^{13}C n.m.r. characterization of soluble polyaniline

Shaoru Ni*, Jinsong Tang and Fosong Wang
Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, People's Republic of China

and Lianfang Shen
Wuhan Institute of Physics, Academia Sinica, Wuhan, Hubei, People's Republic of China
(Received 22 July 1991; revised 7 October 1991; accepted 12 October 1991)

A high-resolution ^{13}C n.m.r. spectrum of soluble polyaniline in DMF-d_7 solution was recorded. The assignment for the various resonance peaks in the spectrum was tentatively performed and the chain structure of polyaniline was analysed. It has been shown that the main chain of pristine state polyaniline is composed of alternating benzoid–quinoid and successive benzoid–quinoid sequences with the former being present in greater concentration. The sequence distribution is random. In addition to the benzoid-type and quinoid-type structures, there is a small amount of other structural units in the main chain.

(Keywords: soluble polyaniline; ^{13}C n.m.r.; characterization; chemical shift; spectrum; structure analysis)

INTRODUCTION

Polyaniline has attracted considerable interest as an electrically conducting polymer of practical potential[1–4]. However, all polyanilines so far reported in the literature are insoluble and infusible, so their proper characterization is very hard to carry out. For example, all solid state high-resolution ^{13}C n.m.r. spectra of the reported polyanilines have very poor resolution and cannot be used to analyse the detail of the chain structure of polyaniline[3]. This is due to the poor molecular mobility of polyaniline resulting from chain stiffness and from strong intermolecular interactions. There may also be some paramagnetic structural units or impurities in the polymer that can lead to a relaxation broadening of n.m.r. linewidths. In order to perform a detailed analysis of chain structure of polyaniline, an adequately resolved ^{13}C n.m.r. spectrum of this polymer must be obtained.

Recently, a soluble polyaniline was successfully synthesized in our laboratory[5], making it possible to investigate the chain structure of polyaniline by n.m.r. and other techniques. In this work, the ^{13}C n.m.r. spectrum and nuclear Overhauser enhancement (NOE) of the soluble polyaniline in the pristine state were measured in DMF-d_7 solution. The assignment for the resulting spectrum was tentatively performed and an analysis of the chain structure of polyaniline was carried out.

EXPERIMENTAL

Soluble polyaniline was synthesized through chemical oxidation of aniline by $(NH_4)_2S_2O_8$ in a 6 mM aqueous solution of HCl. The molar ratio of aniline/$(NH_4)_2S_2O_8$ was 2:1. The polymer thus obtained had a conductivity of 4 S cm^{-1}. The product was converted into the pristine state by treatment with NH_4OH.

N.m.r. measurements were made at 50.3 MHz with a Varian XL-200 n.m.r. spectrometer. The sample was dissolved in a 10 mm n.m.r. tube in DMF-d_7 to a concentration of 10% (w/v). NOE was determined by comparing the intensities of the resonances obtained from completely proton-decoupled and proton-coupled spectra. The measurements were performed at 21–22°C.

RESULTS AND DISCUSSION

High-resolution ^{13}C n.m.r. spectrum of polyaniline

Figure 1 shows the 50.3 MHz ^{13}C n.m.r. spectrum of pristine state polyaniline in DMF-d_7 solution. The resolution of this solution spectrum is much higher than that of the ^{13}C CP-MAS spectrum of solid polyaniline[3]; at least 25 resonance peaks are resolved in the former while only five appear in the latter.

A set of resonance peaks between 110 and 123 ppm appearing in the solution spectrum is highly informative but it could not be resolved in the solid state. In accordance with the ^{13}C CP-MAS spectrum recorded and assigned by Hjertberg *et al.*[3], it is clear that the resonance peaks centred at 124.5, 137.7 and 158.6 ppm are the resonances of the protonated carbons in the benzoid ring and the protonated and unprotonated carbons in the quinoid ring, respectively. However, there has not been a report on the assignment for the other resonance peaks observed in the solution spectrum. In this work, we try to make assignments for these resonance peaks using the additivity rule of substituent chemical shift parameters for benzene derivatives in conjunction with NOE and lineshape analyses.

---

* Current address: Department of Chemistry, University of Toronto, Ontario, Canada M5S 1A1

0032-3861/92/173607-04

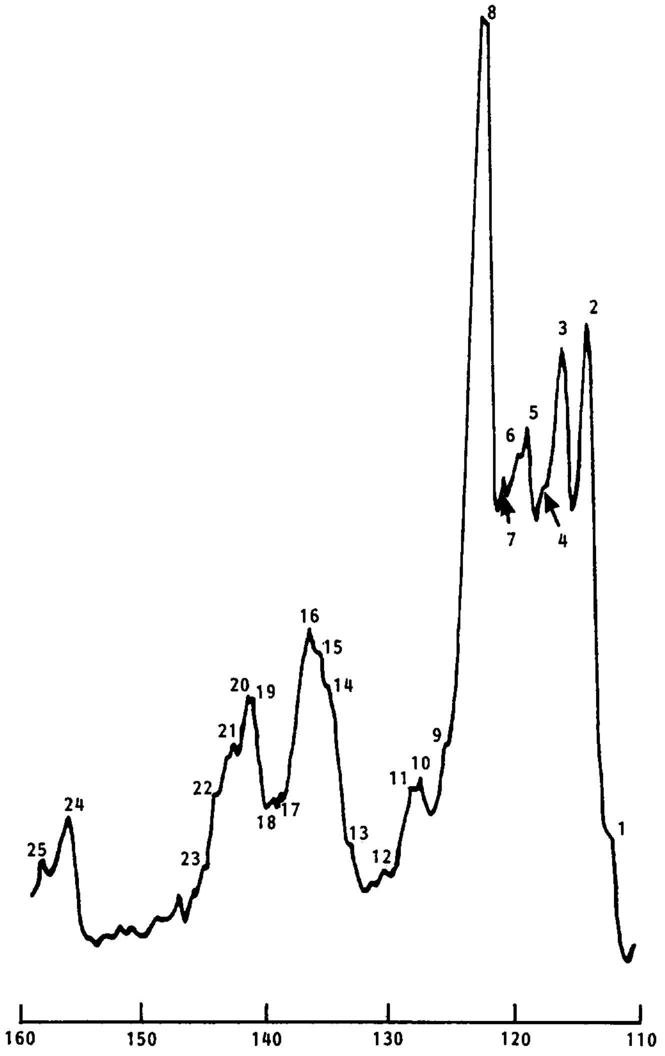
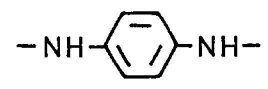


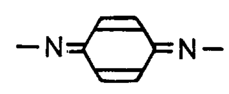
Figure 1 ^{13}C n.m.r. spectrum at 50.3 MHz of the pristine state polyaniline in DMF-d_7: 10000 scans

Calculation of chemical shift

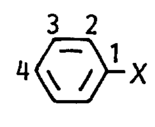
The main chain of pristine state polyaniline is mainly composed of two types of structural units: a substituted benzene-type



and its oxidized form, a substituted quinone-type



The assignment for the resonance peaks of the carbons in the quinoid ring has already been reported. However, the assignment for the resonance peaks associated with the carbons in the benzoid ring remains to be performed. The chemical shift of a carbon in a substituted benzoid ring

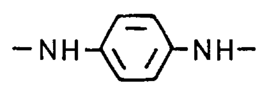


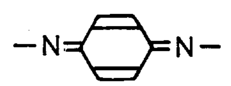
can be predicted by the additivity rule of substituent chemical shift parameters for benzene derivatives[6–8] according to the following relation:

$$\delta_i = 128.5 + Z_i$$

where Z_i is the additivity parameter of the substituent X on the *i*th carbon in the benzoid ring. The additivity parameters of many substituents are readily available from the literature[6,7].

The chemical shifts of the carbons in the benzoid ring of polyaniline are affected not only by groups -NH- or =N- directly bonded to it, but also by the benzoid or quinoid rings neighbouring it and separated by -NH- or =N-. So the major substituents at the benzoid ring in pristine state polyaniline should be





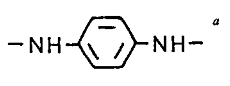
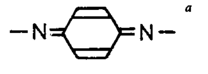
In other words, each of the structural units in the molecular chain would act as a substituent on the adjacent benzoid ring. However, the additivity parameters of these two types of substituents are not available in the literature. In this work, we have obtained them from the ^{13}C n.m.r. measurements of solid polyaniline by Hjertberg *et al.*[3] and aniline oligomers by Cao *et al.*[9] These values are listed in *Table 1*.

I.r. analysis[5] shows that there are possibly five structural units with benzoid ring as centre in the main chain of pristine state polyaniline. The chemical shifts of the carbons in each of these structural units were calculated by the additivity rule; the values are listed in *Table 2*. The chlorine content in the polyaniline used in this work is rather high. Elemental analysis indicates that every three benzoid or quinoid rings contain one chlorine atom on average[5]. We therefore considered the chlorinated benzoid rings to be among the major structural units in the polymer.

The assignment of resonance peaks

The assignment of the ^{13}C n.m.r. spectrum (*Figure 1*) is summarized in *Table 3*. The resonance peaks can be divided into two groups by NOE values: one at 114–142 ppm with NOE values greater than 2.06; the other at 142.6–158.6 ppm with NOE values smaller than 1.5. Because ^{13}C NOE originates from ^{13}C–^{1}H dipolar interaction, NOE values are larger for protonated carbons than for unprotonated carbons. The resonance peaks from 114 to 142 ppm are therefore associated with protonated carbons, and those from 142.6 to 158.6 ppm with unprotonated carbons.

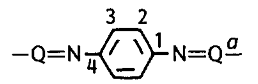
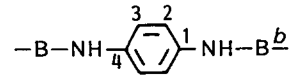
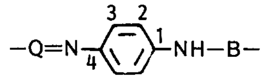
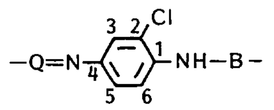
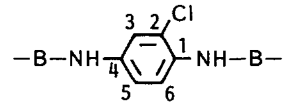
Table 1 Chemical shift parameters of some substituents

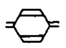
Substituent	Z_1	Z_2	Z_3	Z_4
 [a]	19.1	−13.0	1.2	−5.2
 [a]	21.5	−6.4	2.3	−3.6
$-NH_2$[b]	19.2	−12.4	1.3	−9.5
-Cl[b]	6.4	0.2	1.0	−2.0

[a] Obtained from ^{13}C n.m.r. measurements of solid polyaniline by Hjertberg *et al.*[3] and aniline oligomers by Cao *et al.*[9]

[b] From ref. 8

Table 2 Structural units in pristine state polyaniline and the predicted chemical shifts

No.	Structural unit	C_1	C_2	C_3	C_4	C_5	C_6
1		146.4	124.4	124.4	146.4	124.4	124.4
2		142.4	116.7	116.7	142.4	116.7	116.7
3		144.5	117.8	123.3	144.8	123.3	117.8
4		144.7	124.2	123.5	145.4	121.3	118.8
5		142.6	123.1	116.9	143.4	114.7	117.7

[a] Q represents 

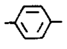
[b] B represents 

Table 3 Assignment of ^{13}C n.m.r. spectrum of polyaniline

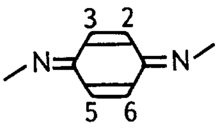
	δ (ppm)			
Peak	Observed	Predicted	NOE	Assignment[a]
1	114.7	114.7		C_{55}
2	116.2	116.7	2.30	C_{22}, C_{23}, C_{25}, C_{26}
3	118.1	117.8	2.24	C_{32}, C_{36}
4	119.3	118.8	2.35	C_{46}
5	121.7	121.3	2.44	C_{45}
6	122.2	123.3		C_{33}, C_{35}
7	122.7	123.5	2.27	C_{43}
8	124.5	124.4	2.06	C_{12}, C_{13}, C_{15}, C_{16}
9–12	125.8–131.0			Unclear
13–19	132.0–142.4			C^b_{q2}, C_{q3}, C_{q5}, C_{q6}
20	142.6	142.4	1.49	C_{21}, C_{24}
21	143.1	144.5	1.29	C_{31}
22	144.2	144.8		C_{34}
23	145.4	146.4		C_{11}, C_{14}
24	156.7		1.50	C_{q1}, C_{q4}
25	158.6		1.17	

[a] First subscript number refers to structural unit in *Table 2*; second subscript number refers to carbon on the benzoic ring

[b] C_q represents a carbon in the quinoid ring

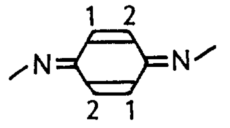
The assignment for the resonance peaks with high resonance intensities from 124 to 158.6 ppm in the solution spectrum is in agreement with the solid state spectral assignments made by Hjertberg *et al.*[3], except that the chemical shift of C_{11} and C_{14} is about 2.6 ppm smaller than that in the solid state spectrum. Now we explain the assignment for the resonance peaks that do not appear in the solid state spectrum.

As seen in *Figure 1*, at least two resonance peaks close to 142.6 ppm can be resolved in the solution spectrum of polyaniline, one at 142.4 ppm and the other at 142.6 ppm, while only one peak can be observed at about 142.6 ppm in the solid spectrum. Hjertberg *et al.*[5] assigned the peak at 142.6 ppm to C_2 and C_5 on the quinoid ring in the *trans* conformation

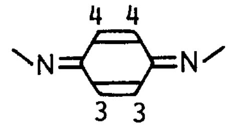


and the peak at 137.7 ppm to C_3 and C_6 on the same ring. In the solution spectrum, the peak at 142.6 ppm has a quite different NOE value and linewidth from the peak at 137.7 ppm, so it is not expected to arise from a quinoid ring carbon. This peak may be assigned to C_{21} and C_{24} based upon the chemical shift calculation and the analysis of NOE and linewidth. The magnetic inequivalence between C_2, C_5 and C_3, C_6 in the quinoid ring in the *trans* conformation would be smaller in solution than in the solid state, owing to the quicker reorientation motions of chain segments in solution, and consequently the difference between the chemical shifts of C_2, C_5 and C_3, C_6 would be smaller in solution than in the solid state, hence the peak at 142.4 ppm in the solution spectrum is more likely to belong to C_2 and C_5 on the quinoid ring in the *trans* conformation.

^1H and ^{13}C n.m.r. spectra of the model compounds of polyaniline indicate that there are *syn* and *trans* conformations about the quinoid ring[10,11]:



trans



syn

Carbons 1, 2, 3 and 4 would all resonate at distinct frequencies (i.e. distinct chemical shifts). The resonance peaks from 132.0 to 142.4 ppm may be associated with these carbons, but the exact assignments for them cannot be made with the present data alone.

A new resonance peak at 156.7 ppm appears in the solution spectrum compared with the solid state spectrum[3]. The low NOE value and larger chemical shift of this peak indicate that it belongs to the unprotonated carbon in the quinoid ring, as does the resonance peak at 158.6 ppm. The appearance of two resonance peaks associated with the unprotonated carbon in the quinoid ring may also be a result of the presence of *trans* and *syn* conformations around it, but the exact origin of these two peaks is, at present, unclear.

A set of resonance peaks from 114 to 123 ppm appear in the solution spectrum but are not observed in the solid state[3]. These peaks have larger NOE values and narrower linewidths, showing them to be associated with protonated carbons which have high mobility. Based on the ^{13}C n.m.r. spectrum of an aniline tetramer in completely reduced form[9], and on the prediction of chemical shifts by the additivity rule, these resonance peaks were assigned to the carbons on the benzoid rings in the successive benzoid–benzoid sequence in the main chain of polyaniline.

The assignment for the resonance peaks from 125 to 131 ppm is unclear at present. They may be related to the carbons in some complex structural units rather than those given in *Table 2*. I.r. analysis has shown the presence of such complex structural units in polyaniline[5].

Analysis of the chain structure of polyaniline

From the assignment of the ^{13}C n.m.r. spectrum of pristine state polyaniline in solution, the chain structure of polyaniline was analysed. The following conclusions may be drawn.

1. The main chain of pristine state polyaniline is mainly composed of alternating benzoid–quinoid and successive benzoid–benzoid sequences with the former being present in greater concentration.
2. The relatively strong resonances of the carbons in the benzoid rings of structure 3 (*Table 2*), a structure unit linking the alternating benzoid–quinoid and successive benzoid–benzoid sequences, imply that the sequence distribution is random.
3. In addition to the main structural units in *Table 2*, there is a small amount of other structural units.

REFERENCES

1 Dorimedoff, M., Hautiere-Cristofini, F., de Surville, R., Jozefowicz, M., Yu, L. T. and Buvet, R. *J. Chem. Phys.* 1971, **68**, 1055

2 MacDiarmid, A. G., Chiang, J.-C., Halpern, M., Huang, W. S., Krawczyk, J. R., Mammone, R. J., Mu, S.-L., Somasiri, N. L. D. and Wu, W. *Am. Chem. Soc. Div. Polym. Chem., Polym. Prepr.* 1984, **25**, 248

3 Hjertberg, T., Salaneck, W. R., Lundström, I., Somasiri, N. L. D. and MacDiarmid, A. G. *J. Polym. Sci., Polym. Lett. Edn* 1985, **23**, 503

4 Stafström, S., Sjogren, S., Wennerström, O. and Hjertberg, T. *Synth. Met.* 1985, **13**, 193

5 Tang, J., Ph.D. thesis, Changchun Institute of Applied Chemistry, Academia Sinica, 1987

6 Levy, G. and Nelson, G. L. 'Carbon-13 Nuclear Magnetic Resonance for Organic Chemistry', Wiley Interscience, New York, 1972

7 Tonelli, A. E. and Schiling, F. C. *Acc. Chem. Res.* 1981, **14**, 233

8 Breitmarier, E. and Voelter, W. '^{13}C-NMR Spectroscopy', 2nd edn, Verlag Chemie, Weinheim, 1978

9 Cao, Y., Li, S., Xue, Z. and Guo, D. *Synth. Met.* 1986, **16**, 305

10 Layer, R. W. and Carman, C. J. *Tetrahedron Lett.* 1968, **11**, 1285

11 Hjertberg, T. and Sandberg, M. *Synth. Met.* 1987, **21**, 31