Synthesis of linear condensation polymer obtained by the reaction of 2,6-diaminotoluene with benzaldehyde

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In the presence of acid, 2,6-diaminotoluene was reacted with benzaldehyde. The obtained polymer was characterized by ^{1}H n.m.r. *FT*i.r. and U.v.–vis. spectroscopy, g.p.c. and elemental analysis. Model compounds were synthesized in order to confirm the chemical structure of the polymer.

(Keywords: synthesis; reaction; characterization)

INTRODUCTION

Aromatic 1,3-diamines were reacted with aldehyde compounds forming tetramine compounds[1]. These type of compounds were used as reactants for making acridine compounds by intramolecular condensation reaction[2–8]. This concept was further developed by Litt and co-workers[9–11] for providing linear condensation polymers as precursors to ladder polymers. However, the obtained polymers did not have good solubility for solvents and had relatively low molecular weight. In order to overcome these problems, a new polymer was synthesized by reacting 2,6-diaminotoluene with benzaldehyde in water/dimethyl sulphoxide mixed solvent in the presence of acid. The obtained polymer was very soluble in common organic solvents. The reaction product was oligomeric with molecular weight of a few thousands due to the steric hindrance or the Schiff base formation which destroyed the stoichiometry of the diamine and the aldehyde.

EXPERIMENTAL

Purification of the chemicals

The sublimation of 2,6-diaminotoluene was performed five times under vacuum. Dimethyl sulphoxide and benzaldehyde were distilled under vacuum. The formation of 2,6-diaminotoluene dihydrochloride was accomplished by treating 2,6-diaminotoluene with concentrated hydrochloric acid.

Synthesis of the model compounds 1 and 2

The synthesis of the model compounds 1 and 2 involved the dissolution of 2,6-diaminotoluene (15.3 g, 0.125 mol) and 2,6-diaminotoluene dihydrochloride (24.4 g, 0.125 mol) in a solution of deionized water (28.5 ml) and dimethyl sulphoxide (30.5 ml). Benzaldehyde (13.25 g, 0.125 mol) was then added dropwise to the solution over a period of 36 h. The solution was stirred at 25°C for 12 h. The solution was neutralized with an excess of sodium hydroxide in an aqueous solution. The precipitate was filtered and washed with deionized water. In order to remove the by-product (Schiff base), the precipitate was suspended in water and subsequently dissolved with 6 N hydrochloric acid. The solution was boiled with ~1 g of activated carbon, filtered hot, and cooled. The solution was washed three times with ether to remove the resulting benzaldehyde. When the solution was treated with excess base, a white precipitate formed. The precipitate was collected via suction filtration, washed with water, then dried in a vacuum desiccator over potassium hydroxide. The crude yield was 26.0 g (62.7%). Thin layer chromatography was used for the determination of the purity. T.l.c. (mobile phase: 70% acetonitrile and 30% benzene; plate: silica gel) showed five components with R_f values = 0.32, 0.16, 0.09, 0.05 and 0.02. The crude material (1 g) was dissolved in mobile phase (2 ml) and separated by column chromatography (column i.d. = 24 mm, length = 30 cm; mobile phase: 30% acetonitrile, 70% benzene; packing material: silica gel). Column chromatography afforded 0.49 g of model compound 1 (fraction 1), m.p. 130–134°C and 0.20 g of model compound 2 (fraction 2), m.p. 157–163°C. The synthetic scheme for model compounds 1 and 2 is shown in *Figure 1*.

Synthesis of the polymer

The synthetic method is based on the work of Kharas and Litt[9] and involves the dissolution of 2,6-diaminotoluene dihydrochloride (9.7 g, 0.05 mol) in a deionized water (57 ml) and dimethyl sulphoxide (61 ml) solution. Benzaldehyde (5.3 g, 0.05 mol) was then added dropwise to the solution over a period of 2 h. The solution turned from light yellow to orange in colour immediately following the addition of the benzaldehyde. The solution was stirred at 25°C for 60 h under argon. The solution was neutralized with an excess of sodium hydroxide in an aqueous solution. The precipitate was filtered and washed with deionized water. In order to remove the by-product (Schiff base), the precipitate was suspended in water and subsequently dissolved with 6 N hydrochloric acid. The solution was washed three times with

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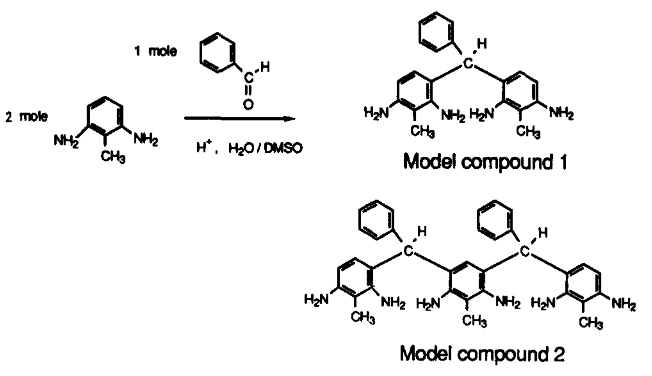

Figure 1 Synthetic scheme for model compounds 1 and 2

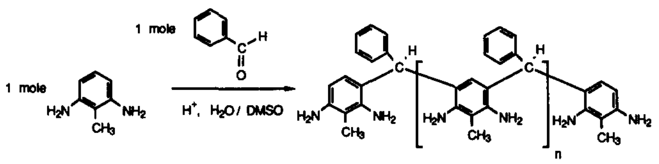

Figure 2 Synthetic scheme for the polymer

ether to remove the resulting benzaldehyde. When the solution was treated with excess base, a light yellow precipitate formed. The precipitate was collected via suction filtration, washed with water, then dried in a vacuum desiccator over potassium hydroxide. The yield was 2.9 g (25.2%). The polymer was soluble in dimethyl sulphoxide (DMSO), dimethyl formamide (DMF), chloroform, tetrahydrofuran (THF), acetone and insoluble in benzene and *n*-hexane. The synthetic scheme for the polymer is shown in *Figure 2*.

Characterization

The ^1H n.m.r. spectra were obtained using a 200 MHz Varian XL-200 *FT*n.m.r. $CDCl_3$ and DMSO-d_6 were used as the n.m.r. solvent. Tetramethyl silane (TMS, $\delta = 0.00$ ppm) was used as a reference. I.r. absorbance spectra were obtained using a Bomem Michelson 110 *FT*i.r. spectrometer. The KBr pellet method was used for sample preparation. A Cary 2300 spectrometer was used to obtain the solution absorbance spectra in the u.v.–visible (vis.) region. Spectrophotometric grade 1,4-dioxane was used as a solvent. The g.p.c. chromatograms were obtained using a Waters Maxima 820 g.p.c./h.p.l.c. chromatograph. Carbon, hydrogen and nitrogen content data were obtained from Galbraith Laboratories.

RESULTS AND DISCUSSION

Model compounds 1 and 2

The g.p.c. chromatograms (*Figure 3*) of the crude product and the separated fractions 1 and 2 show that the molecular weights of fractions 1 and 2 are approximately 400 and 600, respectively. This result is consistent with t.l.c. analysis since the larger molecule, model compound 2 (fraction 2), which is supposed to have more NH_2 groups, has the lower R_f value due to strong adsorption on the silica gel plate.

The ^1H n.m.r. spectra and the peak assignments of model compounds 1 and 2 are given in *Figures 4* and *5* respectively, accompanied by the presumed chemical structures. The chemical shifts and normalized intensities of the peaks are consistent with the expected structures. Furthermore, the molecular weights of the expected chemical structures are 332 and 542, respectively, and are very close to the values found by g.p.c. The n.m.r. spectra for model compounds 1 and 2 show two groups of the peaks downfield in the range 7.4–6.9 ppm which are from the side chain benzene protons (peak a). The ratios of these peaks are approximately 3 to 2, in each case, which indicates that the three protons farthest from methyl carbon, to which the benzene is attached, are in more deshielded environments than the other two protons. In the region of 6.5–6.0 ppm in each spectrum, there are two doublets (peaks b, c) with coupling constants of 9.8 Hz (model compound 1) and 8.9 Hz (model compound 2) which are typical values for spin coupling between two protons at the *ortho* position of a benzene ring[12]. The spectrum for model compound 2 shows a singlet peak arising from the main chain benzene (peak d). These peaks (b, c and d) are very informative for the determination of a molecular weight of a polymer. The singlet peaks, both compounds, arise from the methine proton (peak e) in the region of 5.2–5.1 ppm. The amino protons (peak f) and methyl protons (peak

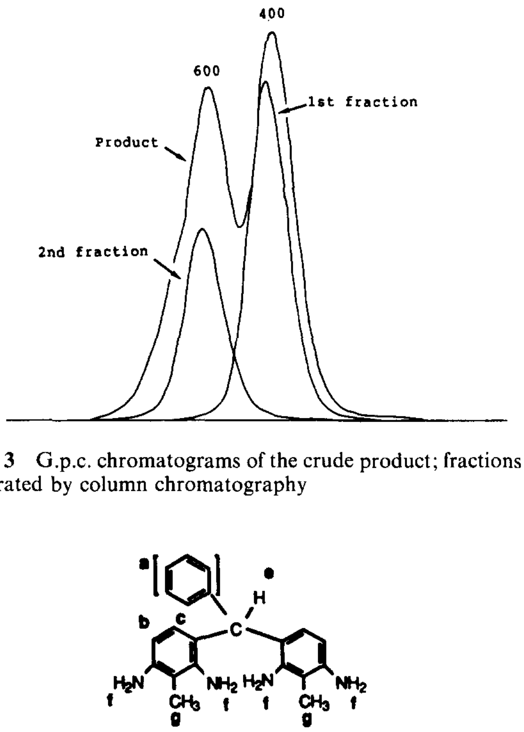

Figure 3 G.p.c. chromatograms of the crude product; fractions 1 and 2 separated by column chromatography

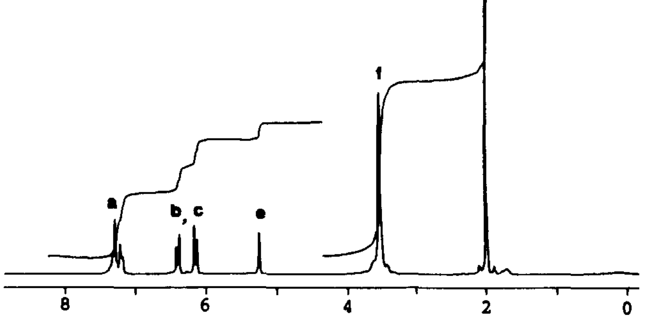

Figure 4 ^1H n.m.r. spectrum and peak assignments of model compound 1

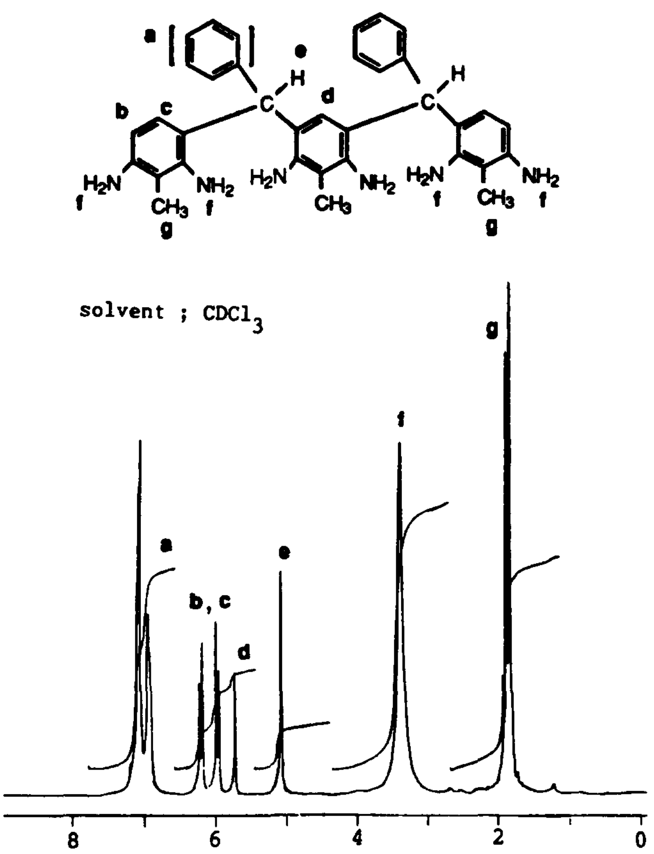

Figure 5 ¹H n.m.r. spectrum and peak assignments of model compound 2

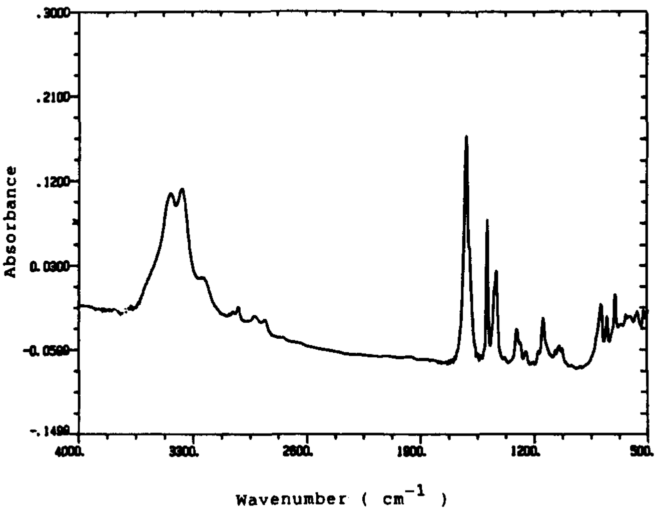

Figure 6 *FT*i.r. spectrum of model compound 1

g) have the chemical shifts in the region of 3.5–3.1 ppm and 2.0–1.9 ppm, respectively. There are two peaks for methyl in the case of model compound 2 which indicates that the inside methyl protons are more shielded than the outside methyl protons.

The *FT*i.r. spectrum of the model compound 1 (*Figure 6*) shows the existence of primary amines NH_3 (antisymmetric NH stretching 3435 cm^{-1}, and symmetric NH stretching 3369 cm^{-1}, NH_2 deformation 1622 cm^{-1}, CN stretching 1314, 1290, 1256 cm^{-1}), benzene rings (aromatic CH stretching 3058 cm^{-1}, aromatic C=C stretching 1599, 1492, 1450, 1438, 1151, 1077, 1033 cm^{-1}, CH out-of-plane bending 793, 757, 707 cm^{-1}) and methyl groups (antisymmetric CH_3 stretching 2925 cm^{-1}, symmetric CH_3 stretching 2862 cm^{-1}, CH_3 deformation 1450 cm^{-1} (overlapped with the C=C stretching)). The *FT*i.r. spectrum of model compound 2 (*Figure 7*) is almost the same as that of model compound 1 except that model compound 2 has the C=C stretching mode originating in a benzene ring with five substituents.

The two compounds have very similar u.v.–vis. absorption spectra (*Figures 8* and *9*) which show B

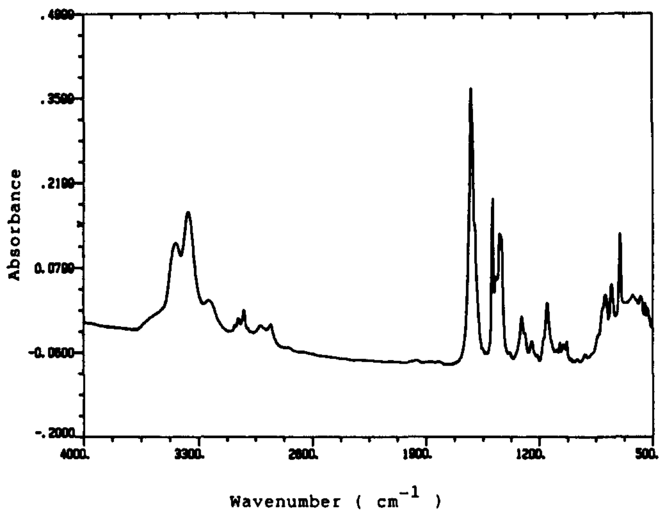

Figure 7 *FT*i.r. spectrum of model compound 2

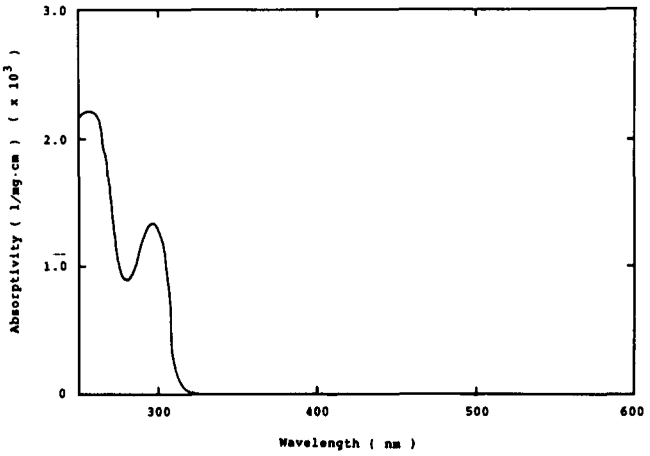

Figure 8 U.V.–vis. spectrum of model compound 1

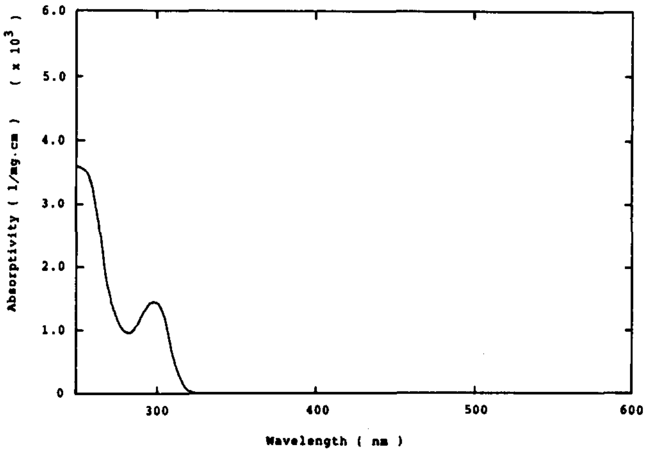

Figure 9 U.v.–vis.spectrum of model compound 2

Table 1 The elemental analysis for model compounds 1 and 2

	Carbon	Hydrogen	Nitrogen
Model compound 1 (experimental)	75.18	7.13	16.74
$C_{21}H_{24}N_40.2H_2O$ (theoretical)	75.09	7.27	16.69
Model compound 2 (experimental)	76.25	7.11	15.23
$C_{35}H_{38}N_60.49H_2O$ (theoretical)	76.26	7.08	15.25

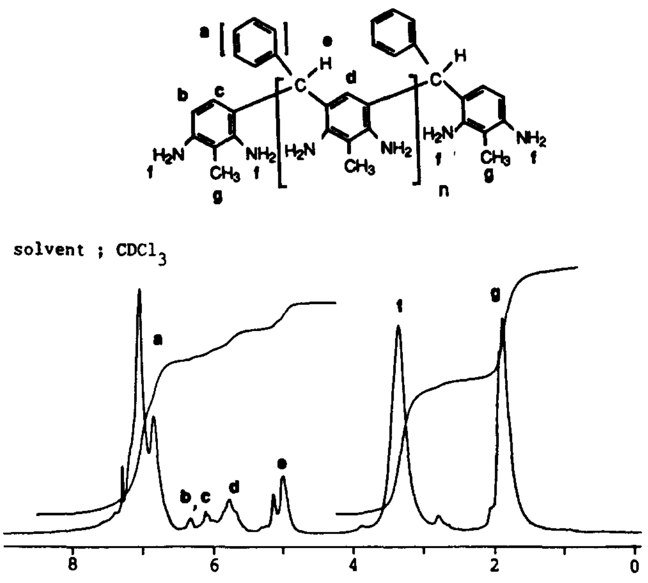

Figure 10 ^1H n.m.r. spectrum and peak assignments of the polymer

bands of π–π* transition at 256.4 nm (ε: 7.37 × 10^2 l mol^{-1} cm^{-1}), 297.2 nm (ε: 4.48 × 10^2 l mol^{-1} cm^{-1}) (model compound 1) and 298.5 nm (ε: 7.80 × 10^2 l mol^{-1} cm^{-1}) (model compound 2).

Finally, the elemental analysis data (*Table 1*) for each compound shows that the theoretical values of carbon, hydrogen and nitrogen content based on the presumed chemical structures are in good agreement with the experimental values.

The polymer

The ^1H n.m.r. spectrum of the polymer is given in *Figure 10*. This spectrum is similar to those of model compounds 1 and 2 except that each peak is broadened due to the polymerization and the two types of methine protons (peak e) exist. The downfield methine proton (5.1 ppm) has the same chemical shift as that of model compound 2 and is close to that of model compound 1 (*Figure 11*). Since the new methine proton of the polymer is located at higher magnetic field (4.9 ppm), it is presumed that the new methine proton is more electrically shielded by the steric hindrance of the polymer. Actually, model compounds 1 and 2 have less steric hindrance than the polymer. The repeating unit *n* was estimated to be 8.0 (calculated from the values of peaks: d/(b + c)) and 6.0 (calculated from the ratio of the two types of methine protons). The g.p.c. chromatogram (*Figure 12*) shows that molecular weight of the polymer is about 1400 (repeating unit $n \simeq 5$) at the peak maxima, which agrees with the end group analysis (main chain benzene, peaks b, c, d and methine proton peak e) within experimental error. The normalized integrated intensity of NH_2 groups is found to be less than 4H, which indicates that partial intramolecular condensation occurred during the polymerization.

This result is supported by the u.v.–vis. spectrum (*Figure 13*) which shows a small amount of the characteristic absorption peak of the acridine moiety at 403.1 nm (refs 13, 14).

The elemental analysis data (*Table 2*) also supports the occurrence of partial intramolecular condensation. The theoretical values of carbon, hydrogen and nitrogen were obtained assuming a repeating unit $n = 5$ and normalized integrated intensities of NH and –N= of 0.149 and 0.008, respectively. The residual amount of the experimental values was assumed to come from oxygen in the form of water.

The *FT*i.r. spectrum of the polymer (*Figure 14*) is similar to those of model compounds 1 and 2 except that

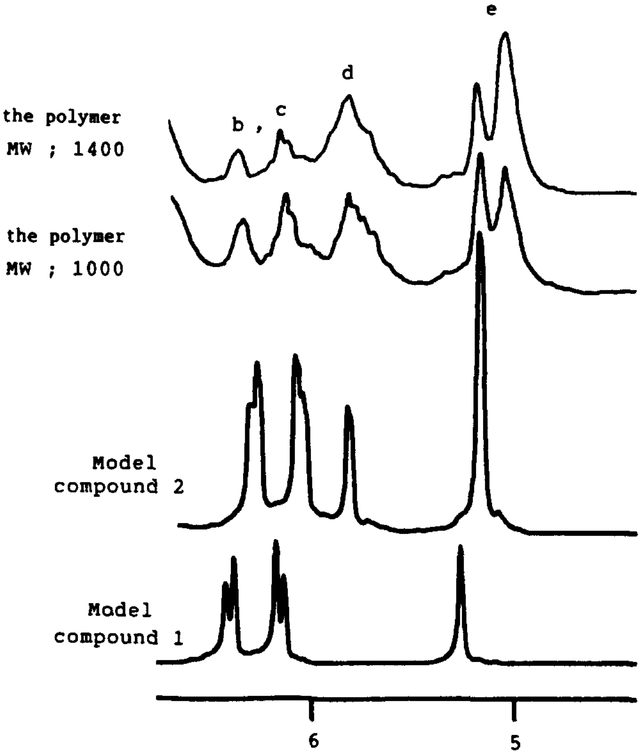

Figure 11 ^1H n.m.r. spectra of model compounds 1 and 2 and the polymers of different molecular weights

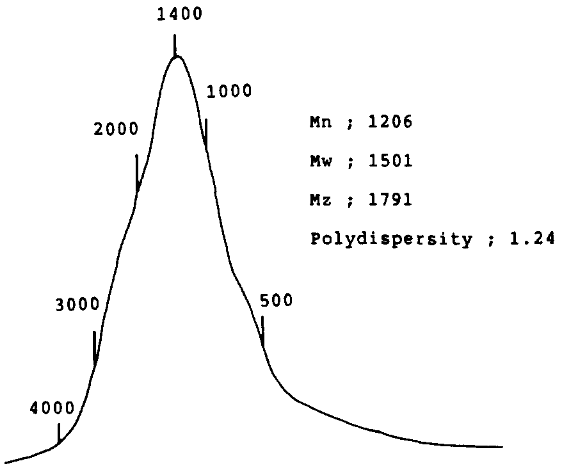

Figure 12 G.p.c. chromatogram of the polymer

Table 2 The elemental analysis for the polymer

	Carbon	Hydrogen	Nitrogen
Prepolymer 1 (experimental)	77.65	6.84	12.97
$C_{91}H_{90.54}N_{12.90}\cdot 2.23H_2O$ (theoretical)	77.81	6.77	12.87
NH; 0.149; -N=; 0.008[a]			

[a]NH and -N= are normalized integrated n.m.r. intensities of acridane (secondary amine) and acridine (tertiary amine)

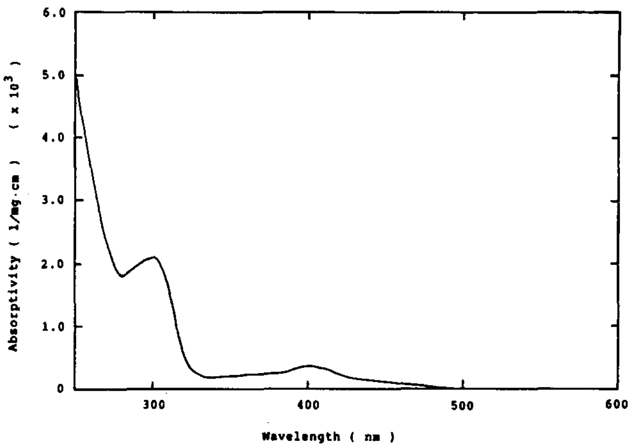

Figure 13 U.v.–vis. spectrum of the polymer

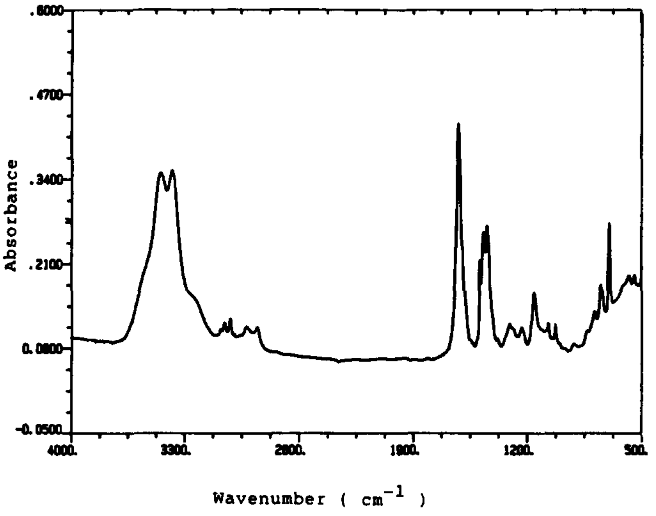

Figure 14 *FT*i.r. spectrum of the polymer

the peak at 1472 cm^{-1} increased. This peak was assigned to the aromatic C=C stretching mode of the internal main chain benzene with five substituents.

Reaction mechanism

The proposed reaction mechanism[15] is shown in *Figure 15*. Nucleophilic addition of the aromatic amine to the carbonyl group readily occurs in a polar solvent (Schiff base formation). In the presence of acid, it rearranges to the corresponding benzyl alcohol, which further reacts with another benzyl alcohol or a diaminotoluene to form the polymer. In order to verify this mechanism, water was used as a solvent instead of water/DMSO mixed solvent used for the synthesis of the polymer. A yellow sticky substance precipitated immediately following the addition of benzaldehyde and did not redissolve in water even after 2 h stirring. The ^1H n.m.r. spectrum of this substance (*Figure 16*) shows the existence of the Schiff base moiety (8.4, 8.0, 7.5 ppm) instead of the NH_2 group. *Figure 17* shows ^1H n.m.r. spectra of the polymer

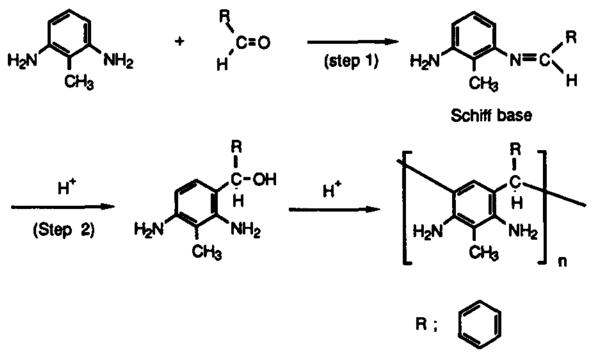

Figure 15 Proposed reaction mechanism of the polymer

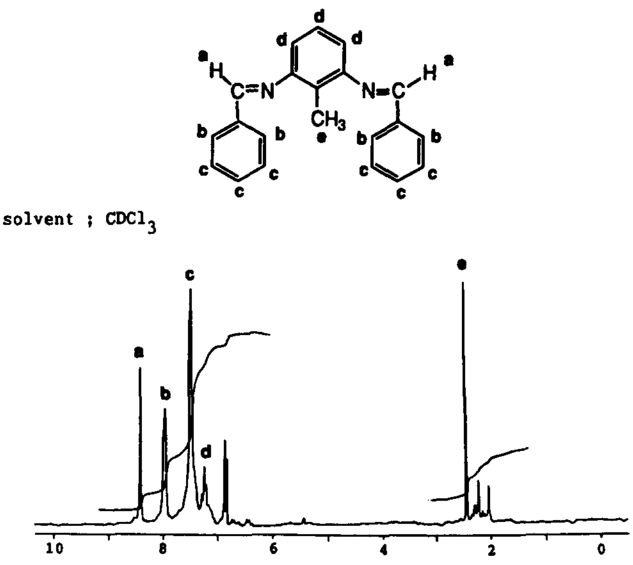

Figure 16 ^1H n.m.r. spectrum of the polymer synthesized in water

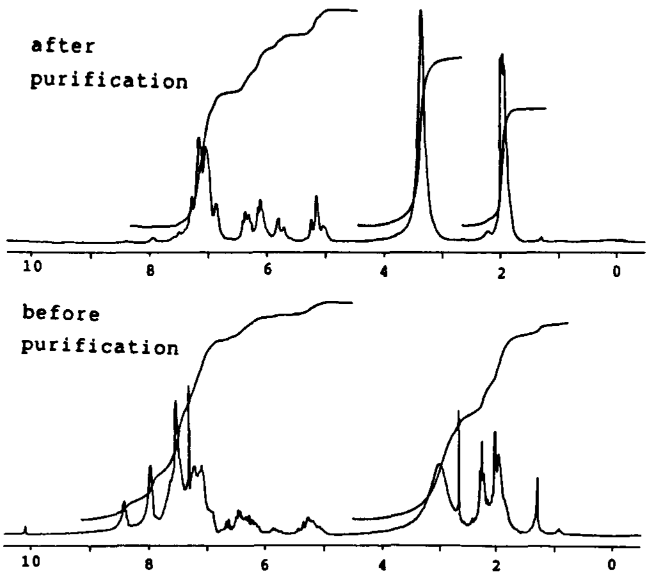

Figure 17 ^1H n.m.r. spectra of the polymer synthesized in a water/DMSO solvent before and after purification

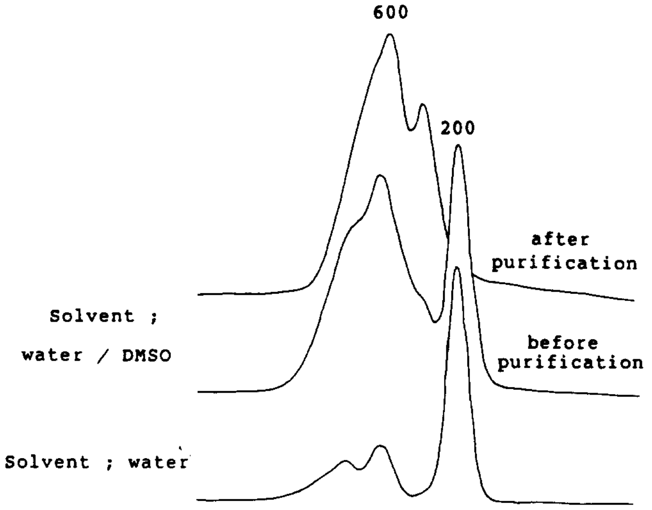

Figure 18 G.p.c. chromatograms of the polymers synthesized in water and in a water/DMSO solvent

synthesized in water/DMSO. There are three peaks which can be assigned to Schiff base moiety at 8.4, 8.0 and 7.5 ppm for the polymer before the purification by aqueous hydrochloric acid. These three peaks almost disappeared from the ^1H n.m.r. spectrum upon purification by aqueous hydrochloric acid. This result is also supported by g.p.c. chromatograms (*Figure 18*). It is well known that stoichiometry has a strong influence on the molecular weight of a polymer synthesized by step polymerization. High molecular weight polymers were not obtained due to the Schiff base formation during the reaction which destroyed the stoichiometry between the diamine and the aldehyde. Therefore, a rapid rearrangement of the Schiff base into the corresponding benzylalcohol is required in order to increase the molecular weight of the polymer. Considering this, DMSO was added to the solvent so that the Schiff base formed was not precipitated out or, if it was, the precipitate was easily redissolved in the mixed solvent which allowed the rearrangement into the corresponding benzyl alcohol to occur. The acidity of the solution is also important for this purpose, but it should be taken into account that too much acidity also reduces the reactivity of diamine compound since NH_3^+ is no longer a nucleophile.

CONCLUSION

A linear polymer can be obtained by reacting 2,6-diaminotoluene with benzaldehyde in water/DMSO mixed solvent in the presence of acid. The reason why only low molecular weight compound was obtained is that Schiff base formation destroyed the stoichiometry between the diamine and the aldehyde. The steric hindrance may also reduce the reactivity. The obtained polymer was soluble in DMSO, DMF, chloroform, THF, acetone and insoluble in benzene and *n*-hexane.

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