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Polyimides with 3,3'-Bipyrrolidine-2,2',5,5'-Tetrone Units

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Summary

New linear polymers with 3,3'-bipyrrolidine-2,2',5,5'-tetrone units were prepared by the ring-coupling reaction of α,α'-bis(chlorosuccinimide)s under the action of dust zinc and iodine. Bis(α-chlorosuccinimide)s were synthesized by the dehydrocyclization of the bismaleamic acids in the presence of thionyl chloride. The IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy and elemental analysis confirmed the structure of monomers and polymers. The thermal behaviour of the polymers was monitored using dynamic thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Introduction

Polyimides have remarkable high temperature resistance and good mechanical and electrical properties. However, condensation type polyimides usually suffer from processing problems due to their insolubility, infusibility and evolution of volatile during the ring formation.

Bismaleimides are a leading class of thermosetting polyimides. Their excellent thermal and mechanical properties have made them extremely popular for advanced composites and electronics [1-4]. When bismaleimides are used alone, they lead to form highly crosslinked networks that are very fragile [5]. Various attempts have been made to improve the impact and fracture toughness of polybismaleimide materials. There are: (i) bismaleimides with flexible or long segment in the backbone [6-9]; (ii) bismaleimide-diamine oligomers prepared by the Michael addition reaction [10-12] followed by the thermal polymerisation; (iii) copolymerisation of bismaleimides with olefinic compound via the Diels-Alder reactions [13-16], bismaleimides and epoxy resin blends [17-18] and bismaleimides-*o*,*o*'-dicyanobisphenol A mixture [19]. Nevertheless, it is very difficult to obtain all the desired properties in one product.

In the present study, various linear aromatic polyimides containing 3,3'-bipyrrolidine-2,2',5,5'-tetrone units were prepared by the ring-coupling reactions of α,α'-bis(chlorosuccinimide)s and investigated their properties.

Experimental

Measurements

The FT-IR spectra were recorded on a Bruker Vertex 70 spectrophotometer. The ^{1}H-NMR spectra were recorded on a Bruker NMR spectrometer, Avance DRX 400 MHz, using DMSO-d_6 as solvents and tetramethylsilane as an internal standard. Melting and softening points were determined with a Gallenkamp hot-block point apparatus. Thermogravimetric analysis (TGA) was carried out in air with a F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) measurements were done using a Mettler TA Instrument DSC 12E with a heating rate of 10°C/min, in nitrogen. Gel permeation chromatographic (GPC) analyses were carried out on a PL-EMD 950 Evaporative light Detect instrument using N,N-dimethylformamide (DMF) as eluant and standard polystyrene sample for calibration.

Reagents and Materials

Maleic anhydride, *p*-toluidine, 1,4-phenylenediamine, 1,3-phenylenediamine, 2,4-diaminotoluene, benzidine, 4,4'-methylenedianiline, 4,4'-ethylenedianiline, 4,4'-oxydianiline, 4,4'-diaminodiphenylsulfone and acetone were used as received. Thionyl chloride was freshly distilled before use. The zinc was activated by several washing with 5% hydrochloric acid through washing with water, methanol and ethyl ether and dried in vacuum [20].

N-phenyl-α-chlorosuccinimides were synthesized by the cyclodehydration of the corresponding maleamic acids with thionyl chloride according to a method described elsewhere [21].

Bismaleamic acids 2(a-j) were prepared by the condensation of maleic anhydride with aromatic diamines in molar ratio 2:1 in acetone at room temperature for 3 hours. The solid products were separated by filtration, washed with freshly acetone and dried in vacuum at 80°C for 6 hours.

General procedure for preparation of bis(α,α'-chlorosuccinimide)s 3(a-h)

To a suspension of bismaleamic acid (0.1 mol) in 1,2-dichloroethane (100-150 mL) was added thionyl chloride (30 mL) and the mixture was stirred and refluxed for 2 hours. The excess of thionyl chloride and solvent was removed under vacuum and the residue was recrystallized.

3-Chloro-1-[4-(3-chloro-2,5-dioxopyrrolidin-1-yl)-phenyl]-pyrrolidine-2,5-dione (3a) was recrystallized from acetic acid, yield 85%, mp>300°C.

Elemental analysis calculated for $C_{14}H_{10}N_2O_4Cl_2$ (340.14), %: C, 49.44; H, 2.96; N, 8.23 and Cl, 20.84. Found: C, 49.17; H, 3.07; N, 8.37 and Cl, 21.03 %.

IR (KBr, cm^{-1}): 1785, 1720, 1385, 1185 (imide I-IV), 1500, 1200 (aromatic structure) and 750 (C-Cl).

^{1}H-NMR ($CDCl_3$), δ (ppm): 7.43 (s, 4H, aromatic protons), 4.73 (dd, J=8.4 Hz, 2H, CH-Cl), 3.42 (dd, J=8.4; 18.4 Hz, 2H, $CH_{succinimide}$), 3.05 (dd, J=4.4; 18.4 Hz, 2H, $CH_{succinimide}$).

^{13}C-NMR ($CDCl_3$), δ (ppm): 39.16 (CH_2), 48.95 (CH-Cl), 127.04, 131.39 (C_{arom}) and 171.89 (C=O).

3-Chloro-1-[3-(3-chloro-2,5-dioxopyrrolidin-1-yl)-phenyl]-pyrrolidine-2,5-dione (3b) was recrystallized from *n*-buthanol, yield 83%, mp=202-205°C.

Elemental analysis calculated for $C_{14}H_{10}N_2O_4Cl_2$ (340.14), %: C, 49.44; H, 2.96; N, 8.23 and Cl, 20.84. Found: C, 48.97; H, 2.53; N, 7.97 and Cl, 21.05 %.
IR (KBr, cm^{-1}): 1795, 1725, 1600, 1500, 1385, 1185, 750 and 725.
^{1}H-NMR ($CDCl_3$, TMS), δ (ppm): 7.54 (t, J=8 Hz, 1H, aromatic), 7.38 (s, 1H, H_{arom}), 7.33 (dd, J=8; 12.4 Hz, 2H, H_{arom}), 4.74 (q, J=3.2; 8 Hz, 2H, CH-Cl), 3.40 (dd, J=8; 18.4 Hz, 2H, $CH_{succinimide}$), 2.98 (dd, J=3.2; 18.4 Hz, 2H, $CH_{succinimide}$).
^{13}C-NMR ($CDCl_3$), δ (ppm): 39.16 (CH_2), 48.95 (CH-Cl), 127.74, 126.22, 129.62, 131.78 (C_{arom}) and 171.89 (C=O imide).

3-Chloro-1-[3-(3-chloro-2,5-dioxopyrrolidin-1-yl)-4-methylphenyl]-pyrrolidine-2,5-dione (3c) was recrystallized from *n*-butanol, yield 87%, mp=135-140°C.
Elemental analysis calculated for $C_{15}H_{12}N_2O_4Cl_2$ (354.167), %: C, 50.87; H, 3.42; N, 7.91 and Cl, 20.02. Found: C, 51.03; H, 3.57; N, 8.05 and Cl, 20.47 %.
IR (KBr, cm^{-1}): 1795, 1715, 1510, 1375, 1185, 830, 760 and 740.
^{1}H-NMR ($CDCl_3$, TMS), δ (ppm): 7.39 (m, 2H, H_{arom}), 7.15 (d, J=7.2 Hz, 1H, H_{arom}), 4.68 (dd, J=3.2; 7.2 Hz, 2H, CH-Cl), 3.38 (dd, J=7.2; 12.4 Hz, 2H, CH_2), 2.95 (dd, J=3.2; 12.4 Hz, 2H, $CH_{succinimide}$) and 2,16 (s, 3H, CH_3).
^{13}C-NMR ($CDCl_3$, TMS), δ (ppm): 17.41 (CH_3), 39.11 (CH_2), 49.12 (CH-Cl), 124.83, 125.35, 129.75, 131.77, 134.42, 136.77 (C_{arom}), 171.62, 171.91 (C=O imide).

3-Chloro-1-[4'-(3-chloro-2,5-dioxopyrrolidin-1-yl)-1,1'-biphenyl]-pyrrolidine-2,5-dione (3d) was recrystallized from dioxane, yield 87%, mp>300°C.
Elemental analysis calculated for $C_{20}H_{14}N_2O_4Cl_2$ (417.238), %: C, 57.57; H, 3.38; N, 6.71 and Cl, 16.99. Found: C, 57.43; H, 3.68; N, 6.53 and Cl, 17.11 %.
IR (KBr, cm^{-1}): 1795, 1720, 1500, 1385, 1185, 810, 760 and 750.
^{1}H-NMR (DMSO-d_6), δ (ppm): 7.63-7.23 (m, 8H, $H_{aromatic}$), 7.38 (s, 1H, H_{arom}), 5.18 (dd, J=3.2; 8 Hz, 2H, CH-Cl), 3.53 (dd, J=8; 17.2 Hz, 2H, $CH_{succinimide}$), 3.09 (dd, J=3.2; 17.2 Hz, 2H, $CH_{succinimide}$).

3-Chloro-1-{4-[4-(3-chloro-2,5-dioxopyrrolidin-1-yl)-1,1'-benzyl]-phenyl}-pyrrolidine-2,5-dione (3e) was recrystallized from acetic acid, yield 89%, mp=159-163°C.
Elemental analysis calculated for $C_{21}H_{16}N_2O_4Cl_2$ (431.265), %: C, 58.49; H, 3.74; N, 6.49 and Cl, 16.44. Found: C, 58.73; H, 3.87; N, 6.57 and Cl, 16.87 %.
IR (KBr, cm^{-1}): 1785, 1730, 1515, 1385, 1185, 950, 755 and 685.
^{1}H-NMR (DMSO-d_6), δ (ppm): 7.17 (dd, J=6.4 Hz, 8H, $H_{aromatic}$), 5.12 (dd, J=6; 9 Hz, 2H, CH-Cl), 4.05 (s, 2H, CH_2), 3.67 (dd, J=9; 18.4 Hz, 2H, $CH_{succinimide}$), 3.17 (dd, J=6; 18.4 Hz, 2H, $CH_{succinimide}$).
^{13}C-NMR (DMSO-d_6), δ (ppm): 38.85 (CH_2 succinimide), 41.37 (CH_2), 50.34 (CH-Cl), 126.91, 129.32, 130.30, 141.80 (C_{arom}), 134.63 (CH maleimide), 172.92, 172.78 (C=O).

3-Chloro-1-{4-{2-[4-(3-chloro-2,5-dioxopyrrolidin-1-yl)-phenyl]-ethyl}-phenyl}-pyrrolidine-2,5-dione (3f) was recrystallized from acetic acid, yield 86%, mp>300°C.
Elemental analysis calculated for $C_{22}H_{18}N_2O_4Cl_2$ (445.292), %: C, 59.34; H, 4.07; N, 6.28 and Cl, 15.92. Found: C, 59.17; H, 3.98; N, 6.13 and Cl, 16.18 %.
IR (KBr, cm^{-1}): 1785, 1725, 1510, 1395, 1185, 1160, 820, 750 and 660.
^{1}H-NMR (DMSO-d_6), δ (ppm): 7.40 (dd, J=7.5 Hz, 8H, $H_{aromatic}$), 5.22 (dd, J=4.5; 7.5 Hz, 2H, CH-Cl), 3.52 (dd, J=7.5; 17.2 Hz, 2H, $CH_{succinimide}$), 3.05 (dd, J=4.5; 17.2 Hz, 2H, $CH_{succinimide}$ and CH_2-CH_2).

3-Chloro-1-{4-[4-(3-chloro-2,5-dioxopyrrolidin-1-yl)-phenoxy]-phenyl}-pyrrolidine-2,5-dione (3g) was recrystallized from acetic acid, yield 88%, mp=192-195°C.

Elemental analysis calculated for $C_{20}H_{14}N_2O_5Cl_2$ (433.238), %: C, 55.45; H, 3.26; N, 6.46 and Cl, 16.36. Found: C, 55.75; H, 3.45; N, 6.36 and Cl, 16.76 %.

IR (KBr, cm^{-1}): 1785 (w), 1730 (s), 1608 (w), 1505 (s), 1395 (s), 1250 (s), 1185 (s), 840 (m), 775 (mb) and 675 (w).

^{1}H-NMR (DMSO-d_6), δ (ppm): 7.37 (dd, J=8.85 Hz, 4H, $H_{aromatic}$), 7.21 (d, J=8.8 Hz, 4H, H_{arom}), 5.17 (dd, J=4.4; 8.4 Hz, 2H, CH-Cl), 3.50 (dd, J=8.4; 18 Hz, 2H, $CH_{succinimide}$), 3.09 (dd, J=4.4; 18 Hz, 2H, $CH_{succinimide}$).

^{13}C-NMR (DMSO-d_6), δ (ppm): 38.85 (CH_2), 50.30 (CH-Cl), 119.37, 127.43, 128.65, 128.87, 156.19 (C_{arom}), 172.94, 172.80 (C=O).

3-Chloro-1-{4-{2-[4-(3-chloro-2,5-dioxopyrrolidin-1-yl)-phenyl]-sulfonyl}-phenyl}-pyrrolidine-2,5-dione (3h) was recrystallized from acetic acid, yield 89%, mp=198-200°C.

Elemental analysis calculated for $C_{20}H_{14}N_2O_6SCl_2$ (481.302), %: C, 49.91; H, 2.93; N, 5.82 and Cl, 14.73. Found: C, 50.07; H, 3.03; N, 5.75 and Cl, 15.07 %.

IR (KBr, cm^{-1}): 1785 (w), 1720 (s), 1590 (m), 1505 (s), 1385 (s), 1330 (m), 1165 (s), 1150 (s), 1100 (m), 840 (m), 740 (m) and 650 (m).

^{1}H-NMR (DMSO-d_6), δ (ppm): 7.75 (d, J=9 Hz, 4H, $H_{aromatic}$), 7.25 (d, J=9 Hz, 4H, $H_{aromatic}$), 5.25 (dd, J=4.5; 9 Hz, 2H, CH-Cl), 3.75 (dd, J=9; 18 Hz, 2H, $CH_{succinimide}$), 3.35 (dd, J=4.5; 18 Hz, 2H, $CH_{succinimide}$).

1,1'-Bis(4-phenyl)-3,3'-bipyrrolidine-2,2',5,5'-tetrone (4)

To a solution of N-phenyl-α-chlorosuccinimide (7.6 mmol) in DMF (10 mL), the dust zinc (0.3 g, 7.6 mmol) and a small amount of I_2 were added. The reaction mixture was stirred and heated at 60°C for 10 hours. Then, the mixture was cooled to room temperature and the solution was precipitated from water and filtered. The yield after recrystallization from methanol was 0.95 g (76 %), mp=261-262°C.

Analysis calculated for $C_{20}H_{16}N_2O_4$ (348.346), %: C, 68.96; H, 4.63 and N, 8.04. Found: C, 69.05; H, 4.87 and N, 7.67 %.

IR (KBr, cm^{-1}): 2950 (w), 1785 (w), 1710 (s), 1630 (m), 1510 (s), 1385 (s), 1290 (w), 1185 (s), 1110 (w), 815 (s), 710 (m), 670 (s), 590 (m) and 500 (m).

^{1}H-NMR (DMSO-d_6), δ (ppm): 7.52-7.40 (m, $6H_{aromatic}$), 7.28-7.20 (m, 4H, $H_{aromatic}$), 3.60 (m, 2H, $CH_{succinimide}$), 3.16 (dd, J =18.82 Hz, 2H), 2.98 (dd, J =18.56 Hz, 2H).

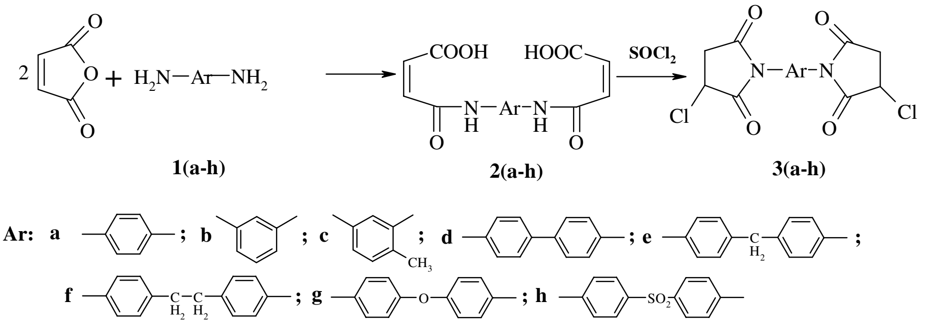
^{13}C-NMR (DMSO-d_6), δ (ppm): 33.40 (c-CH_2 succinimide), 41.60 (CH succinimide), 127.08, 129.80, 130.80, 130.20, 133.60, 176.10 and 178.60.

Synthesis of polymers 5(a-h)

To a solution of bis(α,α'-chlorosuccinimide)s **3(a-h)** (7.6 mmol) in 15 mL DMF, dust zinc (0.3 g, 7.6 mmol) and a small amount of I_2 were added. The reaction mixture was stirred and heated at 80°C for 10 hours. Then, the mixture was cooled to room temperature and the insoluble material was separated by filtration. The filtrate was precipitated in 100 mL water and filtered. The polymer was washed with water and methanol and dried at 80°C in a vacuum oven for 6 hours. The same synthesis was used to prepare all other polymers.

Results and Discussions

Monomers **3(a-h)** were prepared by the cyclodehydration of bismaleamic acids **2(a-h)** with thionyl chloride according to a modified method developed by Pyriadi [22] (Scheme 1).



Scheme 1. Preparation of monomers **3(a-h)**

IR, ^{1}H-NMR, ^{13}C-NMR spectra and elemental analysis confirmed the obtained structures. The IR spectra of monomers **3(a-h)** showed prominent characteristic absorption bands corresponding to the imide ring at 1785, 1720-1710, 1385-1400 and 1185 cm^{-1}, aromatic *p*-substituted ring and C-Cl at 760-750 cm^{-1}. In addition, the IR spectrum of monomer **3g** showed a strong absorption band observed in the range of 1270-1250 cm^{-1} (attributed to the vibration of C-O-C from diphenylether structure) and monomer **3h** showed a strong absorption band at 1330 cm^{-1} (-SO$_2$- asymmetrical vibrations) and at 1160 cm^{-1} (-SO$_2$- symmetrical vibrations).

^{1}H-NMR spectra included characteristic chemical shifts of ABX-type protons (in the range of 5.20-3.00 ppm) and *p*-substituted aromatic protons (Figure 1). In addition the monomer **3c** showed a singlet at 2.187 ppm attributed to the C$\underline{H}_3$-Ar and the monomers **3e** and **3f** showed characteristic chemical shifts of CH$_2$ protons at 4.05 and 3.05 ppm.

^{13}C-NMR spectra included characteristic chemical shifts for: α-chlorosuccinimide rings at 39.20, 48.95 and around 171.90 ppm, aromatic protons in the range of

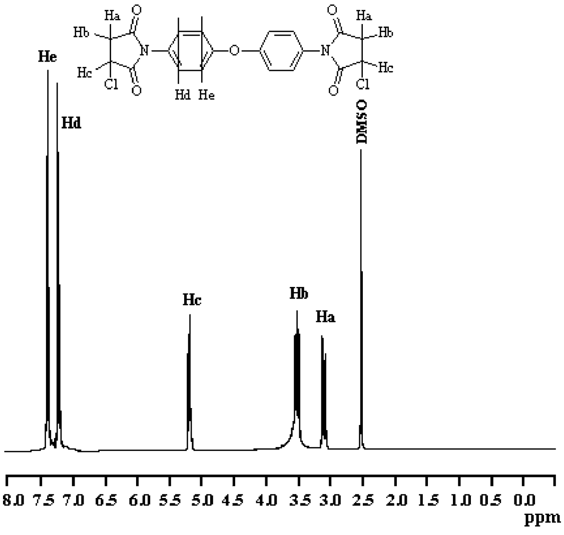


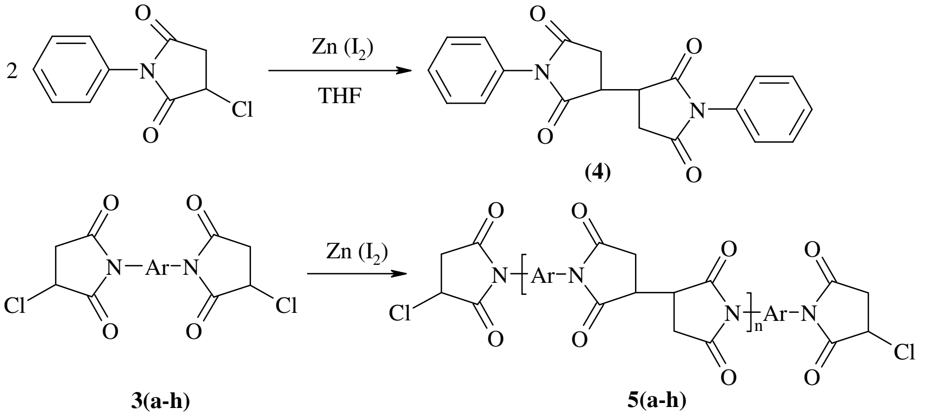
Figure 1. The ^{1}H-NMR spectrum of compound

119-156.20 ppm, aromatic substituted rings, Ar-CH_3, at 17.42 and Ar-CH_2-Ar at 41.37 ppm.

By reaction of α-haloketones with dust zinc in the presence of a small amount of I_2, at 65°C, Ceylon et al. [23] obtained the corresponding 1,4-diketones. By reaction of N-*p*-phenyl-(α-chloro)succinimide with dust zinc in the presence of a small amount of I_2, we obtained bis(*p*-phenyl)-3,3'-bypirrolidine-2,2',5,5'-tetrone (**4**).

The IR, ^{1}H-NMR and ^{13}C-NMR spectra confirmed the purpose structure. The IR spectra showed the disappearance of the absorption band characteristic to C-Cl from 750 cm^{-1}. The ^{1}H-NMR spectra showed the complete disappearance of characteristic chemical shift of an ABX-type proton in the range of 5.20-3.00 ppm and the appearance of new chemical shifts in the range 3.70-2.90 ppm attributed to 3,3'-bipyrrolidine-2,2',5,5'-tetrone.

The polymers were prepared by the reductive coupling reaction of bis(α,α'–chloro) succinimides **3(a-h)** with dust zinc in the presence of a small amount of I_2 (Scheme 2).



Scheme 2. Synthesis of polymers **5(a-h)**

The elemental analysis (C, H, N %) of the polymers are in good agreement with the calculated values (Table 1). The content of chlorine in all the polymers and the difference between calculated and found values for % Cl shows the presence of α-chlorosuccinimide as end groups.

The IR spectra of polymers **5(a-h)** showed prominent characteristic absorption bands for: succinimide structure at 1775, 1720, 1385, 1195 cm^{-1} and distinct aromatic bands in the range of 1600, 1510-1500 cm^{-1}. In addition, the IR spectrum of **5g** showed an absorption band at 1250 cm^{-1} attributed to the vibration of C-O-C from diphenylether structure and the IR spectrum of **5h** showed a strong absorption band at 1330 cm^{-1} ascribed to -SO_2- asymmetrical vibrations and at 1160 cm^{-1} due to -SO_2- symmetrical vibrations. Typical IR spectrum of **3g** monomer and its polymer **5g** are shown in Figure 2. The ^{1}H-NMR spectra of polymers showed characteristic chemical shifts of aromatic protons in the range 7.80-7.10 ppm and chemical shifts attributed to 3,3'-bipyrrolidine-2,2',5,5'-tetrone structures in the range 3.80-2.90 ppm. In addition, ^{1}H-NMR spectra of polymers **5c**, **5e** and **5f** showed chemical shifts of CH_2 protons around 4.00 ppm and CH_3 protons at 2.14 ppm for **5c** polymer.

Table 1. Elemental analysis of polymers **5(a-h)**

Polymer	Molecular formula (formula weight)	Elemental analysis							
		C%		H%		N%		Cl%	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
5a	$C_{14}H_{10}N_2O_4$ (270.234)	62.22	62.60	3.73	3.75	10.36	10.43	0	1.39
5b	$C_{14}H_{10}N_2O_4$ (270.234)	62.22	62.67	3.73	3.83	10.36	10.59	0	1.65
5c	$C_{15}H_{12}N_2O_4$ (284.260)	63.38	63.41	4.25	4.18	9.85	9.71	0	1.53
5d	$C_{20}H_{14}N_2O_4$ (346.332)	69.36	68.58	4.07	4.03	8.08	7.92	0	1.26
5e	$C_{21}H_{10}N_2O_4$ (360.351)	69.70	69.45	4.47	4.35	7.77	7.61	0	0.78
5f	$C_{22}H_{18}N_2O_4$ (374.386)	70.58	69.56	4.85	4.77	7.48	7.37	0	1.44
5g	$C_{20}H_{14}N_2O_5$ (362.332)	66.30	65.86	3.89	3.83	7.73	7.66	0	0.82
5h	$C_{20}H_{14}N_2O_6S$ (410.396)	58.53	57.98	3.44	3.40	6.82	6.73	0	0.96

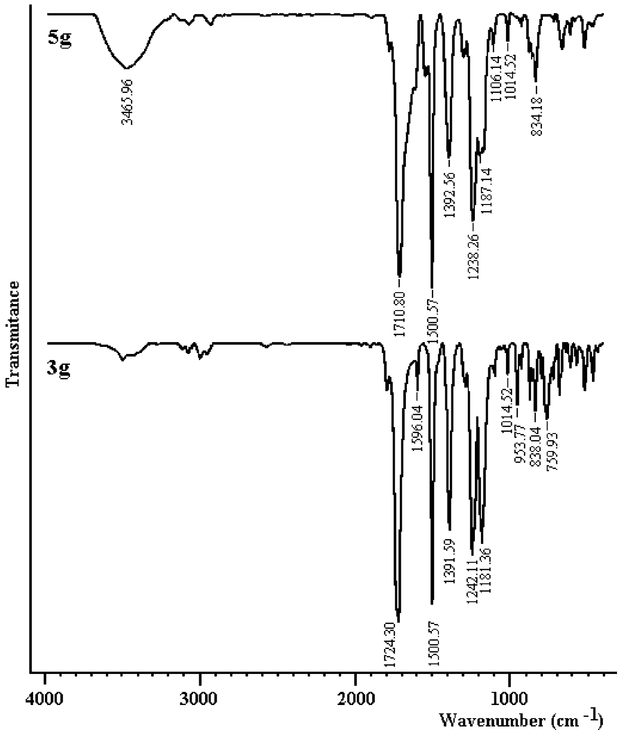


Figure 2. The FT-IR spectra of compounds **3g** and **5g**

The properties of polymers are presented in Table 2. The inherent viscosities of polymers, measured in DMF, ranged between 0.148 and 0.36 dL/g. On the base of purpose structures of polymers and the chlorine analysis data, we calculated the corresponding molecular weights.

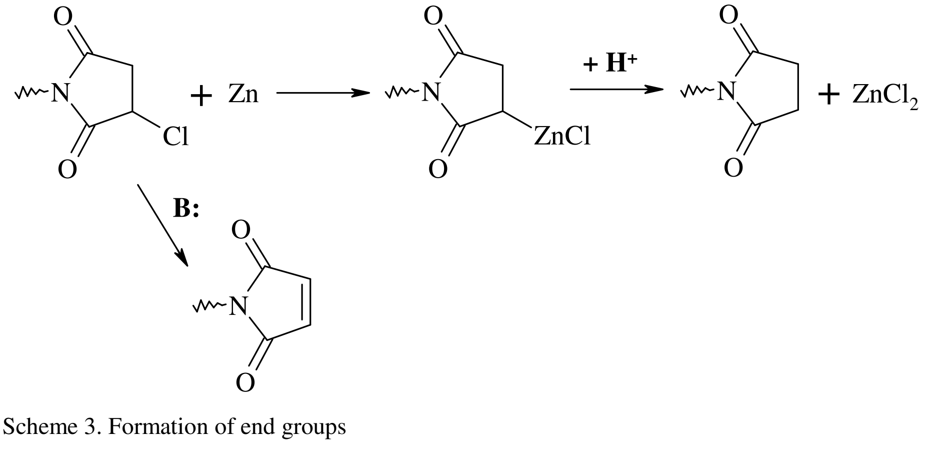
Table 2. Properties of polymers **5(a-h)**

Nr.crt.	Yield (%)	η_{inh}[a] dL/g)	$M_n \cdot 10^{-3}$ ($g \cdot mol^{-1}$)		M_w/M_n	T_g (°C)	IDT (°C)	Temperature (°C) for % weight loss			
			GPC[b]	G_f[c]				5	10	20	50
5a	87	0.183	5.33	5.10	1.63	-	310	323	348	368	500
5b	85	0.196	4.18	4.30	1.45	217	320	328	350	365	493
5c	62	0.148	4.83	4.62	1.37	210	290	310	330	365	450
5d	85	0.212	5.78	5.61	1.89	-	290	298	343	375	510
5e	87	0.230	9.25	9.08	1.48	208	287	308	330	364	460
5f	83	0.260	5.08	4.94	1.58	243	280	295	323	350	460
5g	83	0.296	9.10	8.80	1.39	195	290	312	335	368	480
5h	89	0.360	7.46	7.50	1.11	238	295	315	332	365	476

[a] Inherent viscosity of polymers measured in DMF solution at a concentration of 0.5 g/dL at 25°C; [b] Number-average molecular weight determined by GPC, measured in DMF; [c] Quantitative molecular weight values calculated from the chlorine end group content.

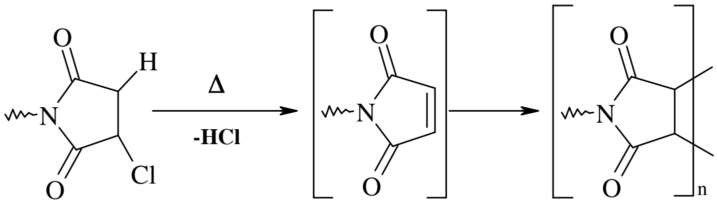
The GPC curves indicate that M_n values of polymers varied between 4180 and 9250 and M_w/M_n ratios, as a measure of the molecular weight distribution, were in range 1.112-1.890. Measured M_n values of polymers showed a good agreement with M_n values calculated from analysis data of chlorine final groups. All polymers exhibited high solubility in aprotic dipolar solvents (DMF, DMSO, NMP, DMAc).

Depending on the reaction conditions, the end groups of polymers can be: α-chlorosuccinimide, when reacted an equivalent of bischlorosuccinimide with an equivalent of zinc and the precipitation was done in acid or neutral medium, and maleimide when the precipitation takes place in basic medium (at pH=8-9), and succinimide when used excess of zinc and the precipitation was made in acid medium. The formation of succinimide or maleimide end groups is presented in Scheme 3.



Scheme 3. Formation of end groups

The thermal behaviour of the polymer was monitored by DSC and dynamic TGA measurements. The glass transition temperatures (T_g) of **5(b-h)**, determined by DSC at second heating cycle, ranged between 195-243°C and its seems to increase with the increasing of η_{inh} values and conformational rigidity. No glass transition temperatures or melting endotherms were detected up to about 300°C for **5a** and **5d** polymers. The thermal stability of the polymers was evaluated by dynamic TGA measurements. All TGA traces of the polymers **5(a-h)** showed a stage of decomposition. The thermal stability of polymers was evaluated by an initial decomposition temperature (IDT), temperature for various weight loss percents (T_5, T_{10}, T_{20}, T_{50}) and their corresponding weight loss and char yield percent at 600°C (Table 2). The initial decomposition temperatures values (IDT) ranged between 270-320°C. All TGA traces of the polymers **5(a-h)** showed a weight loss up to 3% that occurred between 0-300°C due to water desorption and elimination of hydrogen chloride resulted by dehydrochlorination reaction of α-chlorosuccinimide end groups of the polymers. We have already reported on the thermal dehydrochlorination reaction of α-chlorosuccinimides and formation of maleimide [24]. So, by heating of polymers **5(a-h)** formation of maleimide end groups takes place which leads to networks by thermal polymerization (Scheme 4). The same situation was observed by insolubilization of obtained products after their heating at 300°C for 30 minutes and explains also the discrepancy between T_g of polymer **5f** and chemical structure, and lower molecular weight.



Scheme 4. The reaction of end groups from polymers **5(a-h)** by heating

The polymers **5(a-h)** begin to decompose at 290-320°C. The polymers **5e** and **5f** having methylene groups in the structure begin to decompose under 290°C (286°C and 280°C, respectively).

Considering the temperature corresponding to 10% weight loss (T_{10}) as a criterion of thermal stability, the following order may be given for the thermal stability of polymers:

5b > 5a > 5d > 5g > 5h > 5c ≥ 5e >5f

The T_{10} value of the polymer **5f** containing dibenzyl structures was lower compared with those of the polymer containing aromatic structures. The 50% weight loss temperature was ranged between 450-510°C and it is lower than that corresponding to weight loss of polybismaleimides obtained by thermal cure of bismaleimides (530°C) [25].

Conclusion

This paper introduces a new synthesis method of linear polysuccinimide by the ring-coupling reaction of α,α'-bis(chlorosuccinimide)s. The obtained polymers are soluble in aprotic dipolar solvents and the glass transition temperatures (T_g) ranged between 195°C and 243°C.

References

1. Stenzenberger HD (1994) Adv Polym Sci 117:165
2. Chandra R, Rajabi L (1997) J Macromol Sci–Rev Macromol Chim Phys 37:61
3. Mison P, Sillion B (1998) Adv Polym Sci 140:139
4. Tan LS (1999) Polymer Data Handbook. Oxford Univ. Press Inc., pp 306
5. Grenier-Loustalat MF, Gouarderes F, Joubert F, Grenier Ph (1993) Polymer 34:3848
6. Milano JC, Mekkid S, Vernet JL (1997) Eur Polym J 33:1333
7. Hao J, Wang W, Jiang B, Cai X, Jiang L (1999) Polym Int 48:235
8. Gaina V, Gaina C, Sava M, Stoleriu A, Rusu M (1997) J Macromol Sci-Pure Appl Chem 34:2435
9. Mizori FG, Dershem SM (2004) WO 099331A2
10. Dix LR, Ebdon JR, Flint NJ, Hodge P, O'Dells R (1995) Eur Polym J. 31:647
11. Wu W, D Wang, C Ye (1998) J Appl Polym Sci 70:2471
12. Gaina V, Gaina C, Sava M (2001) Polym-Plast Technol Eng 40:89
13. Morgan RJ, Jurek RJ, Yen A, Donnellan T (1993) Polymer 34:835
14. Iijima T, Yuasa N, Tomoi M (1999) Polym Int 48:587
15. Fang Q, Jiang L (2001) J Appl Polym Sci 81:1248
16. Kottner N, Klemm E (1998) Polym Bull 41:153
17. Kumar AA, Alagar M, Rao RMVGK (2001) J Appl Polym Sci 81:38
18. Jeng RJ, Lo GS, Chen CP, Liu YL, Hsiue GH, Su WC (2003) Polym Adv Technol 14:147
19. Reghunadhan Nair CP, Francis T, Vijayan TM, Krishnan K (1999) J Appl Polym Sci 74:2737
20. Tsuda K, Ohki E, Nozoe N (1963) J Org Chem 28:783
21. Gaina V, Gaina C (2004) Materiale Plastice 41:169
22. Pyriadi TM (1972) J Org Chem 37:4184
23. Ceylan M, Gürdere MB, Budak Y, Kazaz C, Seçen H (2004) Synthesis 11:1750
24. Gaina C, Gaina V (2005) Rev Roum Chim 50:655
25. Nanjan MJ, Sivaraj K (1989) J Polym Sci: Part A: Polym Chem 27:375