A comparison of the molecular weights of polyaniline samples obtained from gel permeation chromatography and solid state ^{15}N n.m.r. spectroscopy

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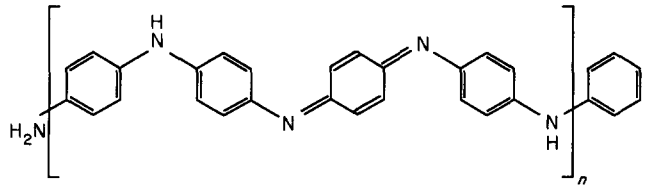
Polyaniline samples of different molecular weights were prepared using aniline enriched with ^{15}N. Molecular weights were determined by gel permeation chromatography (g.p.c.). ^{15}N n.m.r. spectroscopy confirmed that both samples were in the emeraldine oxidation state, and end group analysis techniques were used to compare molecular weights derived from g.p.c. with those from the n.m.r. data. In addition, the ^{15}N solid state n.m.r. spectra of emeraldine hydrochloride and a solvent-cast, oriented film of emeraldine base are presented.

(Keywords: molecular weight; polyaniline; gel permeation chromatography)

INTRODUCTION

Richter *et al.*[1] have previously reported the ^{15}N solid state and solution state n.m.r. spectra of polyaniline in the emeraldine and leucoemeraldine base forms, where secondary (2°) amine and imine but no primary (1°) amine groups were observable. If polyaniline is formed in the 'as-made' emeraldine oxidation state (shown below) as a result of head-to-tail polymerization of aniline at the 1,4-positions, then 1° amine groups should be present at one end of the polymer chain.



Emeraldine base

Similarly gel permeation chromatography (g.p.c.) data for polyaniline have been previously reported[2–4], the latter using monodisperse polystyrene as a molecular weight standard. In this paper, poly(vinyl pyridine) (PVP) was used as it is more soluble in *N*-methyl-2-pyrrolidone (NMP) than the polystyrene. A bimodal distribution is seen when NMP alone is used, but if NMP solvent containing 0.5 wt% LiCl is used, a single large peak is seen[4].

As 1° amine groups were observed in our ^{15}N n.m.r. spectra, end group analysis techniques were used to evaluate the ratio of 2° to 1° amine groups to give values for the molecular weight of polyaniline. These values were then compared to those obtained by g.p.c. analysis.

EXPERIMENTAL

Synthesis of ^{15}N enriched low molecular weight polyaniline

^{15}N enriched aniline (99% enrichment; 0.3106 g, 0.0033 mol) and standard aniline (0.6240 g, 0.0067 mol) were placed in a glass vial (25 ml) and stirred using a small magnetic flea. To this was added 1 M HCl solution (12.0 g, 0.0100 mol). Then 2.2819 g (0.0100 mol) of ammonium persulphate were made up to 6 ml with water and added in a controlled manner to the reaction solution. The reaction solution quickly turned dark blue, then green as the polyaniline was formed and precipitated from solution. After stirring for 1 h, the reaction mixture was filtered, the filter cake was then transferred to a clean glass vial and stirred with 35% ammonia solution (20 ml) for 7 h before refiltering and washing with water (2 × 50 ml) followed by isopropanol (50 ml). Finally, the product was dried for 18 h under vacuum at 50°C to give a purple powder.

Synthesis of ^{15}N enriched high molecular weight polyaniline

As above, except the reaction mixture was allowed to stir for 21 h before filtering, deprotonation, refiltering, washing and drying to give a purple powder. (A constant yield[5] of polyaniline is obtained after 2–3 h.)

Synthesis of ^{15}N enriched polyaniline hydrochloride

Half of the low molecular weight polyaniline was stirred in 1 M HCl solution (20 ml) for 24 h before

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filtering, washing with water (2 × 50 ml) followed by isopropanol (50 ml), and drying for 18 h under vacuum at 50°C.

Solvent-cast oriented ^{15}N enriched polyaniline film

High molecular weight polyaniline (0.2 g) was added to NMP (1.8 g) and dissolved/dispersed with stirring and gentle warming. The solution was poured onto a glass slide to give a coating weight of 0.03 g cm^{-2}. The solvent was removed under vacuum at 80°C until the film was just dry. The film was then peeled from the glass slide and cut into strips (2.5 × 4.0 cm). These were oriented in a stretch rig by heating from room temperature to 60°C to give 100% elongation under a tension of 5 N (ref. 6).

Materials

[4-(Phenylamino)phenyl]-1,4-phenylenediamine, used as a molecular weight standard, was synthesized using the method of Honzl and Tlustakova[7]. *N,N'*-diphenyl-*p*-phenylenediamine, also used as a molecular weight standard, was purchased from Aldrich Chemicals, as were all the other chemicals except the ^{15}N enriched aniline, which was purchased from MSD Isotopes. The PVP molecular weight standards were purchased from Polymer Laboratories Ltd, who also supplied the g.p.c. columns.

Sample preparation for g.p.c.

The polyaniline samples (0.0020 g of each) were dissolved in NMP (4.000 g, containing 0.5 wt% LiCl) to give 0.050 wt% solutions. These were passed through a 0.5 μm filter prior to injection. The u.v. detector was set at 325 nm for these samples. The oligomeric polyaniline standards were made up to 0.005 wt% solutions and detected at 282 nm. The g.p.c. column measured 300 × 7.5 mm and consisted of 5 μm crosslinked polystyrene beads of mixed porosity. This was used with a guard column. H.p.l.c. grade NMP (also containing 0.5 wt% LiCl) was used as the carrier solvent at a flow rate of 0.5 ml min^{-1} and a column pressure of 10 MPa. The g.p.c. system consisted of a Pye Unicam 4011 pump, 4030 controller, 4020 u.v. detector and a 4810 integrator. The sample injection coil size was 20 μl.

N.m.r. spectroscopy

N.m.r. spectra were obtained from a Varian VXR 300 solid state spectrometer using cross-polarization and magic angle spinning. The two emeraldine base samples were run at a spin rate of 4420 Hz, accumulating 2000 transients with a recycle delay of 0.5 s, and cross-polarization contact times of 0.5, 1.0 and 2.0 ms. The oriented film was run at a spin rate of 2760 Hz, accumulating 2000 transients with a recycle delay of 0.5 s, and a cross-polarization contact time of 1.0 ms.

The polyaniline hydrochloride sample was packed with 50% talc to reduce radio frequency reflectance. This was spun at 2760 Hz, accumulating 23 200 transients with a recycle delay of 0.1 s and a cross-polarization contact time of 1.0 ms.

All the samples used enriched NH_4NO_3 as the nitrogen reference.

RESULTS AND DISCUSSION

The chemical shifts for ^{15}N enriched polyaniline have been previously determined by Richter *et al.*[1], but no end groups were detected. The spectra of the four polyaniline samples with a cross-polarization contact time of 1 ms are shown in *Figures 1–4*. The results are shown in *Table 1*.

Neither of the base forms of polyaniline show any discernible splitting of the imine or 2° amine peaks,

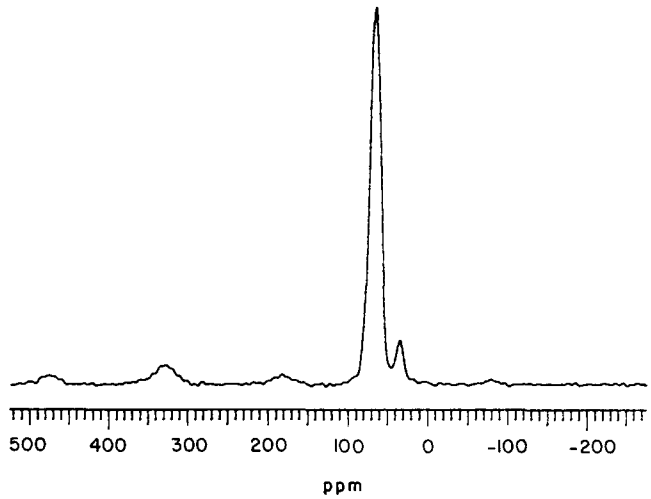

Figure 1 ^{15}N n.m.r. spectrum of low molecular weight deprotonated polyaniline

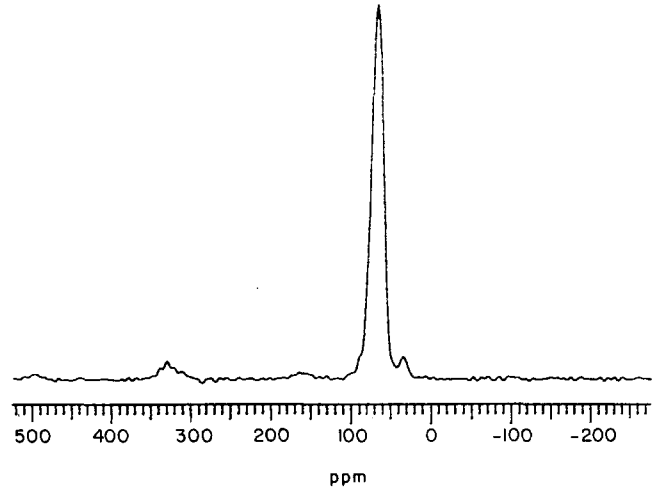

Figure 2 ^{15}N n.m.r. spectrum of high molecular weight deprotonated polyaniline

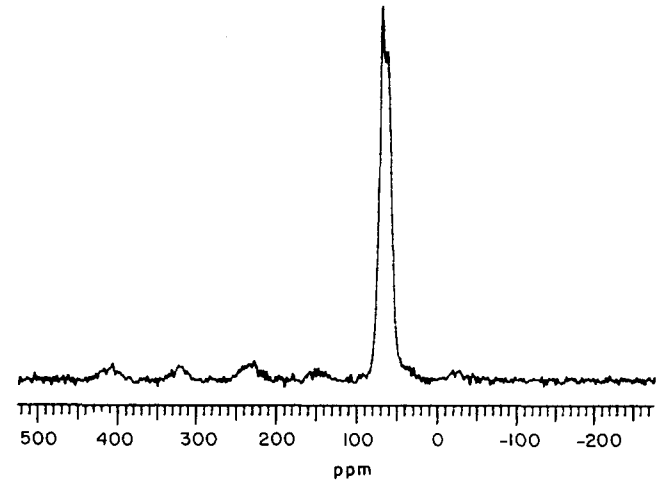

Figure 3 ^{15}N n.m.r. spectrum of solvent-cast polyaniline film

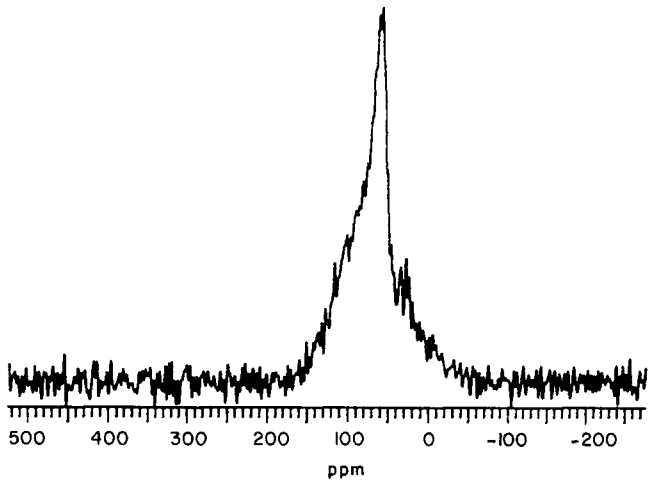

Figure 4 ^{15}N n.m.r. spectrum of polyaniline hydrochloride

Table 1 Chemical shifts of different nitrogen environments in ^{15}N solid state n.m.r. of polyaniline samples

Polyaniline samples (1.0 ms cross-polarization contact time)	Chemical shifts (ppm)		
	Imine N	2° amine N	1° amine N
Low molecular weight emeraldine base	325.8	65.3	33.9
High molecular weight emeraldine base	326.9	66.4	35.9
Solvent-cast, oriented polyaniline film	323.1	68.8, 63.9	–
Polyaniline hydrochloride	102.4	60.9	27.4

indicating that the polyaniline is in the emeraldine oxidation state[1] although these peaks are too broad to show any fine structure. In addition, 1° amine groups are detectable, presumably on the ends of the polyaniline chains. The small peaks on either side of the imine peak are spinning side bands.

When the emeraldine base is dissolved in NMP, cast as a film and oriented, a split occurs in the 2° amine peak of ~5.9 ppm. This is in good agreement with the 5.8 ppm split noted by Richter *et al.*[1] for the solution state spectrum of 'underoxidized emeraldine base'. Here they used a 3:1 mixture of NMP and dimethylsulphoxide as a solvent. It is not known whether the split in this case is due to some effect of the solvent or is a result of orientation of the polymer film.

Protonation of the emeraldine base occurs mainly on the imine nitrogen as the peak at 326 ppm is shifted to 102 ppm, appearing as a shoulder on the 2° amine peak. Both the 2° and 1° amine peaks are also shifted to a slightly lower frequency which is consistent with a decrease in the electron density surrounding all nitrogen atoms upon protonation.

The ratio of 2° to 1° amine groups may be calculated by evaluating the relative peak areas at different contact times. The peak area ratio between 2° and 1° amine groups should be constant for different contact times, but the imine nitrogen will differ as it has no hydrogen atoms attached, so cross-polarization will not be as effective. The ratios are shown in *Table 2*.

The average ratio of 2° to 1° amine groups for the low molecular weight emeraldine base is 14:1. The average ratio for the high molecular weight emeraldine base is 31.3:1. Assuming the polymer chains have one $-NH_2$ end group, a repeat unit value of 28 for the low molecular weight and 63 for the high molecular weight form of emeraldine base is indicated. Because the ratios are similar at different contact times, the intensity of cross-polarization at the two amine groups is equivalent.

The g.p.c. results for the low and high molecular weight emeraldine base samples in NMP/LiCl are shown in *Figures 5* and *6*. The plot of log (molecular weight) *versus* retention volume for the standards shown in *Figure 7* gives a straight line fit of the form:

$$y = -0.996344x + 11.1763$$

where the y value corresponds to log (molecular weight) and the x value corresponds to the retention volume. The results are summarized in *Table 3*.

For an average number of repeat units, g.p.c. gives higher values than n.m.r.; 151 compared to 28 for the

Table 2 Ratio of peak areas for different nitrogen environments in the emeraldine form of polyaniline

	Cross-polarization contact time (ms)	Ratio of peak areas		
		Imine	2° amine	1° amine
Low molecular weight emeraldine base	0.5	1.4	14	1
	1.0	1.9	12	1
	2.0	5.0	16	1
High molecular weight emeraldine base	0.5	3.1	30	1
	1.0	5.6	33	1
	2.0	12.4	31	1

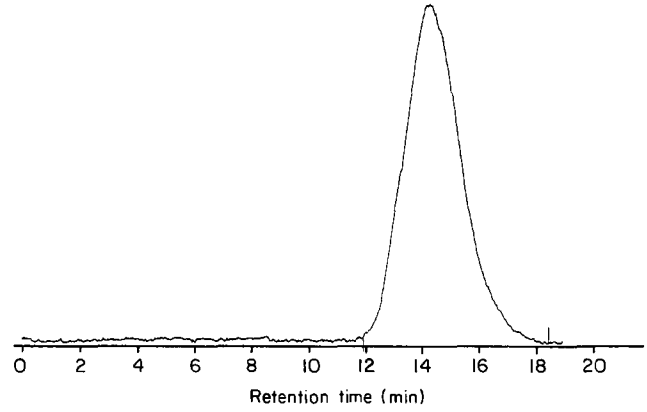

Figure 5 G.p.c. retention times for low molecular weight polyaniline in NMP/LiCl solvent

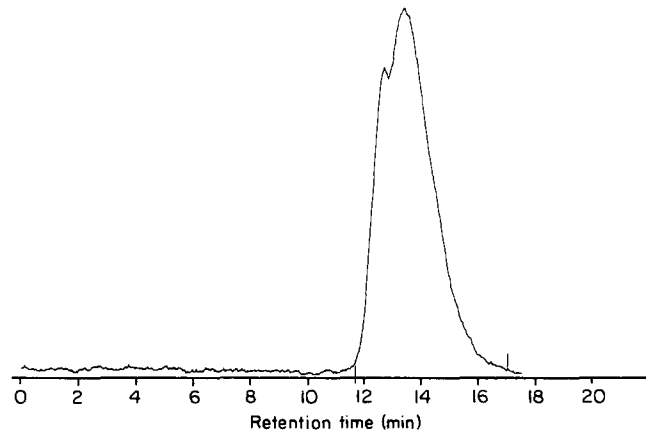

Figure 6 G.p.c. retention times for high molecular weight polyaniline in NMP/LiCl solvent

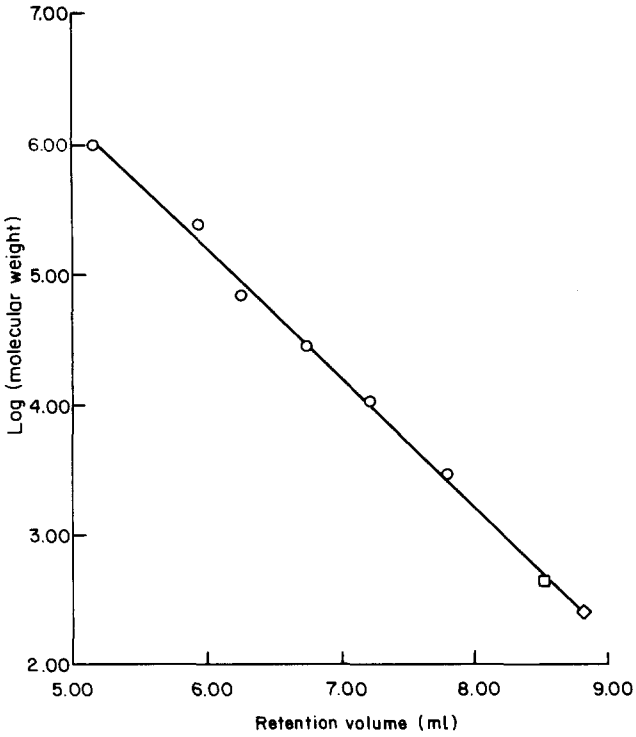

Figure 7 Plot of log (molecular weight) *versus* retention volume for PVP standards used in g.p.c. analysis: (○) PVP standards; (□) [4-(phenylamino)phenyl]-1,4-benzenediamine; (◇) *N,N'*-diphenyl-*p*-phenylenediamine. Column, PL gel 5 μm mixed + guard column; flow rate, 0.5 ml min^{-1}; pressure, 10 MPa; solvent, NMP/LiCl

Table 3 Molecular weight data from g.p.c. analysis of polyaniline in NMP/LiCl solvent

	Retention volume (ml)	Molecular weight	Average number of repeat units
Low molecular weight polyaniline	7.065	13 710	151
High molecular weight polyaniline	6.705	31 320	346

low molecular weight and 346 compared to 63 for the high molecular weight polymer. This could indicate that there are $-NH_2$ groups on polyaniline which are not just on one end of the polymer. The n.m.r. spectra pick these out, but g.p.c. does not. One possible structure which would give these non-terminal $-NH_2$ groups occurs via polymerization through the 2- and 4-positions of aniline. However, solution state ^{13}C n.m.r. spectra of leuco-emeraldine base[8] show that there are no trisubstituted benzenoid rings in polyaniline, and the polymer consists of at least 95% 1,4-phenylene units linked in a regular head-to-tail manner through nitrogen groups. One other possibility is a trisubstituted nitrogen atom where two or three oligomeric polyaniline chains with 1° amine end groups meet, but these would be difficult to detect in ^{15}N n.m.r., and the appropriate carbon atoms would be difficult to pick out in ^{13}C n.m.r.

The ratio of the number of repeat units of the two types of polymers as determined by solid state n.m.r. and g.p.c. is very similar (2.25:1 as determined by n.m.r. and 2.29:1 as determined by g.p.c.). As the ratios are similar but the numbers of repeat units are different, this may indicate either that the g.p.c. results are artificially high, or that the n.m.r. results are artificially low.

It is more probable that the g.p.c. results are artificially high for two reasons:

1. The polyaniline chains clump together in solution. G.p.c. runs performed without LiCl show two or more peaks, with the smaller, initial peaks having molecular weights of up to several million. LiCl aids chain disentanglement, but there is no guarantee that the polymer chains are completely separated in solution, resulting in artificially high molecular weight values. As a comparison, molecular weights obtained on the same samples dissolved in NMP which did not contain LiCl gave the results shown in *Figures 8* and *9*, and which are summarized in *Table 4*. The plot of log (molecular weight) *versus* retention volume for the standards fits a straight line of the form:

$$y = -0.711184x + 9.87474$$

where the y value corresponds to log (molecular weight) and the x value corresponds to the retention volume. The high molecular weight peaks are due to polyaniline chains clumping together.
2. PVP is not the ideal molecular weight standard, but was chosen as it is more soluble in NMP than polystyrene. It is likely to be a more flexible molecule than polyaniline due to rotations around the C–C bonds of both the backbone and of those bonds to the pendant pyridine groups, whereas the emeraldine

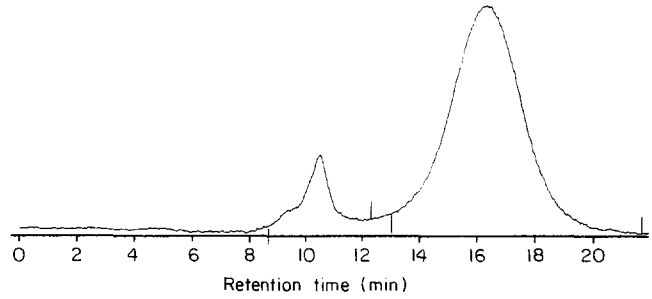

Figure 8 G.p.c. retention times for low molecular weight polyaniline in NMP solvent which does not contain LiCl

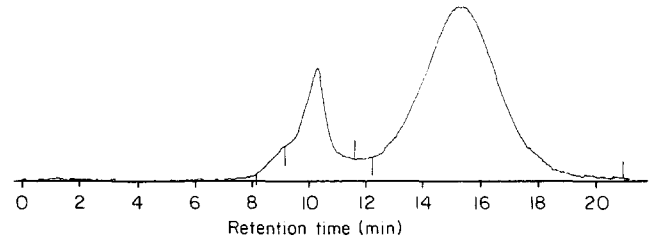

Figure 9 G.p.c. retention times for high molecular weight polyaniline in NMP solvent which does not contain LiCl

Table 4 Molecular weight data from g.p.c. analysis of polyaniline in NMP solvent not containing LiCl

	Retention volume (ml)	Molecular weight	Number of repeat units	Total area (%)
Low molecular weight polyaniline	5.170	1 577 000	17 410	10.04
	8.195	11 130	123	89.96
High molecular weight polyaniline	4.785	2 963 000	32 700	3.56
	5.185	1 539 000	16 990	15.30
	7.745	23 260	257	81.14

base form of polyaniline will be more rigid due to the semiconjugated polymer backbone and the p-orbital overlap of the nitrogen lone pair electrons with the π orbitals in the phenylene rings. As g.p.c. is a size exclusion process, a more rigid, compact molecule will elute more quickly than a flexible, bulky one of comparable molecular weight[9], so the polyaniline has an artificially high molecular weight compared to the PVP standards.

CONCLUSIONS

Oxidatively polymerized polyaniline has been shown to contain 1° amine groups. These are assumed to be on just one end of the polymer chains if the polymerization reaction occurs to give strictly *p*-linked phenyleneamine-imine units. Comparison of the molecular weights obtained from solid state ^{15}N n.m.r. and g.p.c. data give comparable values for the ratio of the number of repeat units for the high and low molecular weight polymers, but it is thought that the g.p.c. results may be artificially high by a factor of 5 or 6 due either to incomplete polyaniline chain disentanglement, or the polyaniline being a stiffer molecule than the PVP used as a molecular weight standard.

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