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Low temperature synthesis of high molecular weight polyaniline

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Oxidative chemical polymerization of aniline in hydrochloric acid solution at sub-zero temperatures leads to polyaniline with a molecular weight five to ten times higher than that prepared at room temperature. The optimum polymerization temperature to give a polymer with the highest yield and molecular weight has been determined, and solution state ^{13}C n.m.r. spectroscopy shows that the improved polyaniline has fewer defect sites compared to the standard polymer. Despite these intrinsic improvements, the conductivity is of the same order of magnitude as standard polyaniline. A solvent-cast film of polyaniline camphorsulfonate had a conductivity of 295 S cm^{-1}, although this rose to 820 S cm^{-1} along the stretch direction after the film had been uniaxially oriented. An oriented film cast from *N*-methyl-2-pyrrolidone solution and protonated with methanesulfonic acid showed a conductivity of 260 S cm^{-1} along the stretch direction and 31 S cm^{-1} perpendicular to this. Copyright © 1996 Elsevier Science Ltd.

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INTRODUCTION

Polyaniline (*Figure 1*) has been well documented as a conductive polymer[1–3], but recent work has shown that the polymer prepared at room temperature is of fairly low molecular weight[4] and contains defect sites[5]. It is hoped that a better quality polyaniline, with fewer defect sites and of a higher molecular weight, may lead to improvements in its mechanical and electrical properties.

Importantly, polyaniline can be made processible in its conductive 'salt' state by using a functional acid such as camphorsulfonic or dodecylbenzenesulfonic acid dissolved in suitable solvents such as *m*-cresol or xylene[6]. The emeraldine base form is also soluble in solvents such as *N*-methyl-2-pyrrolidone[7,8]. Subsequent uniaxial orientation (and protonation) of these solvent cast films leads to higher conductivities along the stretch direction.

Although there is still some uncertainty regarding the exact mechanism of aniline polymerization, it is likely that radical cation species are produced as a result of oxidative attack on the aniline monomers. These then condense with the loss of protons to give the protonated, semi-oxidized emeraldine form of polyaniline as the reaction product[9]. Using aniline hydrochloride and ammonium persulfate as starting reagents the reaction stoichiometry should be:

$$4C_6H_7N.HCl + 5(NH_4)_2S_2O_8 \rightarrow 2HCl + 5(NH_4)_2SO_4 + 5H_2SO_4 + 2(C_{12}H_9N_2.HCl)_x$$

The product is a polysemiquinone radical cation, where x is the number of protonated emeraldine repeat units[1].

If aniline polymerization does indeed follow the proposed theory, it is a difficult reaction to classify as it shows characteristics of both cationic chain polymerization and condensation polymerization reactions[10]. Cationic chain polymerizations are usually carried out at low polymerization temperatures, which favour propagation over competing side reactions, and use solvents with a high dielectric constant, which favours both initiation and propagation leading to high molecular weight polymers. One of the characteristics of condensation polymerization is that the molecular weight of the polymer rises steadily throughout the reaction, and therefore long reaction times are essential to obtain high molecular weights.

Although several previous studies have been made regarding the optimum reaction conditions for the polymerization of aniline[11–13], none of these studied the reaction at low temperatures. There are very few solvents with a higher dielectric constant than water, and most of those which do exist will react with the oxidant used in this polymerization. Although the dielectric constant of water increases as the temperature is lowered, a salt or co-solvent must be present if the temperature is to be lower than 0°C. For very low temperatures, the best salt to use is lithium chloride, due to its low molecular mass and high depression of the freezing point of water. Further, salt addition will also increase the dielectric constant of the medium, whereas using a co-solvent such as methanol may decrease it, so an aqueous solution of lithium

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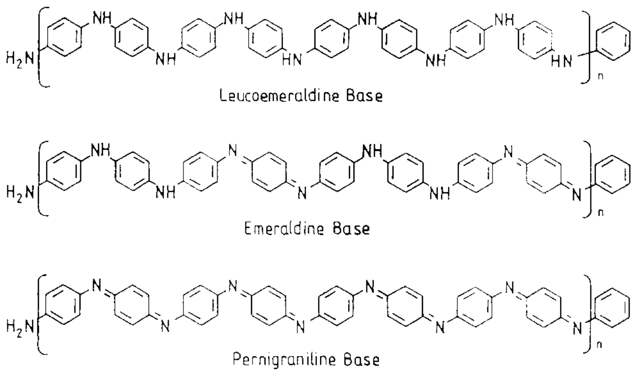

Figure 1 Emeraldine base form of polyaniline, together with the fully oxidized and reduced forms

chloride would appear to be the best reaction medium for aniline polmerization at sub-zero temperatures.

A publication on the effects of starting pH, amount and rate of oxidant addition, and reaction time on molecular weight[14] has been written, which may be considered as a continuation of this paper.

EXPERIMENTAL

Preparation of low molecular weight polyaniline at room temperature

AnalaR aniline (9.313 g, 0.100 mol) was added to AnalaR HCl solution (100 g, 1.0 M) and the pH adjusted to +1.0 by the further addition of a few drops of HCl. AnalaR $(NH_4)_2S_2O_8$ (28.52 g, 0.125 mol) was dissolved in distilled water (51.5 g) and added in one go to the reaction solution which was being stirred at room temperature (~18°C). After 30 min the reaction product was recovered by filtration, washed with distilled water (10 × 200 ml), deprotonated by stirring for 24 h in aqueous ammonia solution (100 ml, 33% w/v), refiltered and washed with water (8 × 200 ml) then with isopropyl alcohol (2 × 200 ml), then dried under vacuum at 60°C for 24 h to give 8.46 g of a purple powder.

Preparation of high molecular weight polyaniline at sub-zero temperatures

This is essentially the same reaction as described in (i), except reaction temperatures between 0 and −35°C were used together with lithium chloride added in sufficient amounts to just prevent the reaction mixture from freezing[15]. A typical reaction at −27.5°C is described below, with the reaction conditions and results summarized in *Table 1*.

The reactions were all carried out in a 1-litre jacketed reaction vessel in the shape of a pot-flask, with a removable flange lid and fitted with an anchor stirrer paddle. This was connected to a Haake F3K circulating chiller unit, which pumped a chilled water/methanol mixture at −27.5°C around the jacketed reaction vessel.

AnalaR aniline (9.313 g, 0.100 mol) was added to AnalaR HCl solution (100 g, 1.0 M). LiCl (23.03 g, 0.542 mol) was added to this solution and stirred until it dissolved. The pH of the reaction mixture was then adjusted to +1.0 by the addition of a few drops of AnalaR HCl (1.0 M). The reaction mixture was left to stir while cooling down to −27.5°C.

AnalaR $(NH_4)_2S_2O_8$ (28.52 g, 0.125 mol) was dissolved in distilled water (51.5 g) and added dropwise, with stirring, to the chilled reaction mixture. This was achieved by using a small peristaltic pump running at approximately 5 ml h^{-1}, so that the total oxidant addition time was $14\frac{1}{4}$ h. The reaction mixture was left to stir for a total of 46 h before filtering, washing, deprotonating, refiltering and washing, then drying overnight under vacuum at 60°C, as described for room temperature (i). Brown powder (9.11 g) was obtained.

Preparation of the sample for solution state ^{13}C n.m.r. spectroscopy

This was as described in an earlier paper[5]. The sample prepared at −30°C was reduced to the leucoemeraldine base form by first dissolving emeraldine (1.0 g) in h.p.l.c.

Table 1 Summary of the salt concentrations, chlorine content and yields for polyaniline samples prepared at various reaction temperatures

Reaction temperature (°C)	Amount of LiCl present (g)	Wt% LiCl	Weight of emeraldine base obtained (g)	Wt% chlorine in polymer	Measured % yield
+18	0	0	8.46	0.42	93.0 $^{+0.9}_{-1.9}$
0	0	0	8.12	0.23	89.4 $^{+0.9}_{-1.8}$
−10.0	10.35	8.65	8.35	0.41	91.8 $^{+0.9}_{-1.8}$
−15.0	13.91	11.29	8.42	0.54	92.4 $^{+0.9}_{-1.8}$
−20.0	17.12	13.54	8.54	0.88	93.4 $^{+0.9}_{-1.9}$
−22.5	18.83	14.69	8.50	1.19	92.7 $^{+0.9}_{-1.9}$
−25.0	20.76	15.96	8.84	0.91	96.7 $^{+1.0}_{-1.9}$
−27.5	23.03	17.40	9.11	1.38	99.2 $^{+1.0}_{-2.0}$
−30.0	25.79	19.09	8.60	1.38	93.6 $^{+0.9}_{-1.9}$
−35.0	33.53	23.47	8.15	2.33	87.9 $^{+0.9}_{-1.8}$

grade *N*-methyl-2-pyrrolidone (NMP, 20.0 g) and adding phenylhydrazine (1.25 g). Stirring with a spatula caused the solution colour to change from dark blue to brown. This sample was then transferred to a nitrogen-atmosphere glove-box. Anhydrous toluene (500 g) was placed in a 1-litre beaker and stirred with an Ultra Turrax T25 homogeniser. The leucoemeraldine solution was slowly added to this with vigorous stirring (20 000 rpm). The resulting suspension was filtered, washed with further toluene (4 × 125 g) and then left to dry on a Buchner funnel before transferring to a vacuum desiccator where it was left under dynamic vacuum for 24 h to give a white solid.

A 1 : 1 by weight mixture of h.p.l.c. grade NMP (2.0 g) and perdeuterated dimethylsulfoxide (d$_6$-DMSO, 2.0 g) was transferred to the glove box and leucoemeraldine base (0.2 g) dissolved in this by stirring with a spatula. The solution was placed in a 10 mm diameter n.m.r. tube which was capped and sealed with 'parafilm'. The ^{13}C spectrum of the sample was obtained on a Bruker AMX-500 spectrometer at an operating frequency of 125.77 MHz and a nominal probe temperature of 303 K. All chemical shifts are quoted relative to tetramethylsilane (TMS), although referencing was done via the d$_6$-DMSO peak, which was taken to be at +39.5 ppm.

Preparation of samples for gel permeation chromatography

This was as described in an earlier paper[4], with some exceptions. The polyaniline samples (0.0020 g of each) were dissolved in h.p.l.c. grade NMP (4.000 g, containing 0.10 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 polyvinylpyridine molecular weight standards were also made up in h.p.l.c. grade NMP (0.50 wt%, 0.1 wt% LiCl) and detected at 285 nm. The gel permeation chromatography (g.p.c.) column (300 × 7.5 mm), consisting of 5 μm crosslinked polystyrene beads, was obtained from Polymer Labs together with the molecular weight standards. A column oven set for 80°C was used which enabled flow rates to be increased to 1 ml min^{-1} at a pressure of 5 MPa. The carrier solvent was h.p.l.c. grade NMP containing LiCl (0.1 wt%) which had been degassed by dynamic vacuum while immersed in an ultrasonic bath. Degassing reduces the noise in the g.p.c. chromatograms. The g.p.c. system consisted of a Pye Unicam 4001 pump, 4030 controller, 4020 u.v. detector and a 4810 integrator. The sample injection coil size was 20 μl.

Preparation of oriented films for conductivity measurements

Emeraldine base (0.50 g) prepared at −27.5°C was dissolved/dispersed in NMP (9.50 g) and homogenized for 5–10 min at 20 000 rpm, then centrifuged at 4000 rpm for 1 h to remove any lumps. The solution was then coated onto a glass microscope slide at a coating weight of about 0.05 g cm^{-2} and the excess solvent removed by heating at 60°C under vacuum. Once the film is dry, it was possible to peel it away from the substrate and orient it by heating at 70–80°C under tension in a specially designed stretching rig, based on a system used to align precursor polyacetylene films[16,17]. The oriented film was then left to soak for 4 h in a suitable acid solution such as CH$_3$SO$_3$H (15 wt% in H$_2$O) and the conductivity measured using a four-probe technique[18,19].

Solvent cast, protonated films of polyaniline camphorsulfonate were also prepared in a similar manner. *Meta*-cresol was first dried with magnesium sulfate then decanted and filtered. Camphorsulfonic acid (0.116 g, 5×10^{-4} mol) was dissolved in *m*-cresol (10 g). Emeraldine base (0.091 g) was dissolved in the *m*-cresol then homogenized and centrifuged as above. The green solution was then poured onto a glass microscope slide and the solvent removed under vacuum as before. Subsequent films used 1.5% by weight solutions and these were cast onto silicon wafers for ease of removal from the substrate. Films were then cut into strips approximately 10 × 1.5 cm in area and oriented by holding under a hot air gun and pulling. Conductivities for these films were measured using four parallel platinum wires, which were found to be less problematic than the Montgomery 4-probe technique[19].

RESULTS AND DISCUSSION

Elemental analyses have shown that in these polyaniline samples both chlorine and sulfur are present as contaminants[5], and are assumed to be ring substituents of either chlorine or sulfonate groups. *Table 1* shows that the chlorine content increases with increasing LiCl content. Sulfur was not determined here, as a scaled-up reaction carried out at −27.5°C gave a sulfur content of <0.15 wt% and a sample prepared at room temperature contained 0.38 wt%[5], so sulfur is a minority contaminant and the amounts present are close to the limits of detection. A percentage yield may be calculated if the chlorine is taken into consideration. These are still subject to an estimated −2 wt% error due to sulfur (and oxygen) contaminants, but the weight of reaction product obtained is reproducible to ±1% in identical reactions. The results show that the yields are close to 100% and that there is some variation in the yield with the reaction temperature. A graph of percent yield *versus* reaction temperature is shown in *Figure 2*.

The g.p.c. results are complex. All the measurements quoted here were made over one 8-h period to try and

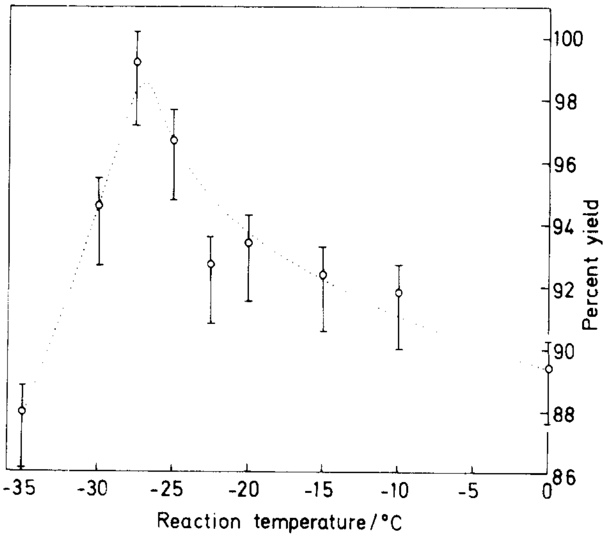

Figure 2 Graph of the percent yield *versus* the reaction temperature for high molecular weight polyaniline

minimize any variations that might occur. The standards were measured first, followed by the 10 samples, including the low molecular weight material as a comparison. This was followed by the standards, then the samples once more, and finally the standards for a third time. For each of the three standards runs, a graph of log(molecular weight), M_p, *versus* peak retention time may be plotted and a straight line plot used to obtain an equation for the line, where y = log(molecular weight) and x = retention time. The average of the three values for each standard may also be taken and a similar equation obtained (*Table 2*). The retention times are shown in *Table 3*. All the results for each standard were found to be within 0.08 min of each other except the value of the highest molecular weight standard on the third run, which was 0.26 min greater than the first run. This point was ignored for deriving the equation for the third run.

The molecular weights of the samples were calculated by taking the average of the two retention times and using the equation for the average molecular weight of the standards. An estimate of the errors for these points was made by taking the longer of the two retention times and calculating the molecular weight using the third of the equations in *Table 2*, followed by the shorter of the two retention times and calculating the molecular weight using the second of the equations. All the retention times are within 0.07 min for each sample, and all but one are within 0.03 min. However, the sample range is from 8.07 to 8.39 min, so 0.03 min represents 10% error in the experimental results. These are shown in *Table 4*.

A graph of the molecular weight *versus* the reaction temperature may be plotted for the reactions below 0°C (*Figure 3*). This shows that a temperature of −26 ± 3°C leads to the highest molecular weight polymer. This is in good agreement with the graph in *Figure 2*, showing that the maximum weight of polymer obtained occurs at around −27 ± 1°C.

The chromatogram for the sample prepared at −27.5°C is shown in *Figure 4*. The weight-average and number-average molecular weights, M_w and M_n, were calculated from the results by the usual method of dividing the space under the chromatogram into equal segments, measuring the heights from the baseline to the

Table 2 Equations used for deriving the molecular weights of the polyaniline samples

Run	Equation	Molecular weight value
1st	$y = 12.046 - 0.85338x$	intermediate
2nd	$y = 12.320 - 0.88163x$	maximum
3rd	$y = 12.117 - 0.86221x$	minimum
average	$y = 12.239 - 0.87420x$	average

Table 3 Summary of the g.p.c. retention times for the three runs of the polyvinylpyridine molecular weight standards

Molecular weight, M_p (daltons)	Log M_p	Retention times (min) rt 1	rt 2	rt 3	Average rt
1000000	6.000	7.17	7.24	7.43[a]	7.21
240000	5.380	7.77	7.85	7.81	7.81
70000	4.845	8.39	8.42	8.45	8.42
28000	4.447	8.80	8.84	8.84	8.83
10500	4.021	9.51	9.51	9.48	9.50
2900	3.462	10.06	10.05	9.99	10.03

[a] Value much higher than rt 1 and rt 2 so ignored in calculations

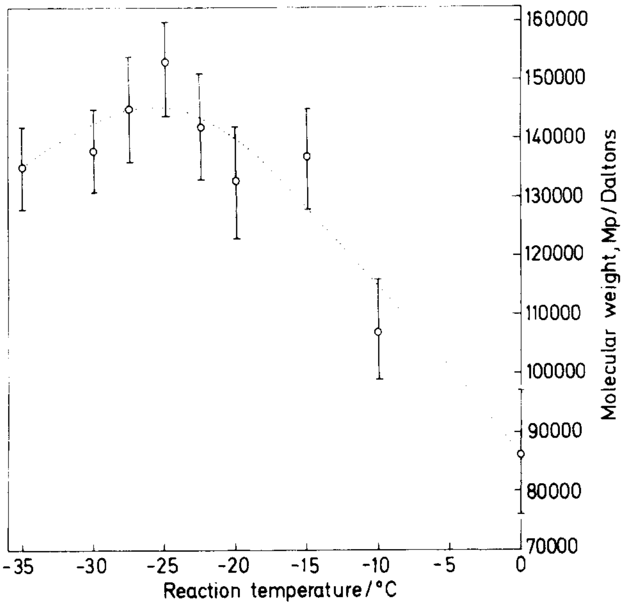

Figure 3 Graph of molecular weight *versus* the reaction temperature for high molecular weight polyaniline

Table 4 Summary of the molecular weights of the polyaniline samples prepared at various reaction temperatures

Preparation temperature (°C)	Retention times (min) 1st Run	2nd Run	Average	Molecular weights (daltons) Maximum	Minimum	Average
−35.0	8.13	8.13	8.13	142000	128000	135000
−30.0	8.12	8.12	8.12	145000	131000	138000
−27.5	8.09	8.10	8.10	154000	136000	145000
−25.0	8.07	8.07	8.07	160000	144000	153000
−22.5	8.11	8.10	8.11	151000	133000	142000
−20.0	8.13	8.15	8.14	142000	123000	133000
−15.0	8.13	8.12	8.13	145000	128000	137000
−10.0	8.26	8.23	8.25	116000	99000	107000
0	8.32	8.39	8.36	97000	76000	86000
+18	9.08	9.11	9.10	20600	18300	19400

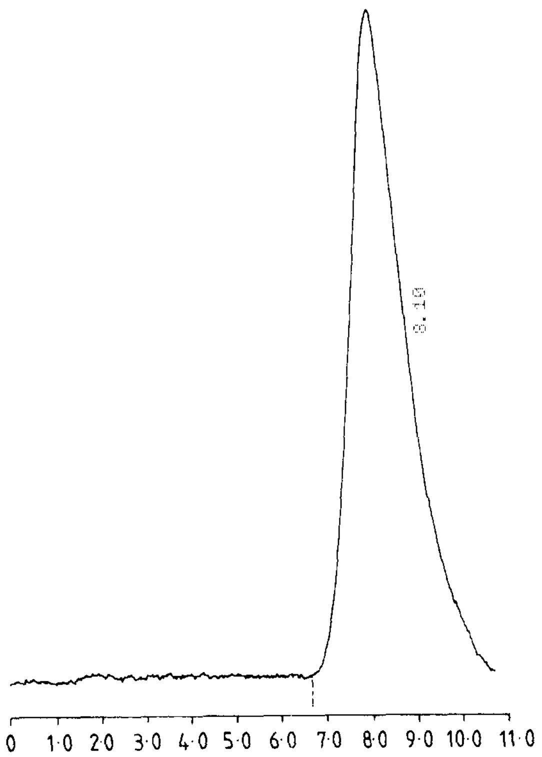

Figure 4 G.p.c. trace of polyaniline sample prepared at −27.5°C

curve and calculating the corresponding molecular weight for each line. From these values,

$$M_w = \frac{\sum h_i M_i}{\sum h_i}$$

and

$$M_n = \frac{\sum h_i}{\sum h_i / M_i}$$

where h_i = height from the baseline to the curve on the chromatogram and M_i = molecular weight corresponding to that retention volume.

The values of M_w and M_n, together with the polydispersity, (M_w/M_n), are shown in *Table 5*. The values for M_w and M_n follow the same variation with reaction temperature as those for M_p in *Figure 3*. The polydispersity reaches a minimum value of 4.8 for the sample with the highest molecular weight, prepared at −25°C, and a maximum of 8.6 for the sample prepared at −35°C. The mean of the ten values is 6.3, but the errors in the results are too great to draw any conclusions from the data.

It should be noted that polystyrene standards do not dissolve well in NMP and should not be used as g.p.c. molecular weight standards in this solvent, as some of our unpublished early work in this area gave artificially high results due to the non-linearity of the calibration graph. Also, the absorption peak at ~252 nm for polystyrene is beyond the cut-off point of the NMP/LiCl carrier solvent. Polyvinylpyridine standards are more soluble, and give a straight line fit for a graph of log(molecular weight) *versus* retention time, which is why they have been used here.

Table 5 Summary of the peak, weight-average and number-average molecular weights and polydispersity for samples prepared at various reaction temperatures

Preparation temperature (°C)	Average molecular weights (daltons) M_p	M_w	M_n	Polydispersity (M_w/M_n)
−35.0	135 000	166 000	19 100	8.6
−30.0	138 000	176 000	27 500	6.4
−27.5	145 000	190 000	31 700	6.0
−25.0	153 000	209 000	43 500	4.8
−22.5	142 000	178 000	25 400	7.0
−20.0	133 000	154 000	24 600	6.2
−15.0	137 000	159 000	26 800	5.9
−10.0	107 000	148 000	28 400	5.2
0	86 000	122 000	20 400	6.0
+18	19 400	29 700	4180	7.1

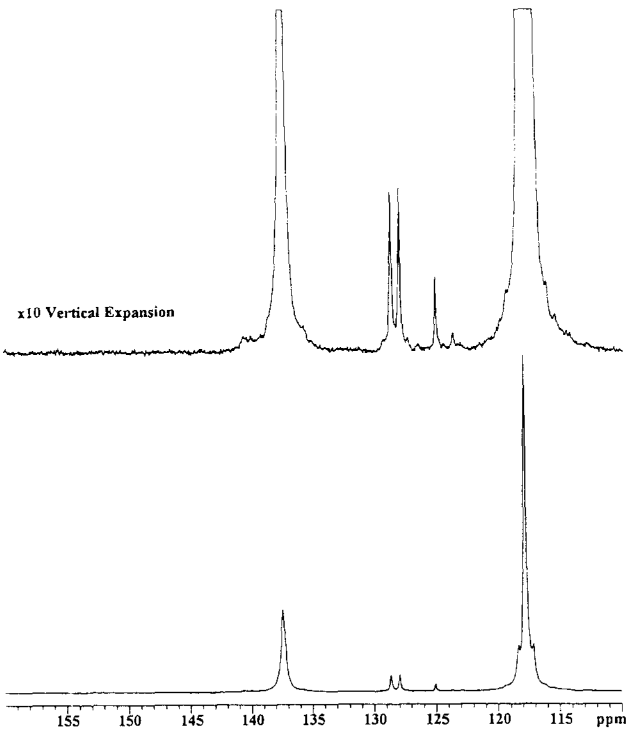

Figure 5 Solution state ^{13}C n.m.r. spectrum of high molecular weight leucoemeraldine base

The solution state ^{13}C n.m.r. spectrum of the reduced leucoemeraldine base form of the high molecular weight polyaniline is shown in *Figure 5*. The three small peaks at 128.66, 127.95 and 125.06 ppm may be ignored as they are toluene residues remaining from the separation of the leucoemeraldine base after reduction of the iminoquinone units in emeraldine.

The peak at 137.41 ppm is due to the two carbons bonded to nitrogen (although the 4th toluene peak is found here as well) and the larger peak at 117.80 is due to the four other carbon atoms in the aromatic rings. The two side peaks at 118.36 and 117.15 are thought to be due either to a restricted rotation of the aromatic rings about the amine groups linking the rings, which is only found in gelled solutions of high molecular weight polyaniline, or spinning side bands.

A comparison of this spectrum with the one shown in *Figure 6*, for standard polyaniline prepared at room temperature[5], shows two main differences. First, the latter shows many more smaller peaks which are

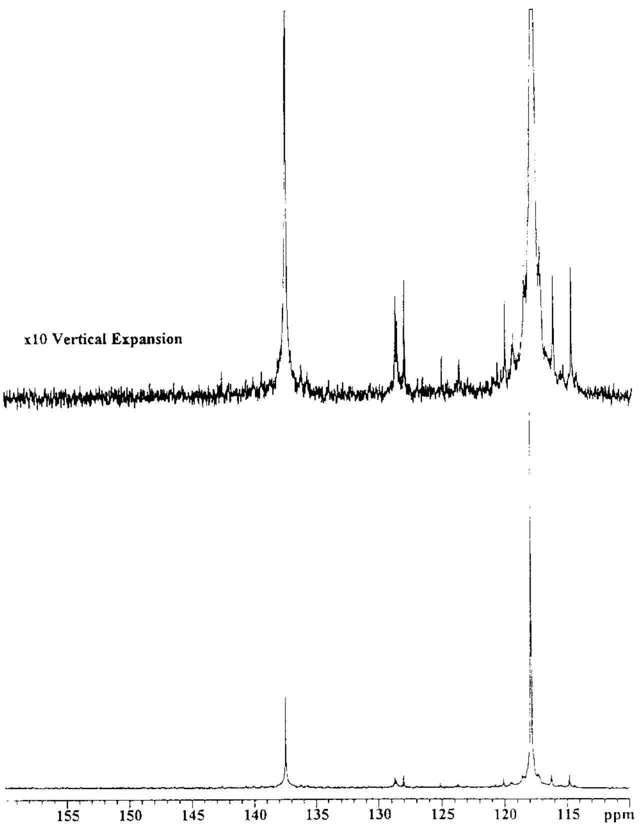

Figure 6 Solution state ^{13}C n.m.r. spectrum of standard (low molecular weight) leucoemeraldine base prepared at room temperature

Table 6 Conductivities for oriented films of polyaniline camphorsulfonate prepared from 1.5% solutions in *m*-cresol

Percent extension	Parallel conductivity (S cm^{-1})	Perpendicular conductivity (S cm^{-1})	Anisotropy	Film thickness (cm)
0	300	300	1.0	0.0012
40	277	125	2.2	0.0016
60	381	101	3.8	0.0016
65	269	67	4.0	0.0016
80	484			0.0015

probably due to defect sites in this leucoemeraldine sample, or possibly end groups. Second, the lines are much narrower, indicating that the standard sample is more mobile in solution and of a lower molecular weight, as may be expected, although the high molecular weight sample had gelled, which broadens the lines in the spectrum. The almost complete absence of small peaks in the n.m.r. spectrum of the high molecular weight polyaniline indicates that this sample contains fewer defect sites than the standard polyaniline in *Figure 6*. Although the higher molecular weight sample contains 1.38 wt% chlorine compared to 0.50 wt% for the sample prepared at room temperature[5], these values equate to one chlorine on every 28 C-6 rings compared to one chlorine on every 78 rings. Both values are too small to give any significant peaks in their n.m.r. spectra.

A film of the polymer prepared at −27.5°C, which had been cast from NMP solution, was oriented under uniaxial stress to give an elongation of 600%. After protonating the film in CH_3SO_3H, the conductivity was measured as 260 S cm^{-1} along the stretch direction and 31 S cm^{-1} perpendicular to this, using the Montgomery method[19]. This result should replace the earlier, erroneous values which were reported[20,21] and were due to a misunderstanding in the calculations involved in the Montgomery method to convert measured resistivity values into anisotropic conductivities. This result indicates that increased molecular weight has no effect on the conductivity compared to previously reported values.

An isotropic solvent cast film of polyaniline camphorsulfonate (cast from a 2.0 wt% solution in *m*-cresol) had a conductivity of 295 S cm^{-1}, measured using van der Pauw's technique. Further films (cast from a 1.5 wt% solution in *m*-cresol) were oriented under stress to give the results in *Table 6*. These conductivities were measured using four parallel wires. The anisotropy increases with increasing degrees of alignment (the 80% extension sample was too narrow to measure the perpendicular conductivity). The parallel conductivity shows a general increase with increasing alignment (the reason the parallel conductivity values for 40 and 65% extensions are less than for 0% is because *m*-cresol is lost during stretching, which is thought to influence the conductivity). More recently, a film stretched to 100% extension in an Instron heated to 150°C showed a parallel conductivity of 820 S cm^{-1} (ref. 22). Again, these results show that higher molecular weight polyaniline essentially free of defect sites does not show any improvement in isotropic conductivity measurements over previously reported values, but oriented polyaniline camphorsulfonate films have been reported for the first time and show increased conductivity along the stretch direction. The reason the conductivity of the oriented film cast from NMP and subsequently protonated with CH_3SO_3H is lower is because not all the film is protonated by soaking in acid solution.

CONCLUSIONS

Polyaniline may be prepared at sub-zero temperatures by the standard chemical oxidative route, using a salt such as lithium chloride to keep the reaction mixture mobile. The low temperature and presence of additional salts in the reaction solution increases the dipole moment and this favours the production of high molecular weight, pure polyaniline compared to materials prepared at room temperature. The highest molecular weight and yield were obtained at temperatures of between −23 and −29°C. Solution state ^{13}C n.m.r. spectroscopy of the leucoemeraldine base prepared from this polyaniline indicates that the polymer consists almost entirely of *para*-substituted phenylene rings linked by amine groups, with fewer small peaks than in the material prepared at room temperature which indicates fewer defect sites, despite containing a greater amount of chlorine substitution on the C-6 rings. Oriented solvent cast films from NMP solution which were protonated with CH_3SO_3H show no increase in conductivity compared to previously reported results for standard polyaniline. Previously reported high conductivity measurements[20,21] were found to be erroneous, whereas the maximum reported conductivity now is 820 S cm^{-1} for an oriented film of polyaniline camphorsulfonate[22]—an order of magnitude lower than our earlier erroneous reported values, but still an improvement on previous reports for CSA route materials, which were nonoriented.

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