20 ml NMP at 90°C. The polymers were precipitated in methanol, filtered off and dried in vacuum until constant weight.

Poly-3 was prepared by one-step polycondensation in o-dichlorobenzene (o-DCB) as follows; diamine **3** (10 mmol), dianhydride **4** (10 mmol) and o-DCB were stirred under reflux with Dean–Stark tramp for 24 h. The polymer solution was precipitated in MeOH, the polymer was filtered off and dried in vacuum until constant weight.

2.3.1. Ring contraction general procedure

Polymer (0.5 g) was dissolved in DMSO (15 ml), a solution containing methanol (20 ml) and KOH (3 g) was added and the reaction mixture was refluxed for 24 h. The resulting solution was poured into diluted HCl, the precipitate formed was filtered off and dried in air and then refluxed for 3 h in a mixture of EtOH (20 ml) and concentrated HCl (5 ml). The reaction mixture was poured in water, the polymer was filtered off, rinsed with water and dried in vacuum at room temperature until constant weight. Elemental analysis data of monomers and polymers are presented in Table 1.

2.3.2. Measurements

The relative molecular weights of polymers were determined using a Varian 9012 GPC instrument at 30°C in $CHCl_3$ with polystyrene standard, universal column and a flow of 1 ml min^{-1}. DSC and TGA were performed at a heating rate of 10°C min^{-1} under nitrogen with a du Pont 2100 machine. ^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, or $CHCl_3$ with TMS as the internal standard. Absorption and emission spectra were measured with an automated Spex-FluoroMax spectrofluorimeter using thin films spin-coated onto a quartz slide. Normal coordinate analysis was performed with MOPAC, using PM3 potential function [5] included in package CS Chem3D Pro version 4.0. Molecular dynamic calculation calculations were carried out with the same package.

Table 1
Element analysis data of synthesized compounds

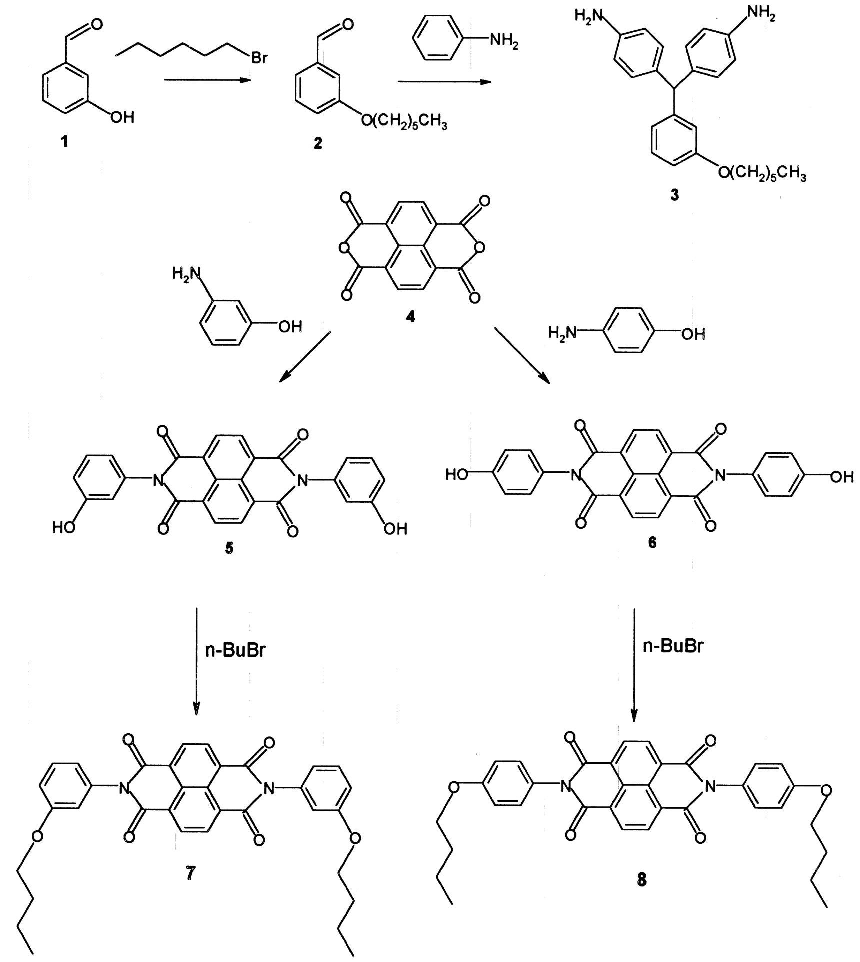
Compound	Formula	Calculated %			Found %		
		C	H	N	C	H	N
2	$C_{13}H_{18}O_2$	75.7	8.74	—	75.2	8.66	—
3	$C_{25}H_{30}N_2O$	80.2	8.02	7.484	79.8	8.06	7.41
5	$C_{26}H_{14}N_2O_6$	69.3	3.11	6.22	69.1	3.08	6.41
6	$C_{26}H_{14}N_2O_6$	69.3	3.11	6.22	68.9	3.14	6.19
7	$C_{34}H_{30}N_2O_6$	72.6	5.34	4.98	72.34	5.41	5.04
8	$C_{34}H_{30}N_2O_6$	72.6	5.34	4.98	73.1	5.33	5.09
Poly-3	$(C_{39}H_{30}N_2O_5)_n$	77.2	4.95	4.62	76.0	4.88	4.62
Poly-5	$(C_{36}H_{34}N_2O_6)_n$	73.2	5.76	4.75	73.8	5.77	4.80
Poly-6	$(C_{36}H_{34}N_2O_6)_n$	73.2	5.76	4.75	73.1	5.72	4.77
i-Poly-3	$(C_{38}H_{30}N_2O_4)_n$	78.9	5.19	4.84	78.0	5.22	5.01
i-Poly-5	$(C_{35}H_{34}N_2O_5)_n$	74.7	6.05	4.98	73.5	5.98	4.99
i-Poly-6	$C_{35}H_{34}N_2O_5$	74.7	6.05	4.98	74.1	6.01	5.02

3. Results and discussion

The synthesis of monomers and polymers are shown in Scheme 1 and Scheme 2, respectively. The choice of polymer structures was determined by two factors; the stability of the polymer chain under the basic condition of the ring contraction and the solubility. Polyimide **Poly-3** was prepared by the high temperature polycondensation of commercially available dianhydride **4** and diamine **3** producing soluble polyimide (**Poly-3**). Diamine **3** was prepared in two steps starting from 3-hydroxybenzaldehyde. The first step was alkylation with *n*-hexylbromide followed by the condensation with aniline of the resulting 3-hexyloxybenzaldehyde. Polymers **Poly-5** and **Poly-6** were synthesized in two steps starting from dianhydride **4** and 3- and 4-aminophenols, respectively. First, bisimide-containing bisphenols **5** and **6** were obtained by the reaction of dianhydride **4** and 3- and 4-aminophenols, respectively, followed by the reaction with 1,10-dibromodecane to give bisimide-containing polyethers **Poly-5** and **Poly-6**. Model compounds **7** and **8** were generated from bisphenols **5** and **6** and butylbromide to assign n.m.r. spectra of polyethers and optimize the polymer synthesis conditions.

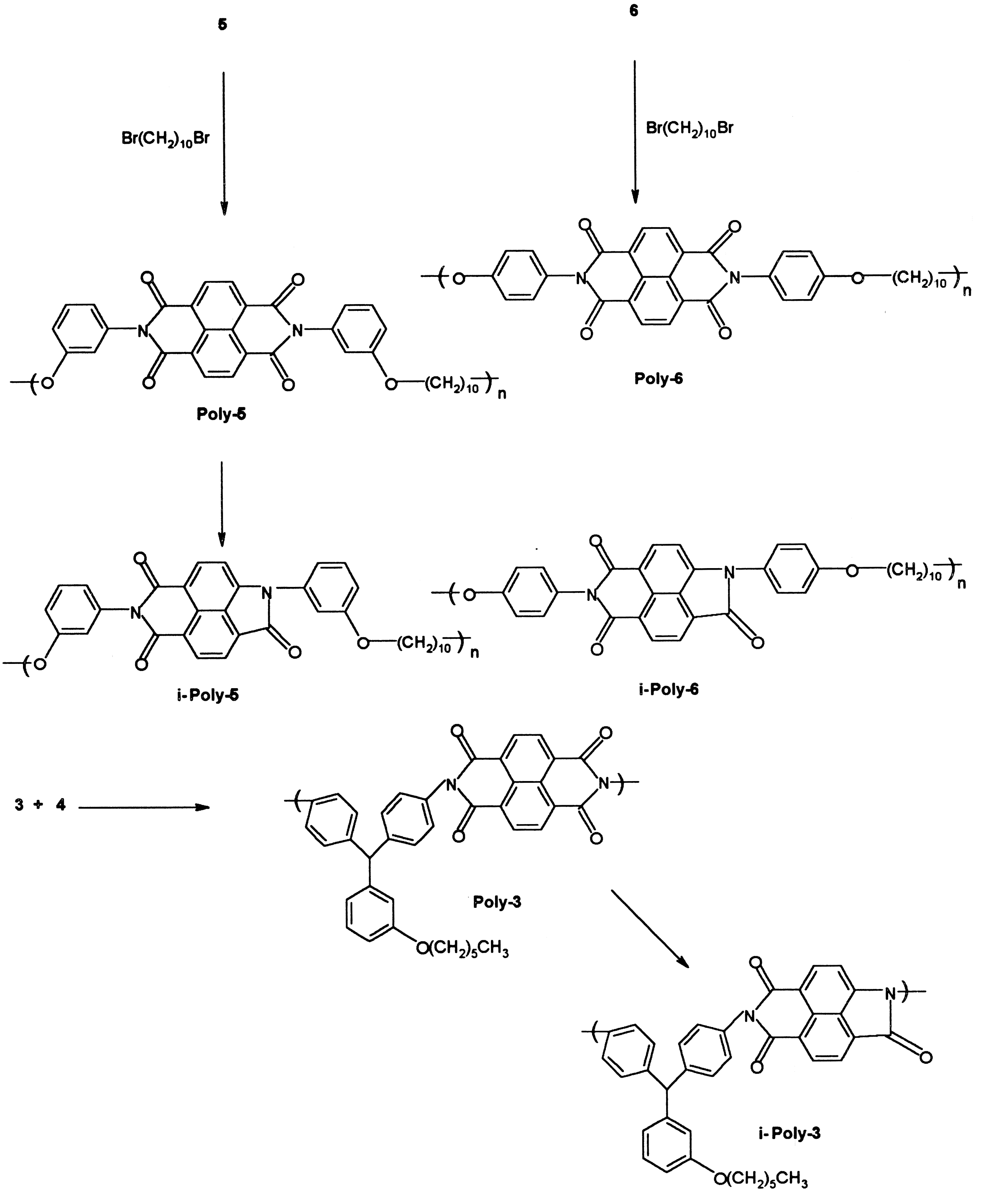
All the polymers show medium molecular weight according to GPC. **Poly-3** was readily soluble in $CHCl_3$ at room temperature, while polymers **Poly-5** and **Poly-6** were only soluble in $CHCl_3$ on heating (Table 2). The ring contraction reaction produced coloured polymers **i-Poly-3, i-Poly-5** and **i-Poly-6**. As seen from the Table 2 all exhibit new long-wave absorption maximums in the region of 426–433 nm, characteristic of lactamimide moieties [3].

Fig. 1 and Fig. 2 present ^{1}H-n.m.r. spectra of **Poly-3** and **Poly-5** before and after the ring contraction reaction. An intense signal near 8.7 ppm corresponding to four equivalent protons of bisimide fragment completely disappeared in the case of **i-Poly-3** and **i-Poly-6** and significantly reduced for **i-Poly-5**. At the same time a series of new signals appeared in the region of 8.5–7.5 ppm assigned to naphthalene protons of lactamimide (H^2, H^3 and H^4). Proton H^1 of the lactamimide moiety appeared in the spectra of **i-Poly-5** at 6.80 ppm, however, in the spectra of **i-Poly-3** and **i-Poly-6** H^1 this peak is masked by protons in the *ortho* position to phenoxy oxygen.



Scheme 1.

The conversion of bisimide moieties was calculated from the integrals of H^1 protons and those of phenyl substituents as a reference. As can be seen from the Table 2, all bisimide moieties were consumed in **Poly-3** and **Poly-6** during the ring contraction reaction, however, in the case of **Poly-5** the conversion was only 60%. To clarify this phenomena molecular mechanics calculations were carried out with oligomers of **Poly-5** and **Poly-6** containing five repeating units. First, the geometry of oligomers was optimized using MM2 potential and then average equilibrium distance at 373 K (temperature of the ring contraction) between the ends of oligomer chains was determined using the molecular dynamic calculation included in the CS Chem3D Pro version 4.0 package. The distance was found to be 12 and 28 A for **Poly-5** and **Poly-6** oligomers, respectively. The results show that the **Poly-6** molecule forms a much looser



Scheme 2.

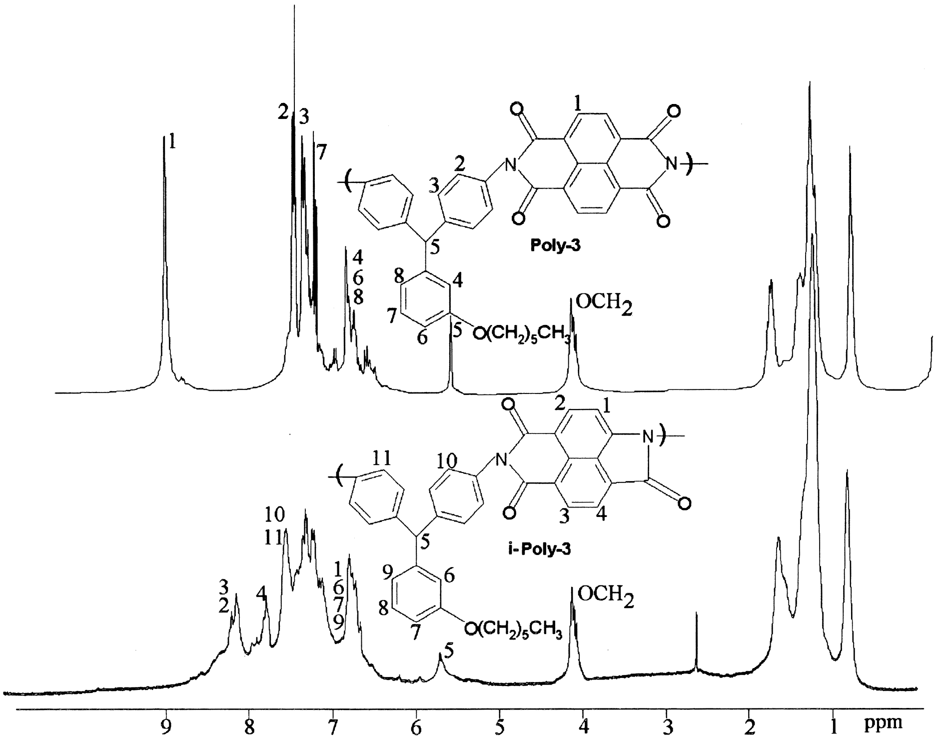


Fig. 1. 1H-n.m.r. spectra of **Poly-3** and **i-Poly-3**.

conformation than **Poly-5**, therefore, the reason for the incomplete conversion of **Poly-5** could be steric hindrance.

The yields of lactamimide moieties were calculated from ^{1}H-n.m.r. spectra using integrals of H^2, H^3 and H^4 of lactamimide. The integrals of phenyl protons were taken as a reference. As shown in Table 2 the yields were less than 100%. The insolubility of the polymer in ethanol during the last step (lactam ring closure) leads to incomplete cyclization. This hypothesis agreed with i.r. data. The i.r. spectra of **i-Poly-3**, **i-Poly-5** and **i-Poly-6** show a broad band in the range of 2800–2600 cm^{-1} attributed to OH stretching of the carboxy group. Taking into account that no significant hydrolytic degradation of the polymer chain occurred during the ring contraction, as followed from GPC data (Table 2) this absorption band should be assigned to uncyclized carboxy groups.

The i.r. spectra of **Poly-3, Poly-5** and **Poly-6** show two absorption bands in the carbonyl region corresponding to C–O stretching of imide carbonyls. The spectra of **i-Poly-3, i-Poly-5** and **i-Poly-6** present three absorption bands in the same region. Fig. 3 show charts of *F.T.*i.r. spectra of **Poly-5** and **i-Poly-5** as examples. Normal coordinate analysis of bisimide and lactamimide carbonyl vibrations was performed to assign the i.r. spectra of the polymers and the results are listed in Table 3. Vibrational frequencies were computed by determining the second derivatives of the energy with respect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates at

Table 2
Some physicochemical properties of synthesized polymers

Polymer	Yield %	Conversion of imid%[a]	Yield of lactam%[a]	T_g,°C	T_{10}°C[b]	$M_n \times 10^3$[c]	λ_{max}nm[d]	λ_{em}, nm[e]	Solubility in $ChCl_3$	Solubility in DMSO
Poly-3	93	—	—	—	485	18	380	555	+	+
Poly-5	89	—	—	175	425	13	379	543	f	+
Poly-6	89	—	—	205	430	12.5	379	534	f	+
i-Poly-3	97	100	75	—	475	14.5	426	573	+	+
i-Poly-5	96	60	60	115	425	11.3	436	602	+	+
i-Poly-6	90	100	80	135	430	9.9	433	605	f	+

[a] From ^{1}H-n.m.r. spectra.

[b] Temperature of 10% weight loss.

[c] Determined by GPC in DMSO.

[d] Long-wave absorption maximum of thin film spin-coated onto a quartz plate.

[e] Emission maximum of thin film spin-coated onto a quartz plate when excited at 350 nm.

[f] On heating.

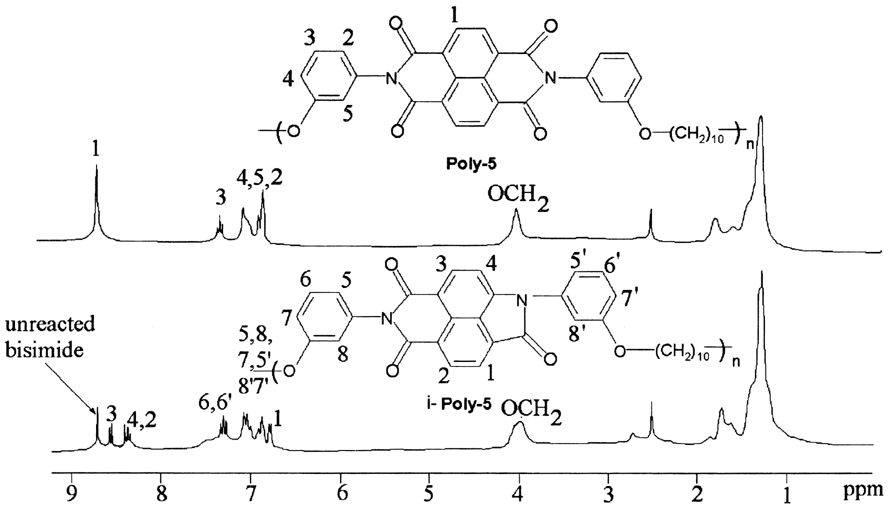
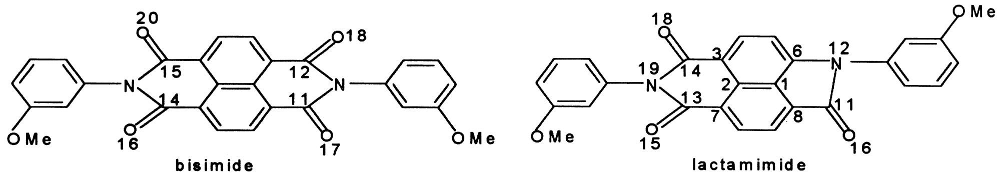


Fig. 2. 1H-n.m.r. spectra of **Poly-5** and **i-Poly-5**.

Table 3
Normal coordiante analysis data of bisimide and lactamimide moieties



Compound	Calculated vibration frequency (cm^{-1})	Symmetry of mode	Transitional dipole (D)	Atom pair[a]	Radial%[b]	Observed vibration frequency (cm^{-1})[c]
Bisimide	1736	Ag	0.000	C14–O16	99.8	
				C15–O20	99.8	
				C12–O18	99.8	
				C11–O17	99.8	
	1731	Bu	4.51	C14–O16	99.9	1714
				C15–O20	99.9	
				C12–O18	99.9	
				C11–O17	99.9	
	1711	Au	9.19	C14–O16	99.5	1678
				C15–O20	99.5	
				C12–O18	99.6	
				C11–O17	99.5	
	1711	Bg	0.000	C14–O16	99.6	
				C15–O20	99.6	
				C12–O18	99.6	
				C11–O17	99.6	
Lactamimide	1792	A	6.22	C11–O16	99.7	1735
				C8–C11	59.5	
				C11–N12	21.1	
				C1–C6	100.00	
	1736	A	4.06	C14–O18	99.7	1715
				C13–O15	99.8	
				C3–C14	42.6	
				C14–O19	12.1	
	1717	A	6.54	C13–O15	99.5	1680
				C14–O18	99.3	
				C7–C13	47.3	
				C13–N19	14.3	
				C3–C14	50.5	

[a] All pairs of atoms that contribute significantly to the energy of the mode.

[b] The percentage of radial motion.

[c] Thin film *F.T.*i.r. spectra of **Poly-5** and **i-Poly-5**.

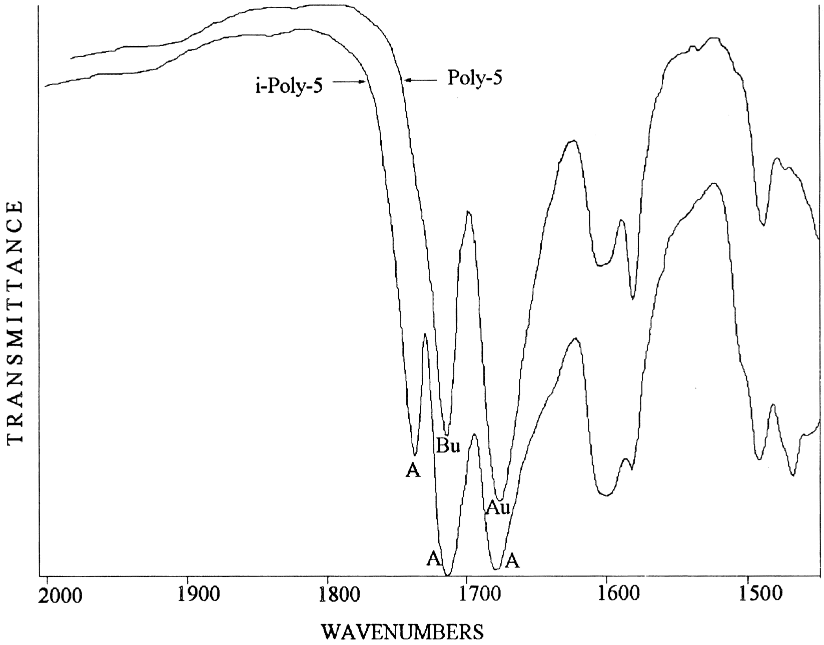


Fig. 3. *F.T.*i.r. spectra of **Poly-5** and **i-Poly-5**.

stationary point geometry [6], [7]. As can be seen, bisimide has four normal modes each involving four carbonyl groups. Two of theses (Ag and Bg modes) are not active in i.r. due to zero transitional moment. Thus, the observed absorption bands at 1714 and 1678 cm^{-1} should be assigned to Bu and Au modes, respectively. The calculations for the lactamimide moiety give three vibrational modes involving carbonyl groups all belonging to irreducible representation A and active in i.r. in agreement with the experiment (Fig. 3). Unlike bisimide these modes are not purely carbonyl and include C–C, C=C and C–N contributions, as seen in Table 3. These data provide additional proof of the polymer structures.

Unlike **Poly-3, Poly-5** and **Poly-6**, polymers **i-Poly-3, i-Poly-5** and **i-Poly-6** were readily soluble in chloroform at room temperature due to the presence of lactamimide units. All polymers were found to be rather thermostable showing temperatures of 10% weight loss (T_{10}) above 400°C. It is noteworthy that the thermostability of the bisimide moiety is approximately the same as that of lactamimide judged from almost equal T_{10} for polyimide and polylactamimides (Table 2). All polymers were found to be photoluminescent. The emission properties of polymer films are listed in Table 2. As seen, the emission maxima of polylactamimides are red-shifted compared with those of polyimides which correlated with their absorption spectra and this is due to the intramolecular charge transfer in lactamimides.

4. Conclusions

Novel lactamimide-containing polymers were first synthesized by the bisimide-lactamimide ring contraction of 1,8:4,5-tetracarboxylic bisimide-containing polymers. The conversion of bisimide moieties was in the range of 60–100% depending on polymer chain flexibility. Yields of lactamimide units were between 75 and 100% with respect to bisimide conversion due to insolubility of polymers during the ring closure step. No appreciable hydrolytic degradation of polymers was observed as followed from GPC data. Both u.v. long-wave absorption and emission maxims in polylactamimides were 20–50 nm red-shifted compared with those of polyimides due to intramolecular charge transfer. It was found that the thermostability of the lactamimide unit was close to that of bisimide, as proved by TGA.

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