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Preparation and properties of polyamines. Part I. Polymers containing dinitro substituted aromatic groups

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Abstract

Relatively high molecular weight polyamines with aromatic nitro groups in the repeat units were prepared by the reactions of aliphatic diamines, and 1,5-difluoro-2,4-dinitrobenzene, at elevated temperatures in diphenyl sulfone. The physical characteristics, including solubility, thermal stability, and viscosity of the resulting polyamines were found to be strongly dependent on the aliphatic chain length of the diamines used. All polymers exhibited exceptional solvent resistance. Except for strong acids with bulky counter-ions, including sulfuric, perchloric, and nitric acids, the polymers were found to be insoluble in all common organic solvents at room temperature.

Keywords: Polyamines; H-Bonding; Solvent resistance

1. Introduction

Branched and linear polyalkylenimines are prepared from aziridine and as the post-hydrolysis product of linear poly(2-ethyl-2-oxazoline), respectively [1–3], and polymers with varying molecular weights are available for a wide range of applications [4].

2,4-Dinitrofluorobenzene (DNFB), the well-known Sanger's Reagent, is used extensively to label terminal amino groups of polypeptide chains, to derivatize mixture of amino acids prior to chromatographic separations, and to detect primary amine containing substances by spectrophotometric techniques [5]. In addition, the primary amine end groups of polyurethanes and polyureas have been capped using DNFB [6]. These nucleophilic displacement reactions of the fluorine atom by a primary amine group, a relatively weak nucleophile, can be carried out with ease, due to the presence of the two nitro groups in ortho and para positions relative to the fluorine atom.

1,5-Difluoro-2,4-dinitrobenzene (DFDNB) is used as a reagent for histochemical applications [7], and as a possible fungicide [8]. To the best of our knowledge, polymerization reactions of diamino compounds with DFDNB have not been reported. Furthermore, reduction of the nitro groups to amino groups after the polymerization reactions, may allow one to prepare water-soluble polymers with greater thermal stability than the conventional aliphatic polyimines. We report herein the preparation and characteristics of relatively high molecular weight, nitro group containing polymers, **1**. These polymers may find applications as suitable proton exchange membranes in fuel cell applications [9].

2. Experimental section

2.1. Materials

N,*N*-Dimethylacetamide (DMAC) (Aldrich), toluene (Fisher) were dried over calcium hydride and then distilled at reduced pressure. Dipheyl sulfone (Aldrich) was recrystallized from acetone. All α, ω diamines were purchased from Aldrich. The liquid homologs (containing up to five methylene units) were purified by distillation at reduced pressure immediately prior to use. The remainder (solid) diamines, (with six to twelve methylene units) were recrystallized from low boiling (bp 35–50 °C) ligroin, and then dried in a vacuum oven at room temperature. DFDNB was recrystallized from anhydrous ether. All other chemicals were used as received.

2.2. Measurements

Proton and carbon-13 NMR spectra were recorded using a Varian 500 MHz or a GE QE-300 instrument. Aqueous concentrated sulfuric acid was used as the solvent of choice for NMR measurements. A co-axial tube containing either

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dueterated dimethyl sulfoxide (DMSO-d_6) or dueterated benzene (C_6D_6) was placed inside the NMR tube during these measurements. The NMR spectra of the model compounds were run in a similar fashion. IR spectra were obtained with a Nicolet DxB FT-IR spectrophotometer using KBr pallets containing the model compounds. Mass spectra were obtained using a Hewlett–Packard Model 5995A gas chromatograph/mass spectrometer (GC/MS) with an ionization potential of 70 eV or a Bruker Auto Flex MALDI-TOF instrument using 2,5-dihydroxybenzoic acid (DHB) as the matrix for high molecular weight model compounds. Instrumentation details for the single crystal X-ray analysis are provided in the supplementary data section. Electronic absorption spectral measurements were carried out on Perkin–Elmer lambda 20 instrument, using a 1 cm cuvet. Intrinsic viscosity measurements of the polymers were conducted using a Cannon–Ubbelode dilution viscometer and solutions in aqueous concentrated sulfuric acid (25 °C). Thermogravimetric analysis (TGA) of the polymer samples was conducted at a heating rate of 10 °C/min in nitrogen using Dupont 2100 instrument. Wide-angle X-ray scan were performed on Philips wide-angle X-ray instrument using Cu Kα radiation.

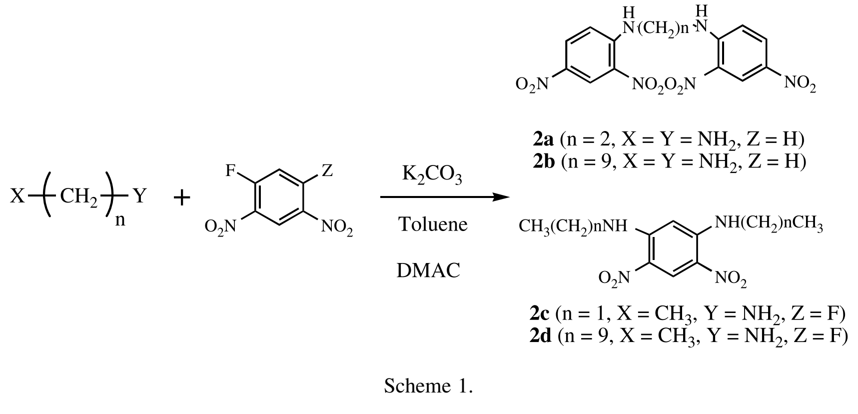
*2.3. General procedure for synthesis of model compounds **2(a–d)***

The reaction vessel consisted of a four-necked, 100 mL, round-bottomed flask fitted with an over-head stirrer, a nitrogen inlet, a thermometer, and a Dean–Stark trap fitted with a condenser. The procedure outlined below is for the preparation of compound **2d**. Decylamine (1.57 g, 0.01 mol), DFDNB (1.02 g, 0.005 mol), anhydrous potassium carbonate (2.20 g, excess), DMAC (20 mL), and toluene (20 mL) were charged into the reaction vessel. The reaction vessel was heated by an external oil-bath to an initial reaction mixture temperature of 60 °C, and the reaction was allowed to continue at this temperature, with stirring, for 30 min. The temperature of the reaction mixture was gradually raised to 150 °C over a period of 2 h. Water, the by-product of the reaction mixture, was removed by azeotropic distillation with toluene. After complete removal of water, the reaction mixture was cooled to room temperature, diluted with 25 mL of tetrahydrofuran (THF), filtered, and the filtrate was poured into rapidly stirring mixture (50:50) water/acetic acid mixture. The product, which precipitated out, was isolated by filtration. The crude yellow solid was washed with saturated sodium bicarbonate solution to remove residual acetic acid. It was air-dried under suction overnight, dissolved in dichloromethane, washed twice with water, and the organic layer was dried over anhydrous magnesium sulfate. It was filtered and the volume of the solution was reduced using a rotary evaporator. It was then allowed to crystallize from the concentrated solution.

Model compound, **2a**, derived from ethylene diamine was insoluble in DMAC at its reflux temperature. The purification of this compound was carried out by Soxhlet extraction using acetone, water, and acetone, in that order to remove residual salts and DMAC. The compound could not be purified further by recrystallization from common solvents.

*2.4. General procedure for polymer synthesis **1(a–k)***

Polymerization reactions were carried out in a four-necked 100 mL round-bottomed flask fitted with an over-head stirrer, a nitrogen inlet, a thermometer, and a Dean–Stark trap fitted with a condenser. An oil bath was used as the external heat source. A typical procedure for the preparation of a polyimine, **1j**, from 1,11-diaminoundecane and DFDNB, is provided below. The diamine (1.862 g, 0.01 mol), and DFDNB (2.04 g, 0.10 mol) were accurately weighed and transferred carefully into the reaction vessel. Anhydrous potassium carbonate (2.20 g, 0.016 mol), diphenylsulfone (20 g), and toluene (20 mL) were added to the reaction vessel. The color of the reaction mixture turned deep yellow, and a slight exotherm was observed. The temperature rose to approximately 35 °C. The reaction mixture was heated to 60 °C and the reaction was allowed to continue at this temperature for 30 min. The temperature was gradually increased to solvent reflux and water, the by-product of the reaction, was removed by azeotropic distillation with toluene. Toluene was then removed via the trap and temperature was increased gradually to 210 °C over a period of 2 h and held at that temperature for a period of 15–30 min. The color of the reaction mixture gradually became deep reddish brown, and its viscosity increased. The reaction mixture, while hot, was then poured into rapidly stirring acetone containing acetic acid 20% v/v, and the precipitated polymer was collected by filtration. The polymer was then



2a (n = 2, X = Y = NH_2, Z = H)
2b (n = 9, X = Y = NH_2, Z = H)

2c (n = 1, X = CH_3, Y = NH_2, Z = F)
2d (n = 9, X = CH_3, Y = NH_2, Z = F)

Scheme 1.

extracted with a Soxhlet extractor with acetone, water, and acetone, in that order, to remove residual potassium carbonate and diphenyl sulfone.

3. Results and discussions

3.1. Preparation and characteristics of model compounds **2(a–d)**

The nucleophilic displacement reactions of a halogen atom from 1-substituted-2-4-dinitrobenzenes by amines via S_NAr reactions have been well documented [10]. Displacement of the fluorine atom of DNFB by an aliphatic amino group falls into this category of reactions. For the sake of simplicity, we chose to utilize amines and diamines with one and nine methylene units for our model compound studies, to better understand how the conformational degrees of freedom can influence solubility behaviors. The solubility behaviors and the ease of preparations of these compounds would help in predicting the necessary polymerization reaction conditions (Scheme 1). Compounds **2**(**b**–**d**) could be prepared in DMAC with relative ease in quantitative yields. During the preparation of these compounds, an initial exotherm was observed upon the addition of the fluorinated compound. The byproduct, HF, is removed by anhydrous potassium carbonate, present in the reaction mixture. Water, which is produced by these acid–base reactions, is removed via azeotropic distillation with toluene. The model compounds could be prepared during a short reaction period of 2 h. The preparation of compound **2a**, was more problematic, due to its lack of solubility in refluxing DMAC. Analytical data of the model compounds **2**(**a**–**d**) are displayed in Table 1. An examination of the data in Table 1 indicates the following. Compound **2a** does not melt up to a temperature of 280 °C, significantly above that exhibited by compound **2b**, which may appear at first glance as a consequence of enhanced spacer length in compound **2b** in contrast to **2a**. However, as our discussion unfold, we will provide evidence for the possibility of through space interactions of two aromatic rings due to conformational rigidity of this molecule, in addition to the H-bonding, possible between the amino group with the nitro group ortho to it [11]. For **2b**, chain flexibility may not force the aromatic rings to be on top of each other. An examination of the IR spectral data in Table 1 indicates in case of **2a**, the bands due to the nitro groups (1519, 1329 cm^{-1}) are shifted to lower frequencies than those of **2b** (1524 and 1334 cm^{-1}). Although these changes are not significant, it is noteworthy that the C–H band ortho to the amine group of **2a** shifts to lower frequency (3328 cm^{-1}) in contrast to the band at 3351 cm^{-1} due to the same group of **2b**. The absorbances due to the C–H bonds meta to the amine groups appear essentially at the same position (3094 cm^{-1}). This may be due to a higher degree of intermolecular H-bonding possible for **2a** as opposed to **2b**. However, the aromatic proton absorbances in the H-1 NMR spectra of these two compounds (concentrated sulfuric acid) were identical. That this should be the case is not unexpected due to the loss of H-bonding interactions in a strongly acidic medium. In addition to the H-1 NMR studies (Table 1), it was possible to obtain a single crystal X-ray analysis of one compound (with eight methylene bridging units) belonging this category of model compounds (please see supporting information). The structures of this group of model compounds were also further confirmed by mass spectral analyses (Table 1). Mass spectral data for the remainder of model compounds are included as supporting information.

Table 1
Analytical data **2**(**a**–**d**)

Compound **2**	Mp (°C)	IR (KBr)	Proton NMR data[a]	Mass spectrum$_{(\text{relative intensity})}$ (m/z)
a	>280	3328	3.99 (s, 4H)	$392_{(5)}$
		3094	7.60 (d, 2H)	$196_{(100)}$
		2931	8.50 (d, 2H)	$179_{(90)}$
		1519	9.09 (s, 2H)	$104_{(46)}$
		1329		
b	118–121	3351	1.20 (m, 12H)	$220_{(0.05)}$
		3095	1.77 (m, 4H)	$196_{(100)}$
		2927	3.55 (m, 4H)	$180_{(68)}$
		1524	7.92 (d, 2H)	$164_{(18)}$
		1334	8.70 (d, 2H)	
			9.18 (s, 2H)	
c	158–162	3352	1.45 (t, 3H)	$293_{(0.05)}$
		2916	3.75 (q, 2H)	$254_{(100)}$
		1560	8.09 (s, 1H)	$221_{(100)}$
		1542	9.39 (s, 1H)	$174_{(29)}$
		1362		
d	88–89	3378	0.73 (t, 6H)	$478_{(15)}$
		2919	1.20 (m, 28H)	$443_{(100)}$
		1581	1.77 (m, 4H)	$375_{(32)}$
		1541	3.63 (m, 4H)	$351_{(47)}$
		1409	8.05 (s, 1H)	
		1343	9.37 (s, 1H)	

[a] Aqueous concentrated sulfuric acid.

In contrast to compound the excellent solubility behaviors of **2b** in a variety of solvents, compound **2a** is soluble only in aqueous concentrated sulfuric acid at room temperature. This is due to the stronger inter and intra molecular forces which can exist for compound **2a** (Table 2). Further evidence in support of this argument comes from electronic absorption spectral measurements of **2a** and **2b** (3 μL of 15 μM solution of each compound in aqueous concentrated sulfuric acid was diluted in 3 mL of water). The electronic absorption spectra before and after addition of water to **2a** and **2b** solutions are displayed in Fig. 1(a) and (b), respectively. An examination of Fig. 1 indicates the following. First, prior to the addition of water, both compounds show sharp absorptions at 250 nm and **2a** exhibits a well-defined peak at 360 nm, which is absent for **2b**.

Table 2
Solubility behavior of **2**(**a**–**d**)

Compound **2**	THF	CH_2Cl_2	$CHCl_3$	DMAC	DMSO	Conc. H_2SO_4	NMP
a	I	I	I	S*	S*	S	S*
b	S	S	S	S*	S	S	S
c	S	S	S	S*	S	S	S
d	S	S	S	S*	S	S	S

S, soluble at room temp; S*, soluble upon heating to reflux temperature; I, insoluble.

This suggests that even in aqueous concentrated sulfuric acid, aggregation persists for **2a** due to the short spacer length leading to stacking interactions [12,13]. Thus, it is clear that one observes a bathochromic (300–360 nm) shift, with the change in the spacer lengths from ten methylene to two methylene units. This can arise due to both inter and intra molecular stacking interactions. The possible existence of intramolecular π–π interactions were further confirmed by the energy-minimized models of **2a** and **2b** are shown in Fig. 2. The minimizations were run from Xchemedit, Version 0.95 [14a], using BOSS Version 4.3 program [14b].

Second, absorbances due to both these compounds exhibit solvatochromic red shifts upon addition of a poor solvent, water, in this instance. The strong absorbance at 250 nm, present before the addition of water for compound **2a** loses most of its intensity, and a strong band, appears 410 nm with the concurrent loss of the weak peak at 360 nm. This remarkable red shift was observed in case of **2b** also (Fig. 1(b)). Therefore, it is likely that in the presence of water, a non-solvent for these compounds, the molecules start exhibiting both intra and inter-chain H-bonding associations, in

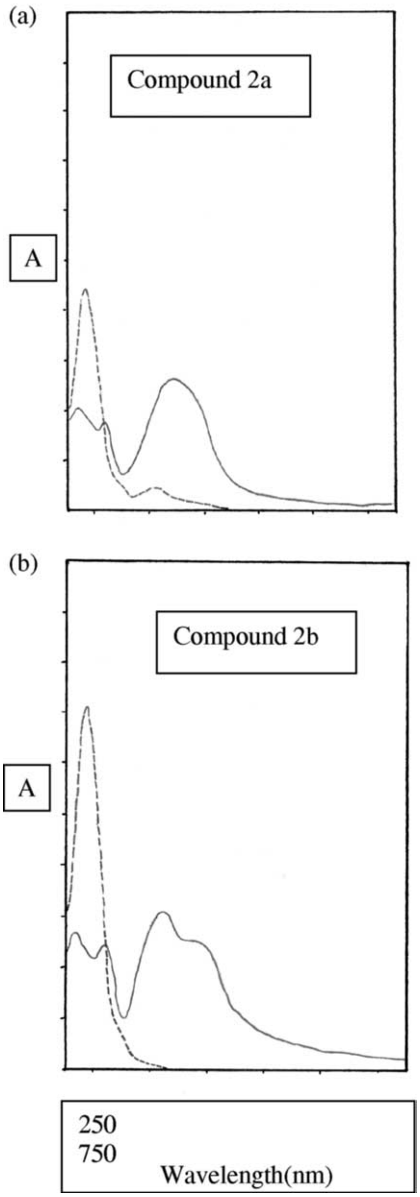
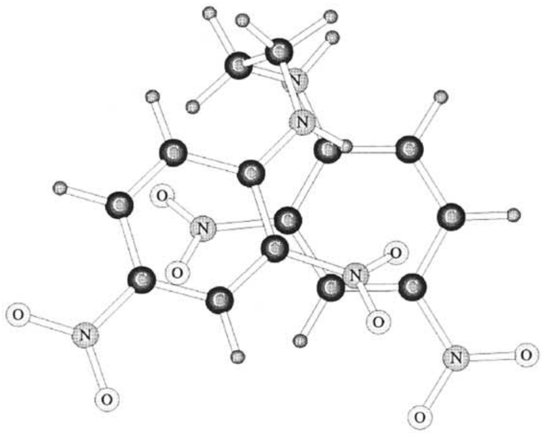
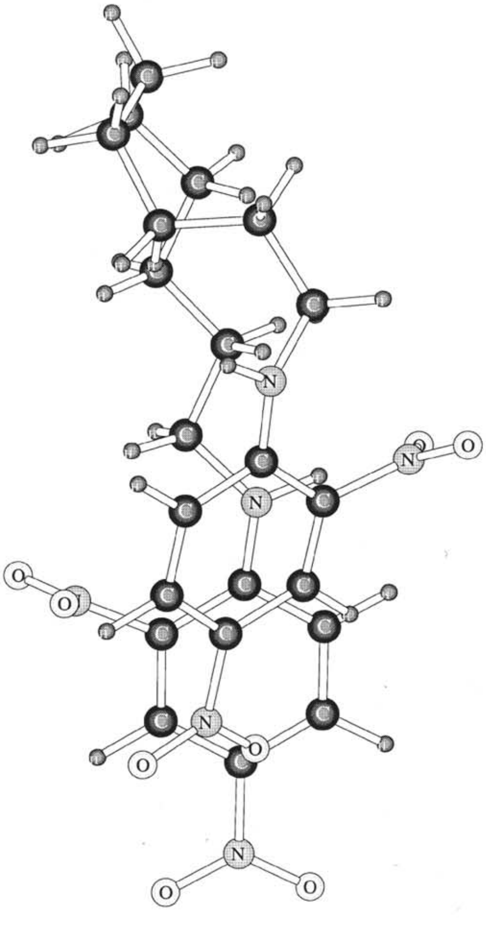


Fig. 1. (a) Absorption spectra of **2a** and (b) **2b** before (– – –) and after (solid line) addition of water. Spectra were obtained at ambient temperatures.

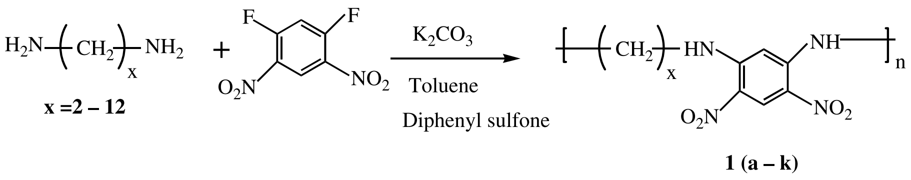


Compound **2a**



Compound **2b**

Fig. 2. Energy minimized structures of **2a** and **2b**.



Scheme 2.

addition to the stacking interactions of the aromatic rings. This results in a greater degree of conjugation resulting in bathochromic shifts.

Model compounds **2c** and **2d** were prepared to examine the reactivity of the remaining fluorine atom after the displacement of the first one by one amine group. These compounds could be prepared in essentially quantitative yields. As discussed in the section above for **2a** and **2b**, model compounds **2c** and **2d**, exhibited similar spectral (IR and NMR) characteristics. The first evidence comes from the significantly different melting points of these two compounds (Table 1). Compound **2c**, containing two short arms of two carbon atoms is likely to exhibit a higher degree of inter-molecular H-bonding than **2d**, which can result in high melting point. This is further supported by the IR (KBr) data. The absorbances due to the C–H group ortho to the two amine groups in **2c** and **2d** appear at 3352 and 3378 cm^{-1}, respectively; indicative of the higher extent of H-bonding in the former compound. Furthermore, the peaks due to the nitro groups appear at 1362 (**2c**) and 1409 cm^{-1} (**2d**). These facts suggest that the extent of inter-molecular H-bonding is significant in case of **2c** in contrast to **2d**. In solution, H-bonding is likely to be lost in both these compounds. This is borne out by the proton NMR spectral data (aqueous concentrated H_2SO_4). The absorbances due to the two aromatic protons appear as singlets and exhibit essentially identical chemical shifts in the vicinity of 8.25 ppm (ortho to two amino groups) and 9.30 ppm (ortho to the two nitro groups) (Table 1).

*3.2. Preparation and characteristics of polymers **1(a–k)***

The solubility behaviors of the model compounds indicated that for the preparation of relatively high molecular weight polymers one has to resort to high temperatures in dipolar aprotic solvents. Furthermore, with increasing molecular weights, it would be necessary to conduct reactions beyond the temperature achievable by using DMAC as the solvent. We have used diphenyl sulfone (DPS) as a solvent of choice for the preparation of high melting, semicrystalline aromatic poly ether ketones [15]. These observations led us to attempt polymerization reactions in DPS in the presence of toluene and anhydrous potassium carbonate (as the acid scavenger) (Scheme 2).

The solubility behaviors of the polymers **1**(**a**–**k**) are displayed in Table 3. All polymers exhibited very good solubility in aqueous concentrated sulfuric acid at room temperature. Similar observations were made (not shown in Table 3) with aqueous concentrated nitric and perchloric acids. Interestingly, the polymers were insoluble in concentrated hydrochloric acid, 48% aqueous hydrobromic acid, and phosphoric acid. This suggests that both the acid strength and the size of the counter-ion may play a critical role; strong acid can protonate the secondary nitrogen atom attached to the benzene ring, and bulkier groups interfere with inter-chain interactions. Polymers with more rigid backbones, **1**(**a**–**c**), were only slightly soluble in refluxing DMAC. Thus, these polymerizations were also carried out in DPS at elevated temperatures (>200 °C). On the other hand, polymers with

Table 3
Solubility behavior and intrinsic viscosity for **1**(**a**–**k**)

1	Number of methylene unit per repeating unit (*x*)	THF	CH_2Cl_2	$CHCl_3$	DMAC	NMP	Conc. H_2SO_4	Viscosity (*n*)[a]
a	2	I	I	I	SS*	I	S	0.083
b	3	I	I	I	SS*	I	S	0.114
c	4	I	I	I	SS*	I	S	0.171
d	5	I	S*	I	SS*	S*	S	0.394
e	6	S*	S*	S*	S*	S*	S	0.347
f	7	S*	S*	S*	S*	S*	S	0.770
g	8	S*	S*	S*	S*	S*	S	0.406
h	9	S*	S*	S*	S*	S*	S	0.394
i	10	S*	S*	S*	S*	S*	S	0.431
j	11	S*	S*	S*	S*	S*	S	0.348
k	12	S*	S*	S*	S*	S*	S	1.351

S, soluble at room temp; S*, soluble upon heating to reflux temperature; SS*: slightly soluble upon heating to reflux temperature; I, insoluble.

[a] Aqueous concentrated H_2SO_4 solution at 25 °C.

more flexible backbones, **1**(**d**–**k**), (containing from five up to twelve methylene units) were soluble in refluxing DMAC, and it was possible to achieve relatively higher molecular weight polymers by doing the polymerization reactions in the same solvent.

Due to their solubility behaviors, conventional size exclusion chromatography could not be performed to ascertain and compare molecular weights of this series of polymers. Nevertheless, the intrinsic viscosity measurements in concentrated sulfuric acid could be carried at room temperature. These values are displayed in Table 3. A comparison of these values indicates that with the exception of polymers **1**(**a**–**c**), the remainder, exhibit intrinsic viscosity values indicative of moderate to high molecular weight natures of the polymers.

The chemical constitutions of the polymer backbones were ascertained by C-13 NMR. The C-13 NMR spectrum of (aqueous concentrated sulfuric acid) of **1i** with ten methylene units is shown in Fig. 3. An examination of the spectrum indicates the presence of absorbances due to five different types of aliphatic and four types of aromatic carbon atoms. Due to the nature of the solvent used for conducting NMR experiments, it was not possible to assign the peaks to the corresponding carbon atoms by using the chemical shift contribution values [16].

The electronic absorption spectra of polymers solutions in concentrated sulfuric acid **1**(**a**–**k**) of similar concentrations are shown in Fig. 4(a). A sample (5 μL, of 1 mg/ml) of this solution was diluted with 3 mL of concentrated sulfuric acid. Extremely dilute solutions were used to avoid complications arising from inter-chain interactions and the spectra were recorded at room temperature. An examination of Fig. 4(a) indicates the presence of a sharp absorbance at 360 nm for **1a**, and a gradual blue shift of this absorbance with increasing spacer lengths (from two to twelve methylene units). Since the polymers have different molecular weights, one observes sample-to-sample variations in peak intensities. These observations suggest that with increasing spacer lengths, the degrees of conformational freedom increases, the chain rigidity decreases, and the possible stacking interactions between the benzene rings of juxtaposed repeat units become less likely. As discussed earlier for the model compounds **2a** and **2b**, this lowers the extent of conjugation, resulting in the observed blue shift. However, in a poorer solvent, both inter and intra chain interactions H-bonding interactions, and stacking interactions should play a critical role in determining the conformation of a chain in solution. In order to confirm this in the present system, 5 μL of each of the polymer sample solution (1 mg/mL), was diluted with 3 mL of de-ionized water (a non-solvent for the polymers) and the electronic absorption spectra of these samples were measured. The spectra of **1a**, **1d**, and **1i**, with two, five, and ten methylene units, respectively, before and after the addition of water, are displayed in Fig. 4(b). One observes trends similar to the ones discussed earlier for the model compounds. Furthermore, the spectra of the three polymers, after the addition of water, do not exhibit significant and discernable differences. The shift of absorbance around 420 nm to higher wavelength can be ascribed to possible intra, inter chain H-bonding, and stacking interactions. This is wholly consistent with the fact that all possible non-covalent

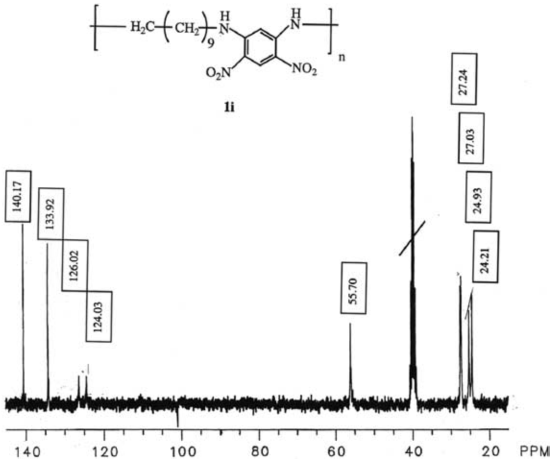


Fig. 3. C-13 NMR (concentrated sulfuric acid) spectrum of polymer **1i**.

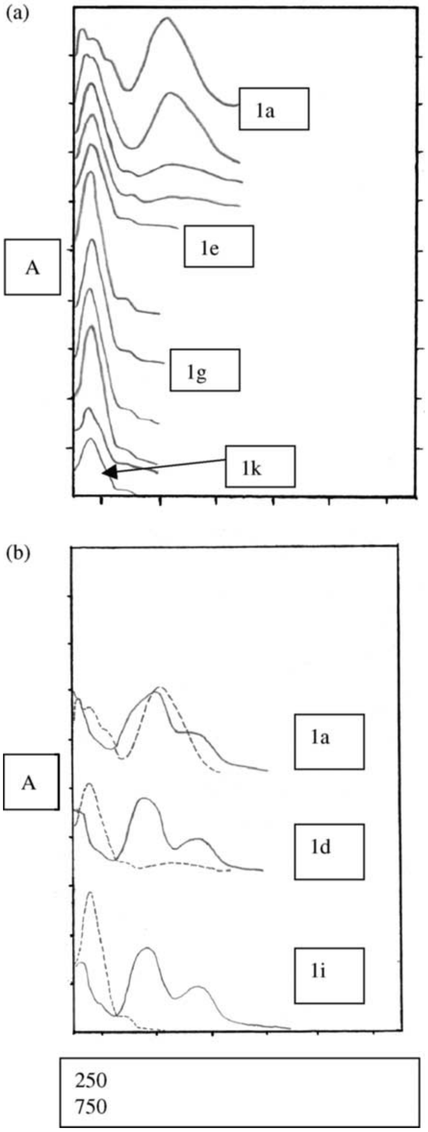


Fig. 4. (a) Absorption spectra of polymers **1**(**a**–**k**). (b) Absorption spectra of polymers **1a**, **1d**, and **1i** before (– – –) and after (solid line) addition of water.

Table 4
Thermogravimetric analysis data of **1**(**a**–**k**)

1	Number of methylene unit per repeating unit (x)	Percent residue at 850 °C	Isothermal loss[a] (%)
a	2	22.77	1.62
b	3	29.37	4.44
c	4	29.84	3.53
d	5	52.25	9.56
e	6	53.17	9.19
f	7	44.65	9.13
g	8	40.12	9.40
h	9	36.46	8.92
i	10	32.84	8.74
j	11	32.10	8.02
k	12	26.86	7.07

TGA heating rate: 10°/min, N_2.

[a] 240 °C, 1 h, N_2.

interactions come into play in a hostile environment to minimize the energy of the system, a scenario akin to polymers in their solid states.

Table 5
Data from DSC analyses (first heating, heating rate 10°C/min) of polymers **1**(**a**–**k**)

Polymer **1**	First endotherm peak maxima (°C)	Second endotherm peak maxima (°C)
a	n/a	n/a
b	n/a	n/a
c	n/a	n/a
d	n/a	n/a
e	147.7	n/a
f	133.3	n/a
g	99.9	152.2
h	120.8	149.5
i	110.9	128.5
j	94.0	110.9
k	104.4	n/a

The thermal stabilities of the polymers were examined by both dynamic and isothermal TG analysis. Data collected from these experiments are displayed in Table 4. The thermograms obtained from dynamic TG analysis are displayed in Fig. 5(a) and (b). Polymers with short spacers (up to four methylene units), **1**(**a**–**c**) (Fig. 5(a)), display similar pattern of decomposition, which is significantly different from the one displayed by **1**(**d**–**k**), (Fig. 5(b)) with longer spacer groups (from five to twelve methylene units). Furthermore, an examination of Fig. 5(b), indicates that the percent residue at 850 °C, decreases, with the increasing aliphatic chain length, consistent with generally observed lower degree of char formation from aliphatic units. These polymers decompose in two steps-the onset temperature for the first decomposition (∼20% loss) occurs in the vicinity of 275 °C. The second decomposition with the major weight loss (∼30%) takes place between 420 and 440 °C. Polymers **1**(**a**–**c**), are of relatively lower molecular weights, thus, a high concentration of chain ends can contribute significantly to the thermal decomposition pattern and also to the extent of char formation at elevated temperature (850 °C). These observations are consistent with the data obtained from the isothermal studies (Table 4). Polymers **1**(**d**–**k**), show somewhat similar percent weight losses (between 8 and 10%), higher than those observed for low molecular weight polymers with two, three and four methylene units. This may be due to the fact that a large proportion of these rigid chains must contain aromatic moieties at their chain termini. An examination of Fig. 2(a) suggests significant steric crowding. Thus, in addition to the stiffness of the chain, the aromatic groups at the chain termini cannot exhibit as high a degree of freedom as an amino alkyl chain end. This would render the chain inactive for further growth.

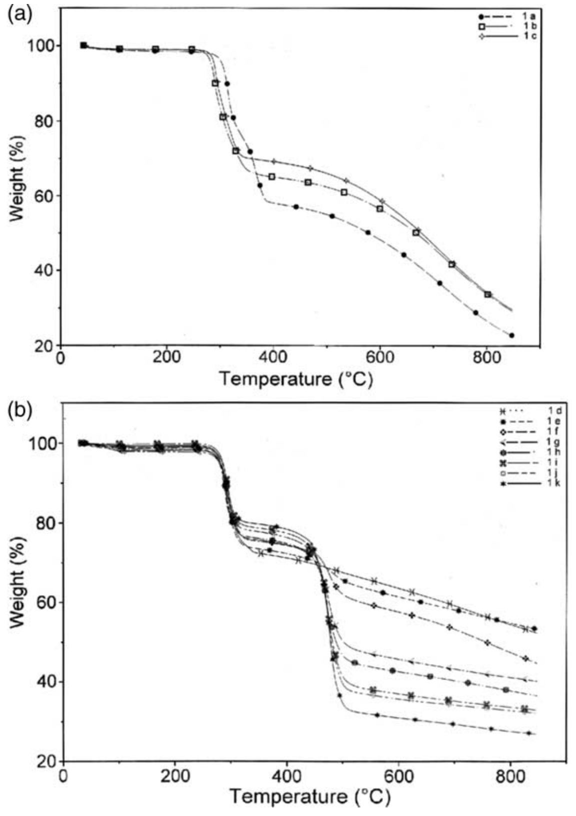


Fig. 5. (a) TG thermograms of polymer **1**(**a**–**c**) (nitrogen, 10°/min). (b) TG thermograms of polymer **1**(**d**–**k**) (nitrogen, 10°/min).

The data collected from the differential scanning calorimetry studies for polymers **1**(**a**–**k**) are displayed in Table 5. An

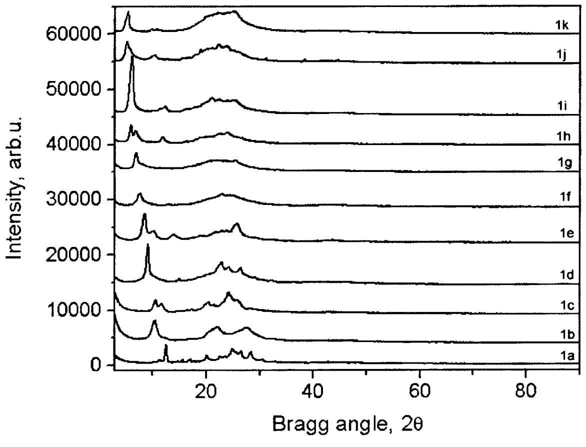


Fig. 6. WDAX scans of polymers **1**(**a**–**k**).

examination of these findings suggests that the polymers with more than five methylene units, **1**(**e**–**k**), in the repeat units exhibit melting point endotherms in the first heating. Furthermore, four members of this subgroup, **1**(**g**–**j**), exhibit multiple endotherms—a possible consequence of both inter and intra chain interactions. Our understanding as to why the remaining three polymers do not show this behavior is meager. Irrespective of the number of methylene units in the repeat units, these polymers **1**(**e**–**k**) fail to recrystallize upon slow cooling (2.5 °C/min). This group of materials could be compression molded above their melting transitions to afford tough transparent films. Polymers with shorter aliphatic chains, (up to five methylene units) **1**(**a**–**d**), are devoid of thermal transitions below their decomposition temperatures, which suggest that they are not amenable to thermal processing. As discussed below, these materials are likely to possess melting points above their decomposition temperatures.

Wide-angle X-ray analyses of the polymers **1**(**a**–**k**) (Fig. 6) provided additional evidences in support of these observations. First, polymers containing up to six methylene units, **1**(**a**–**e**) are semicrystalline in nature. With the increase in the number of methylene units beyond six, the degree of crystallinity decreases—an expected consequence of higher degrees of conformational freedom. The sizes of the crystallites, as evident from the half peak width at the lower angles, fluctuate randomly. One also observes a step-wise shifts to higher values of the characteristic length between the scattering units with the increase in the number of methylene units. These complexities arise from three major factors including spacer lengths, H-bonding interactions, and edge-to-face [17] aromatic ring interactions.

4. Conclusions

A novel class of secondary amine containing polymers with dinitro substituted benzene ring in each repeat unit has been prepared. Moderate to high molecular weight polymers with excellent solvent resistance were prepared via nucleophilic aromatic substitution reactions. Detailed electronic absorption spectral studies, and molecular modeling analysis on model compounds were carried out to better understand the roles of H-bonding, edge-to-face interactions of aromatic rings, and the spacer lengths on the solubility, molecular weights of the polymers, and thermal stability behaviors. Post modifications of the nitro group, the secondary amino groups, the aromatic ring, are presently under way. Findings from these studies will be reported soon.

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