

Proton NMR study on the molecular motion and conformation of polyaniline doped with HCl

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SUMMARY

Proton NMR spectra and spin–lattice relaxation time (T_1) for polyaniline doped with HCl were measured at 90MHz over a temperature range of 110–430K. A narrow line with a width of about 1–2KHz superimposed on broad NMR peak was observed above 210K, and it was tentatively assigned to the protons in dopant and absorbed water. The analysis of linewidths and second moments for the broad lines reveal two distinct relaxation processes with activation energies of 1.9 and 7.8Kcal./mole, respectively. The former may be associated with the motion of the dopant and water absorbed and the latter with the rotation of benzoid ring about C–N bond axis. The second moment data suggest that the twist angle between the adjacent rings decreases with rising the doping ratio. Proton NMR relaxation rate was fitted with a theoretical equation containing the contributions from nuclear dipolar interaction and from electron–proton interaction, R_d and R_p , respectively. R_d is negligible below room temperature and R_p has little change above 100K. The total relaxation rate is dominated by R_p near room temperature.

INTRODUCTION

In our previous work (1,2), it has been shown by high resolution NMR and IR investigations that the main–chain of the pristine state polyaniline is composed of alternating benzoid–quinoid and successive benzoid–benzoid sequences with a ratio of

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benzoid/quinoid rings of 3:1. The pristine polyaniline has a conductivity lower than 10^{-10} S/cm and therefore is not electrically conductive. Upon doping with some electron donors, the conductivity of its can reach up to 10 S/cm, being more than 10 orders of magnitude as high as that of the pristine state. Therefore, it is believed that the doping profoundly modifies the structure of the polyaniline. However, the doped polymers are very intractable and their chain structure can not be detected by high resolution NMR in solution due to their insolubility and infusibility. And their NMR spectra measured by solid-state high-resolution NMR technique like combined cross-polarization and Magic-angle sample spinning are also too broad to solve (3) and so can not be used to analyze the chain structure. Consequently, the exact chain structure and conformation of doped polyaniline remain unknown so far.

Broad line nuclear magnetic resonance has proved very useful in studying the morphology, relaxation process and conformation of conductive polymers (4) and some information on structure and molecular motion of doped polymers can be extracted from such studies.

In this work, the proton NMR linewidth, second moment and spin-lattice relaxation time T_1 for polyaniline doped with HCl were measured at 90 MHz as a function of temperature from 110 K to 430 K and the molecular motion and conformation of doped polyaniline were analyzed.

EXPERIMENTAL

Polyaniline samples in this work were prepared by chemically oxidation of aniline with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in a 6 M aqueous solution of HCl. The molar ratio of aniline to $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is 2:1. The samples with different doping ratios were obtained by mixing the pristine polyaniline with the aqueous solutions of HCl in different pH values. The doping ratio was determined by means of element analysis, the conductivity by the four-point contact method and the spin number of electrons by ESR. The parameters thus obtained for the various samples are tabulated in Table I.

The NMR measurement was made on a Bruker CXP 100 pulse NMR spectrometer. The 90° pulse time is 1.5 s. The powder samples were filled in 10 mm tube for the NMR measurements. T_1 was determined using the conventional $180^\circ-t-90^\circ$ pulse sequence, where t is the pulse interval time, and the t were 1–2 ms in this work. All the measurements were performed at 90 MHz.

TABLE I

The Doping ratio(P), Conductivity(δ) and Number of Electron Spins(N_s) of the Various Samples

Sample	CHP4	CHP3	CHP2.5	CHP0
P	1.1	9.2	28.5	49.8
δ , S/cm	5.3×10^{-10}	1.8×10^{-5}	5.3×10^{-2}	6.0
N_s , S/g	3.7×10^{18}	7.8×10^{19}	1.0×10^{20}	2.9×10^{20}

$P = 6 \cdot [Cl] \cdot 100\% / [C]$, where [Cl] and [C] are the molar numbers of chlorine and carbon, respectively.

RESULTS AND DISCUSSION

1. Proton NMR spectra

Fig.1 shows the broad line proton NMR spectra for sample CHP0 at different temperatures. As seen, a narrow line superimposed on the broad line appears above 210K. The intensity of the narrow line increases with rising temperature in a low temperature range and attains a maximum at about room temperature following a drop in its intensity above room temperature.

The appearance of narrow line superimposed on broad line means that there is a species of highly mobile proton with quite long spin-spin relaxation time T_2 compared with that of the protons in the polymer matrix. The widths of the narrow line is only 1-2KHz, much smaller than those of the broad line (ca. 40-50KHz). So the T_2 for the mobile protons are 20-50 times as long as those of the protons responsible for the broad line.

Nechtschein et al. (4) also observed the narrow line in the broad line NMR spectra of polyaniline and assigned it to the protons in the water absorbed in the samples. The similar narrow line in pristine poly(p-phenylene sulphide) was also detected by Schlick et al. (5), but they proposed that the narrow line arises from the larger scale motion in the amorphous phase in the polymer. From our observation, it seems to be more plausible to assign the narrow line to the proton in both dopant and water absorbed in the polymers.

First, the content of the mobile proton increases with rising doping ratio. The contents of the mobile protons in the samples CHP0 and CHP2.5 are, respectively, 27% and 15% measured from the relative intensities or the area of the narrow line and broad line while the intensities of the narrow lines in the sample CHP3 and CHP4 are too weak to be used to estimate the contents of the mobile protons.

Next, in the samples doped with some protonless dopants like I_2 , no narrow line can

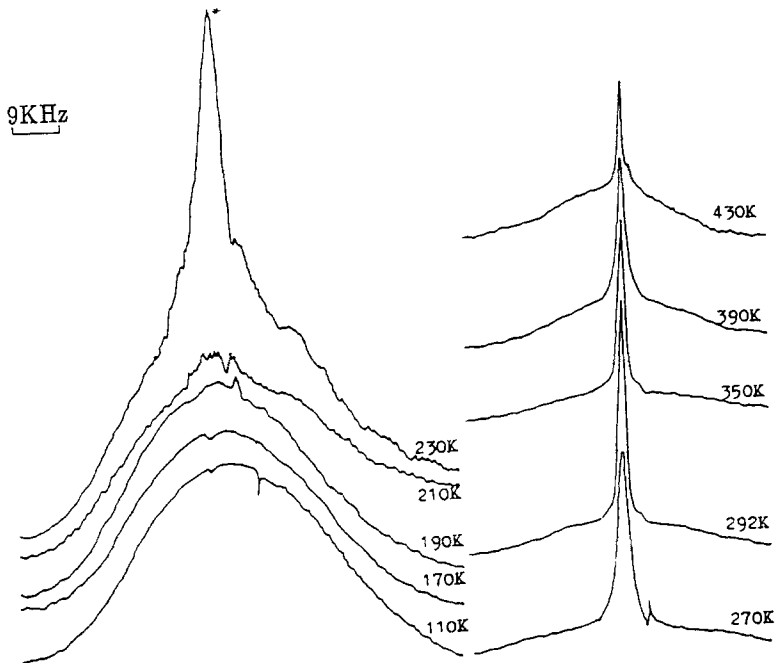


Figure 1 Proton NMR spectra of the sample CHP0 at different temperatures
 * Extended scale vertically by about 6 times.

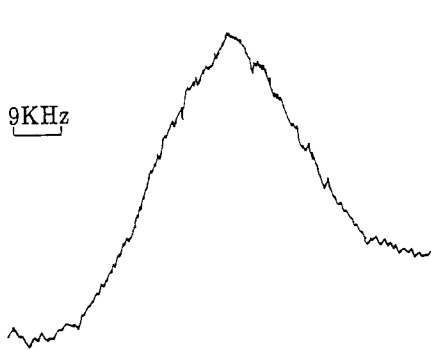


Figure 2 Proton NMR spectrum of the sample doped with I_2

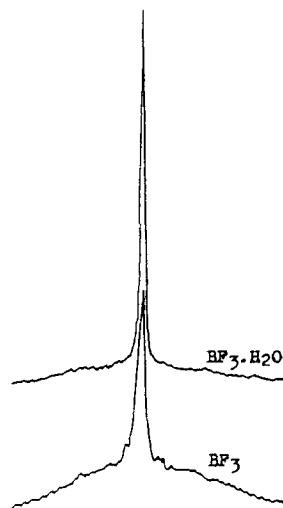


Figure 3 proton NMR spectra of the samples doped with BF_3 and $BF_3 \cdot H_2O$

be detected in the broad line proton NMR spectra (Fig. 2). This indicates that the narrow line comes from the protons in dopant.

Third, as shown in Fig. 3, the intensity of the narrow line in the sample doped with BF_3 containing water is much higher than that in the sample doped with waterless BF_3 . The combination of BF_3 and H_2O may yield HF and $\text{B}(\text{OH})_3$.

Besides, it was found that the decrease in the intensity of narrow line above temperature was caused by the escape of the dopant and water absorbed due to elevated temperature.

All the observations we have done support the conclusion that the narrow line superimposed on broad proton NMR line in conductive polymers arise from the protons both in dopant and in water absorbed.

2. Linewidth and second moment

The linewidth and second moment of the broad line for the sample CHP0 are shown in Fig. 4 as a function of temperature. Two distinct relaxation processes can be observed in both linewidth and second moment vs. $1/T$ plots. The analysis for molecular motion based on linewidth of NMR in solids can be performed by the following equations (6)

$$\ln\left[\frac{1}{W}-\frac{1}{A}\right] = -\frac{E_a}{RT} + \ln\left[\frac{1}{B}-\frac{1}{A}\right] \quad (1)$$

where w is the linewidth at temperature T , A and B are the limiting values of the linewidth at low and high temperature, respectively, E_a is the motional activation energy. A plot of eq.1 usually reveals the existence of different relaxation processes and from it the motional activation energies for various processes can be evaluated. Our data are shown, plotted according to eq.1, in Fig.5, and the plot shows two distinct linear regions with activation energies 7.8 and 1.9Kcal./mole, respectively. The low temperature relaxation process starts from about 210K, just corresponding to the onset of the narrow line in the spectra, implying that it is associated with the motions of dopant and water absorbed. And this is also supported by the activation energy value of 1.9Kcal./mole. According Flory (7), the motional activation energy for a single-bond molecule is about 2Kcal./mole.

In the high-temperature relaxation process, the linewidth decreases about by 20KHz and the second moment about by 10Gass^2 , and the activation energy of the process is as high as 7.8Kcal./mole. So this relaxation should arise from some large-size motional units. But it is certainly not the glass transition because the activation energy for glass transition is usually 20-100Kcal./mole and for the doped polyaniline the activation energy of glass transition would be more higher due to its stiff molecular chain and strong intermolecular interaction. Mishra, et al. (8) once reported that aniline

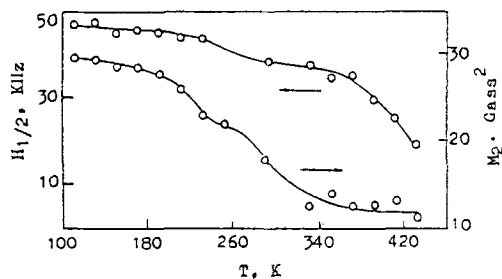


Figure 4 Linewidth and moment as a function of temperature for the sample CHP0

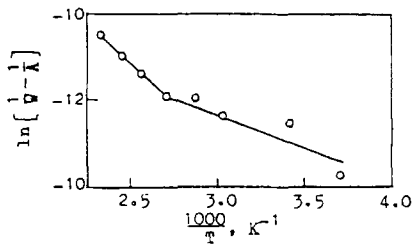


Figure 5 Plot of linewidth as a function of $1/T$

hydrochloride (corresponding to the repeat unit in HCl-doped polyaniline) has a transition in the same temperature range in the proton linewidth and second moment vs. temperature plots as that of HCl-doped polyaniline and the activation energy was estimated by an empirically express $E_a = 37T_c$ to be about 8Kcal./mole, where T_c is the temperature at which the narrowing of proton NMR line starts. Therefore, it is likely that the rotation motion of benzoid rings about C-N bond axis may be responsible for the high-temperature relaxation process.

Second moment is dependent on the conformation of molecular chain in solids. In a rigid solid that is in the absence of any NMR-active molecular motion and the orientation of molecular chains is random, the theoretical second moment proposed by Van Vleck (9) can be expressed as

$$M_2 = (6/5)I(I+1)g_n^2 B_n^2 (1/n) \sum_{j>i} r_{ji}^{-6} \quad (2)$$

where I is the nuclear spin number, g is the nuclear g factor, B is the nuclear magneton, n is the total number of interacting protons, and r_{ji} is the distance between proton j and i . The sum $\sum_{j>i} r_{ji}^{-6}$ mainly depends upon the conformation of chain. If some structure data have been known, the conformation of molecular chain can be deduced from relating the theoretical second moment to the observed one. For the doped polyaniline, such data are quite absent, so their conformation cannot be exactly investigated from the second moment measurements for the moment. In spite of that, some informations related to their conformation can be extracted.

From the inverse sixth power dependence of second moment on internuclear distance r_{ji} , it is clear that the change in second moment is caused by the change in internuclear distance r_{ji} . In the case of benzoid ring rotating about C-N bond axis, the interproton distances in the same ring remain approximately unchange when the change in temperature is not too much and the contribution to the change in second moment so mainly comes from the change in the interproton distances between the adjacent rings, especially from the change in the distances between H^1-H^1 or $H^{2'}-H^{2'}$, because the twist

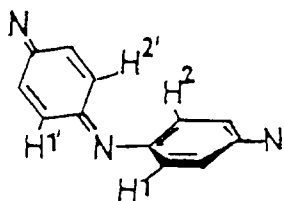


Figure 6 Schematically the chain structure of polyaniline

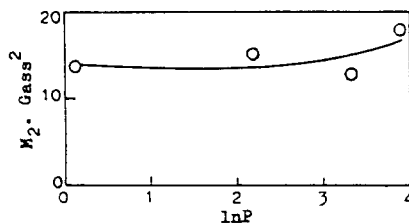


Figure 7 Second moment vs. doping ratio

angle between the adjacent rings varies with the free rotation of rings about C–N bond axis and therefore causes a great change in the distances between $H^{1'}-H^1$ or $H^{2'}-H^2$. as shown in fig.6. So the second moment is sensitively dependent on the twist angle between the adjacent rings in polyaniline. Fig.7 shows the plot of the second moment vs. doping ratio. As seen, the second moment of the broad line NMR spectra in HCl-doped polyanilines increases with rising the doping ratio. It means that the doping causes the shortening of the interproton distances, and further means that the doping causes a decrease in the twist angle between the adjacent rings. This is consistent with the results from theoretical calculation of the ground state geometry of polyaniline (10).

3. Temperature dependence of spin–lattice relaxation rate

Two NMR relaxation mechanisms are to be considered at least in conductive polymers (4), one being the thermally modulated nuclear dipolar interaction, the other the interaction of nuclei with unpaired electrons. The relaxation rates due to the former and the latter can be, respectively, expressed as (11)

$$R_d = C \exp(-E_a/KT) \quad (3)$$

and

$$R_p = R_o \exp(E_p/KT) \quad (4)$$

where C and R_o are constants, and E_a and E_p are the activation energies.

The total relaxation rate is then obtained by combining the eqs.3 and 4

$$R = 1/T_1 = R_d + R_p = C \exp(-E_a/KT) + R_o \exp(E_p/KT) \quad (5)$$

The experimental R values for the sample CHP0 is depicted in Fig.8 as a function of reciprocal temperature. An attempt was made to fit the experimental R data with the theoretical eq.5 for R . The result is shown in Fig.8 as solid line. The calculated results are in good accordance with the experimental ones. The various parameters in eq.5 obtained from the fitting process are as follows: $C = 4.1 \times 10^5 \text{ s}^{-1}$, $R_o = 16.6 \text{ s}^{-1}$,

$E_a = 6.95 \text{ Kcal./mole}$ and $E_p = 0.04 \text{ Kcal./mole}$. The E_a is close to the activation energy obtained from the linewidth vs. $1/T$ plot for the high-temperature relaxation.

Fig.9 shows the plots of R vs. $1/T$ according eqs.3 and 4 with the corresponding parameters given above. As shown, the contribution from the unpaired electrons to relaxation rate is almost constant above 100K and that from the nuclear dipolar interaction is negligible below room temperature. And at room temperature (298K), $R_d=3$ and $R_p=18$. Therefore, a conclusion can be drawn that the proton NMR relaxation in HCl-doped polyaniline is dominated by the interaction between the protons and unpaired electrons near room temperature.

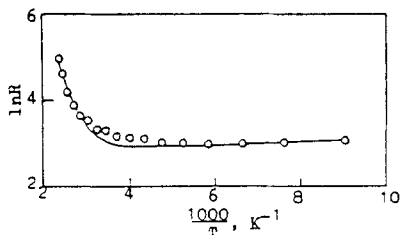


Figure 8 $\ln R$ vs. $1/T$.
Circle: Experimental,
Solid line: Calculated

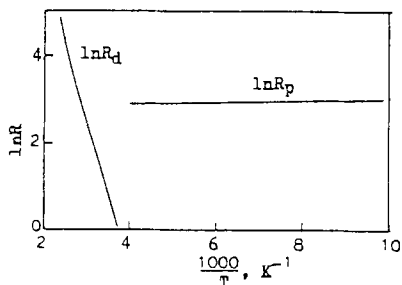


Figure 9 $\ln R$ vs. $1/T$ plots according to eqs.3 and 4

REFERENCES

1. Shaoru Ni, Jinsong Tang and Fosong Wang, manuscript in preparation.
2. Jinsong Tang, thesis, 1987.
3. T. Hjertberg, M. Sandberg, O. Wennerström and I. Lagerstedt, *J. Polym. Sci., Lett. Ed.*, 21, 31 (1987).
4. M. Nechtschein, C. Santier, J.P. Travers, J. Chrobczek, A. Alik and M. Ripert, *Synth. Met.*, 18, 311 (1987).
5. S. Schlick and B.R. McGarvey, *Polym. Commun.*, 25, 369 (1984).
6. J.R. Hendrickson and P.J. Bray, *J. Magn. Reson.*, 9, 341 (1973).
7. P. Flory, "Statistical Mechanics of Chain Molecules", Interscience Publ., New York, 1969.
8. S.C. Mishra, R.C. Gupta and U. Bajpai, *Cur. Sci.*, 47, 37 (1978).
9. J.H. Van Vleck, *Phys. Rev.*, 74, 1168 (1948).
10. S. Stafström, *Chem. Phys. Lett.*, 131, 410 (1986).
11. A. Carrington and A.D.M. Clachlan, "Introduction to Magnetic Resonance", Harper and Row, 1967.