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Synthesis and Characterization of New Tetraaza-bridged Polymeric Phthalocyanines

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ABSTRACT

New tetraaza-bridged metal-free and metal phthalocyanine polymers were prepared. The metal-free phthalocyanine polymer was obtained by the reaction of 4,4'-(octane-1,5,8,12-tetra-p-tolysulphonyl-1,5,8,12-tetraamine)-diphthalonitrile with hydroquinone. The chlorides of Cu(II), Ni(II) and Co(II) were employed in order to synthesize the corresponding metal-phthalocyanine polymer, $Zn(CH_3CO_2)_2$ was used for the preparation of the zinc phthalocyanine, and $Fe(CO)_5$ was used for the preparation of the Fe-analog. For the preparation of the Co-containing polymer, ammonium molybdate had to be added as catalyst. The new polymers have been characterized by elemental analyses, IR, NMR and UV-VIS spectroscopy. The electrical conductivities of the phthalocyanine polymers measured as gold sandwiches are about 10^{-9} Sm^{-1} in vacuo *and 10^{-8} Sm^{-1} in air.* © *1997 Elsevier Science Ltd*

Keywords: tetraaza-bridged, polymeric phthalocyanines.

INTRODUCTION

Unsubstituted and substituted phthalocyanines are widely used as pigments and dyes [1]. Owing to their thermal stability and facile accessibility, metallophthalocyanines have been of great interest in the preparation of organic conductors and semiconductors. Using different main group or transition metals in the centre of the macrocycles, oxygen-bridged, e.g. [Pc(SiO)]n (Pc: phthalocyanine) and other bridged systems with organic ligands, e.g.

[Pc(FeL)]n with L: e.g. pyrazine, diisocyanobenzene and tetrazine, can be obtained, exhibiting good semiconducting properties with and without doping [2]. One of the important aims of research in the chemistry of phthalocyanines (Pc) is to enhance their solubility in various solvents. While benzo-18-crown-6 ether [3] and dithia-oxa ether [4] bridged or 9-membered dithia-oxa macrocycle [5] lead to Pc derivatives slightly soluble in common organic solvents, an additional advantage of using monoazacrown ether [6,7] and 8- or 9-membered diaza and 11- or 13-membered triaza [8] and 12-membered [9,10] tetraaza macrocycles are water-soluble compounds resulting from quaternization of the aza function. Low molecular-weight metal phthalocyanine polymers are generally prepared in high yield by cyclotetramerization of phthalic acid derivaties, e.g. 1,2-dicyanobenzene or benzene-1,2-dicarboxylic anhydride with urea and metal salts. Starting with bifunctional reactants, such as 1,2,4,5-benzene tetracarboxylic dianhydrides or 1,2,4,5-benzene tetracarbonitrile, metal polymeric phthalocyanines can be prepared via polytetracyclomerization [11–13].

The present paper describes the synthesis and properties of some tetraaza-bridged polymeric phthalocyanines.

RESULTS AND DISCUSSION

4,4′-(Octane-1,5,8,12-tetra-p-tolysulphonyl-1,5,8,12-tetraamino)diphthalonitrile (1) was synthesized by treating 4-nitrophthalonitrile with octane-1,5,8,12-tetra p-tolysulphonyl-1,5,8,12-tetraamine in DMSO using K_2CO_3 as the base for this nucleophilic addition reaction [14, 15] (Scheme 1). The metal-free phthalocyanine polymer (2) was synthesized by heating a mixture of the dinitrile compound (1) with hydroquinone [16]. Cyclotetramerization of the phthalonitrile (1) in the presence of metal salts gave the metal phthalocyanine polymer (3–7). The high boiling solvents used for these reactions were urea for the Cu(II) polymer (3), dry quinoline for the Ni(II) (4) and Zn(II) (6) polymers, and ethylene glycol for the Co(II) (5) and Fe(II) (7) polymers.

In order to obtain the Co-containing phthalocyanine (5), ammonium molybdate was added as a catalyst, leading to the desired product in relatively high yields. Detosylation of the bridged aza groups of 3 and 5 with conc. H_2SO_4 (96%) and then treatment with ethanol led to the Cu(II) and Co(II) phthalocyanine polymers (3b,5b) containing free amino groups.

The polymers (2,3,4,6 and 7) were soluble in common organic solvents such as chloroform, dichloromethane, DMSO and DMF. The conversion of compounds 2–7 to the imido analogous 2a–7a, and detosylation of the aza groups of compounds 3a and 5a to 3b and 5b increased the solubility of the polymer in DMSO and DMF, but decreased it in chloroform and

dichloromethane. Decomposition of the polymeric phthalocyanines is above 200°C.

Although the aim of this work was to isolate, model polymers with homogenous end groups, the IR spectrum of compounds of 2–7, however, indicated the presence of both cyano (2220 cm^{-1}) and imido groups (1770 and 1710 cm^{-1}). Wöhrle *et al.* [17] reported a similar phenomenon to be the result of an easy saponification of the cyano groups in the presence of moisture during work-up. Therefore, all the end groups were transformed into imido groups by dissolving the product in conc. sulfuric acid and subsequent precipitation by addition of water. After this treatment, the C≡N vibration disappeared and the sym and asym C=O stretching vibrations became more intense [18].

Elemental analyses results of the starting material and of the phthalocyanine polymers are also given in Table 1.

The IR spectra of the polymeric phthalocyanines provide evidence for the structural skeleton of phthalocyanine and the nature of the end groups. The intense absorption at 1100 cm^{-1} and 1300 cm^{-1}, corresponding to vibrations of the pyrrole or benzene rings [19], as observed in the IR spectra of the polymeric phthalocyanines.

The IR spectra of 1 showed intense stretching bands at 3080–2860 (CH_2) and 2220 (CN) and 1340, 1160 cm^{-1} (SO_2). The similar spectra of the metal phthalocyanine polymers and of the metal-free phthalocyanine polymer are clear from the presence of imido and CN vibrations for 2–7 at 3330–3310 and 2445–2225 cm^{-1}. Comparison the IR spectra data clearly indicated the formation of the polymeric phthalocyanines 3b and 5b by the disappearance of the -SO_2 band at 1340, 1160 cm^{-1} in the polymeric phthalocyanines 3 and 5, and the appearance of new intense -NH bands at 3400–3380 cm^{-1} [9]. The M-N vibrations were expected to appear at 400–100 cm^{-1} but they were not observed in KBr pellets [20]. The polymers synthezised contain cyano and imido end groups which cannot be transformed into carboxylic groups under mild conditions (at 90°C in NaOH/NaCl) [11].

In the ^{1}H-NMR spectrum (DMSO-d_6) of 1, the aromatic protons appear as a multiplet at 7.77–7.26 ppm and the aliphatic protons as the expected triplet between 3.66 and 3.07 (N-CH_2CH_2-N), a singlet at 2.44 (Ar-CH_3) and a multiplet at 1.75 ppm (C-CH_2-C).

The ^{13}C-NMR spectrum of 1 shows different signals for the unsaturated C-atoms, one arising from CN (116.21 115.25 115.10). Aliphatic C-atoms also give signals at 49.81 47.91 47.55 (C-N-C), 27.62 (Ar-CH_3), 21.60 (C-CH_2-C), and 145.12 144.83 139.85 134.73 134.49 132.64 132.02 130.21 130.13 129.93 127.45 127.39 127.21 127.01 ppm (Ar).

The best indications for a phthalocyanine system are given by their UV-VIS spectra in solution. The UV-VIS absorption spectra of these polymers exhibit Q and B bands, which are the characteristic bands for phthalocyanine

TABLE 1
Analytical Data for the Starting Material and the Phthalocyanine Polymers

Compound	*Formula*	*Analysis (%)* *C*	*H*	*N*	*S*
1	$C_{52}H_{50}N_8S_4O_4$	59.88	4.80	10.75	12.28
		(59.92)	(4.76)	(10.71)	(12.33)
2	$C_{208}H_{202}N_{32}S_{16}O_{32}$	59.86	4.84	10.74	12.28
		(55.45)	(5.28)	(9.25)	(10.04)
2a	$C_{208}H_{206}N_{28}S_{16}O_{40}$	58.76	4.85	9.23	12.06
		(54.26)	(5.16)	(11.85)	(9.21)
3	$C_{208}H_{200}N_{32}S_{16}O_{32}Cu$	58.99	4.73	10.59	12.10
		(56.27)	(5.11)	(8.66)	(10.82)
3a	$C_{208}H_{204}N_{28}S_{16}O_{40}Cu$	57.95	4.74	9.10	11.89
		(53.70)	(5.23)	(10.97)	(9.61)
3b	$C_{96}H_{108}N_{28}O_8Cu$	62.49	5.86	21.26	
		(57.94)	(6.64)	(22.87)	
4	$C_{208}H_{200}N_{32}S_{16}O_{32}Ni$	59.10	4.73	10.60	12.11
		(56.73)	(5.25)	(8.48)	(10.62)
4a	$C_{208}H_{204}N_{28}S_{16}O_{40}Ni$	58.01	4.74	9.11	11.89
		(51.24)	(4.97)	(11.12)	(9.05)
5	$C_{208}H_{200}N_{32}S_{16}O_{32}Co$	59.10	4.73	10.60	12.11
		(55.11)	(5.37)	(9.17)	(9.55)
5a	$C_{208}H_{204}N_{28}S_{16}O_{40}Co$	58.00	4.74	9.11	11.90
		(53.62)	(5.16)	(10.81)	(9.34)
5b	$C_{96}H_{108}N_{28}O_8Co$	62.64	5.87	21.32	
		(58.46)	(6.25)	(23.15)	
6	$C_{208}H_{200}N_{32}S_{16}O_{32}Zn$	59.00	4.72	10.58	12.10
		(55.24)	(5.20)	(8.92)	(9.91)
6a	$C_{208}H_{204}N_{28}S_{16}O_{40}Zn$	57.91	4.73	9.10	11.89
		(52.66)	(5.12)	(11.87)	(10.02)
7	$C_{208}H_{200}N_{32}S_{16}O_{32}Fe$	59.10	4.74	10.60	12.12
		(56.05)	(5.17)	(9.01)	(10.05)
7a	$C_{208}H_{204}N_{28}S_{16}O_{40}Fe$	58.00	4.74	9.12	11.90
		(53.24)	(5.13)	(11.03)	(9.94)

Required values are given in parentheses. 2–7 phthalocyanine polymers were calculated for monomeric phthalocyanines (for CN end groups). 2a–7a, 3b and 5b phthalocyanine polymers were calculated for monomeric phthalocyanines (for imide end groups).

polymers [1]. The UV-VIS data of the phthalocyanine polymers in chloroform and DMSO are given in Table 2.

There is a shoulder at the slightly higher energy side for all products. The longer wavelength encountered for the intense band compounds of 2–7 with respect to compounds 2a–7a, 3b and 5b is a result of mixed end groups (imide and cyano groups).

The UV-VIS spectra of the polymeric phthalocyanines are very similar to those of crown ether [3], alkyl chain [21], ester-imide [22], oxa-thia [4] -substituted phthalocyanine polymers. The experimental UV-VIS bands of the polymeric phthalocyanines were slightly different from theoretical values [23],

TABLE 2
UV/VIS Spectra of the Polymeric Phthalocyanines in $CHCl_3$ and DMSO (λ max and ε are in nm and $g^{-1}cm^{-1}$ L., respectively)

Compound	
2	241(61.28) 343(15.36) 612(4.88)† 644(7.84) 667(16.96) 701(19.76) 759(1.68)
2a*	230(410.00) 324(724.00) 439(260.00) 620(410.00)† 730(785.00)
3	260(23.00) 345(11.68) 615(6.00)† 681(25.44) 760(0.08)
3a*	235(382.88) 322(313.51) 440(88.28) 660(165.16)† 734(254.95)
3b*	281(208.00) 350(20.00) 650(16.00) 733(25.44)
4	274(28.48) 607(5.36)† 672(19.44) 760(2.08)
4a*	230(450.45) 320(931.23) 448(278.08) 664(371.47)† 735(666.37)
5*	327(6.00) 625(3.28)† 650(3.84) 690(3.92) 760(2.88)
5a*	240(1300.00) 334(1027.00) 450(220.00) 605(347.00)† 671(912.00)
5b*	280(260.00) 370(40.00) 640(24.00) 732(60.00)
6	242(63.12) 330(7.60) 618(2.08)† 684(12.24) 759(1.60)
6a*	240(390.39) 360(539.90) 430(160.66) 659(199.70)† 735(695.00)
7	340(9.44) 615(3.20)† 684(9.84) 759(0.72)
7a*	240(1400.00) 330(808.00) 434(340.00) 604(278.00)† 666(541.00)

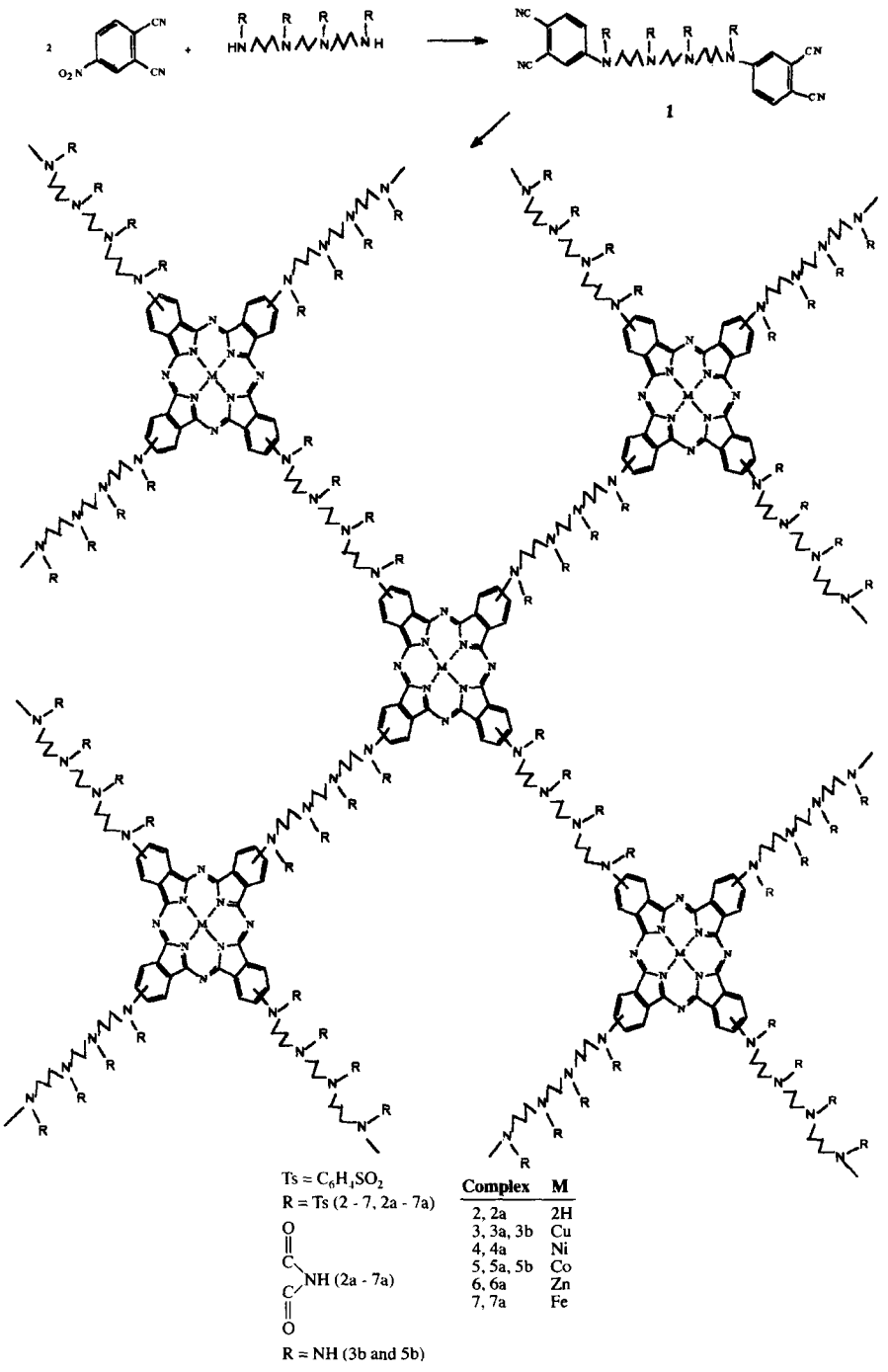
(C: 1.0 10^{-2} g/L) (for 2–7, 3b and 5b), (C: 3.3 10^{-3} g/L) (for 2a–7a).
*in DMSO.
†:shoulder.

and the results of mononuclear [8], binuclear [24], five-nuclear [25] and nona-nuclear [9] phthalocyanine. The spectral line shapes are similar and absorption maxima occur at the near-IR region with respect to the corresponding phthalocyanine model compounds.

The DC electrical conductivities of the polymeric phthalocyanines measured at room temperature in air and vacuum as a sandwich type are also given in Table 3. For the N-tosylated polymeric phthalocyanines (2–7 and

TABLE 3
Electrical Properties of the Polymeric Phthalocyanines

Compound	*Conduct. in vacuum* (σ *dc*/Sm^{-1})	*Conduct. in air* (σ *dc*/Sm^{-1})
2	$4.27\ 10^{-9}$	$1.34\ 10^{-8}$
3	$9.51\ 10^{-9}$	$1.22\ 10^{-8}$
4	$2.47\ 10^{-9}$	$4.96\ 10^{-9}$
5	$2.05\ 10^{-9}$	$3.10\ 10^{-9}$
6	$2.79\ 10^{-9}$	$2.08\ 10^{-8}$
7	$2.91\ 10^{-9}$	$1.62\ 10^{-8}$
2a	$5.26\ 10^{-9}$	$5.71\ 10^{-9}$
3a	$6.84\ 10^{-10}$	$7.69\ 10^{-10}$
4a	$1.63\ 10^{-9}$	$1.73\ 10^{-9}$
5a	$1.24\ 10^{-9}$	$3.92\ 10^{-9}$
6a	$1.37\ 10^{-9}$	$1.41\ 10^{-9}$
7a	$1.78\ 10^{-9}$	$2.18\ 10^{-9}$
3b	$3.26\ 10^{-8}$	$9.71\ 10^{-8}$
5b	$1.38\ 10^{-8}$	$6.12\ 10^{-8}$



Scheme 1. Synthesis of the Ligand and Complexes

2a–7a) are lowest with respect to detosylated polymers (3b and 5b). The bulky tosyl groups probably prevent the interaction of delocalized π electrons on the phthalocyanine moiety. The conductivity values obtained in air for all polymers show an increase of about 10^{-1}. The enhancement of the conductivity in air for the polymers has been reported to be due to absorbed oxygen [26, 27]. The higher values are comparable with those of monoaza-crown ether [28] and oxa-thia [4] substituted polymeric phthalocyanines.

EXPERIMENTAL

IR spectra were recorded on a Mattson 1000 FTIR spectrometer (KBr). Electronic spectra were recorded on a Unicam UV-VIS spectrometer. ^{1}H-NMR and ^{13}C-NMR studies were made on a Bruker AC-200 FT-NMR spectrometer. Elemental analysis was performed by the Instrumental Analysis Laboratory of Tübitak Gebze Research Center. 4-nitrophthalonitrile [29] and octane-1,5,8,12-tetra-p-tolysulphonyl-1,5,8,12-tetraamine [30] were synthesized according to the reported procedures:-

Synthesis of 4,4′-(octane-1,5,8,12-tetra-p-tolysulphonyl-1,5,8,12-tetraamine)-diphthalonitrile (1):

Octane-1,5,8,12-tetra-p-tolysulphonyl-1,5,8,12-tetraamine (23.7 g. 30 mmol) was dissolved in dry DMF (500 ml) under nitrogen and 4-nitrophthalonitrile (10.38 g. 60 mmol) was added. After stirring for 10 min, finely ground anhydrous K_2CO_3 (20.7 g. 150 mmol) was added portionwise in 2 h with efficient stirring. The reaction mixture was stirred under nitrogen at room temperature for 20 h. Water was then added and the product filtered and washed with water until the filtrate was neutral. The product was then refluxed in methanol, filtered, and the residue washed with hot methanol, and diethyl ether and dried. Yield 25 g. (80%). This compound was soluble in chloroform, dichloro methane, ethyl acetate, DMF and DMSO. M.p. 112–114°C. IR (vmax/cm^{-1}): 3080–2880, 2220, 1595, 1490, 1450, 1340, 1160, 1090, 1060, 1015–1000, 950, 810, 750–730, 695, 655, 560. ^{1}H-NMR($CDCl_3$): 1.75 (4H, m), 2.44 (12H, s), 3.07–3.66 (12H, t), 7.26–7.77 (20H, m) ^{13}C-NMR($CDCl_3$): 21.60 27.62 47.55 47.91 49.81 110.85 115.10 115.25 116.21 127.01 127.21 127.39 127.45 129.93 130.13 130.21 132.02 132.64 134.49 134.73 139.85 144.83 145.12.

Metal-free phthalocyanine polymer (2):

A mixture of 1 (1.042 g. 1.0 mmol) and hydroquinone (0.11 g. 1.0 mmol) (purified by sublimation) was heated under nitrogen by gentle heating in a sealed tube and then cooled. This mixture was heated up to 200°C under a nitrogen atmosphere and held at this temperature for 3 h. After cooling to room temperature, it was diluted with hot ethanol and the product filtered

and then refluxed with ethanol. The dark green product was dissolved in chloroform (100 ml) and added dropwise into stirred ethyl acetate (250 ml). The resulting green precipitate was filtered, washed with ethanol and diethyl ether and dried. This polymer was soluble in chloroform, dichloro methane, ethyl acetate, DMF and DMSO. Yield 0.30 g. IR (v max/cm^{-1}): 3310, 3060–2880, 2245, 1735, 1600, 1495, 1450, 1345, 1305, 1160, 1095, 1030, 945, 850, 825, 730, 665, 560.

Cu-containing polymer (3):

A mixture of 1(1.042 g. 1.0 mmol) and CuCl (0.025 g. 0.25 mmol) and urea (0.04 g. 1.0 mmol) was heated at 180–190°C for 2 h under nitrogen. After cooling, the reaction mixture was diluted with ethanol and refluxed and the residue filtered off. The dark green product was washed with NH_4OH (24%, 50 ml) and then with water until the filtrate became neutral. It was then refluxed with ethyl acetate, the liquor filtered and the dark green product recrystallized from chloroform. This polymer was soluble in chloroform, dichloromethane, DMF and DMSO. Yield 0.40 g. IR (v max/cm^{-1}): 3330, 3075–2875, 2235, 1725, 1600, 1510, 1470, 1350, 1300, 1165, 1100, 1070, 1020, 955, 820, 750, 725, 660, 555.

Ni-containing polymer (4):

A mixture of 1 (1.042 g. 1.0 mmol), $NiCl_2$ (0.033 g. 0.25 mmol) and dry quinoline (30 ml) was heated and stirred at 220°C for 6 h under nitrogen. After cooling, the reaction mixture was diluted with methanol and the precipitate was filtered off. It was treated with boiling ethanol twice to dissolve any unreacted metal salts. The green product was purified by chromatography (silica gel, $CHCl_3/CH_3OH$ 20:1). This polymer was soluble in chloroform, dichloromethane, DMF and DMSO. Yield 0.32 g. IR (v max/cm^{-1}): 3325, 3055–2890, 2230, 1735, 1595, 1490, 1455, 1350, 1300, 1170, 1095, 1020, 955, 815, 780, 725. 670, 555.

Co-containing polymer (5):

A mixture of 1 (1.042 g. 1.0 mmol), $CoCl_2$ (0.033 g. 0.25 mmol), ammonium molybdate (0.05 g) and ethylene glycol (30 ml) was refluxed and stirred at 220–230°C for 5 h under nitrogen. After cooling, the liquor was filtered and the residue digested with ethanol and ethyl acetate, washed with hot chloroform and diethyl ether and dried. This polymer was soluble in DMF and DMSO. Yield 0.60 g. IR (v max/cm^{-1}): 3330, 3060–2865, 2230, 1730, 1605, 1510, 1490, 1460, 1340, 1300, 1160, 1095, 1050, 955, 810, 765, 725, 660, 550.

Zn-containing polymer (6):

A mixture of 1 (1.042 g. 1.0 mmol), anhydrous $Zn(CH_3CO_2)_2$ (0.045 g. 0.25 mmol) and dry quinoline (30 ml) was heated and stirred at 210–220°C for 5 h under nitrogen. After cooling, the reaction mixture was diluted with methanol and the precipitate was filtered off. The green product was washed with ethanol, ethyl acetate and diethyl ether and dried. This polymer was

soluble in chloroform, DMF and DMSO. Yield 0.2 g. IR (v max/cm^{-1}): 3315, 3060–2880, 2235, 1735, 1605, 1505, 1485, 1455, 1350, 1300, 1170, 1095, 1055, 955, 815, 760, 725, 670, 560.

Fe-containing polymer (7):

A mixture of 1(1.042 g. 1.0 mmol) and ethylene glycol (30 ml) was rapidly heated and stirred at 200°C under nitrogen. At this temperature, (0.1 ml. 0.75 mmol) of $Fe(CO)_5$ was added slowly by means of a syringe and the liquor heated at 200°C for 4 h. After cooling, the reaction mixture was diluted with ethanol and filtered. The green product was washed with ethanol, ethyl acetate, and diethyl ether and dried. This polymer was soluble in chloroform, DMF and DMSO. Yield 0.2 g. IR (v max/cm^{-1}): 3325, 3050–2880, 2225, 1730, 1600, 1500, 1460, 1345, 1300, 1165, 1100, 1065, 1010, 960, 815, 760, 725, 660, 550.

Conversion of cyano end groups of polymers 2–7 into imido groups in polymers 2a–7a:

This was accomplished by dissolving the polymer in conc. sulfuric acid with stirring at room temperature. After filtration, the filtrate was poured into ice/water. The dark green precipitates were filtered, washed first with water until the filtrate became neutral and then with ethanol and diethyl ether and dried. IR (v max/cm^{-1}): 3400–3380 (NH), 1770–1760 (C=O), 1725–1710 (C=O).

Detosylation of 3 and 5 with H_2SO_4 (3b,5b):

Polymers 3 and 5 (1.0 g) were treated with conc (96%) H_2SO_4 (20 ml) at 130–135°C for 10 h. After cooling to room temperature and pouring into excess cold ethanol, the products were filtered and washed with cold ethanol until the filtrate was neutral, and then washed further with (5%) NaOH. The products were finally washed with water and diethyl ether and dried. These polymers were soluble in DMSO and DMF IR (v max/cm^{-1}): 3400–3380 (NH).

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