

Electronic motion of HClO₄-doped polytoluidine studied by varying-frequency proton NMR relaxation

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SUMMARY

Proton spin-lattice relaxation times (T_1) in poly-o-toluidine doped with HClO₄ were measured over a frequency range from 20 to 90 MHz at room temperature. It was found that there are at least two kinds of phase structures with definitely distinguishable T_1 values in moderate doped samples. The spin-lattice relaxation rate $(T_1)^{-1}$ exhibits a maximum at the doping ratio of about 20%. The frequency dependence of $(T_1)^{-1}$ reveals that the electrons predominantly perform an intrachain diffusive motion above 50 MHz and below this frequency an interchain hopping of electrons takes place.

INTRODUCTION

Polyaniline (PAn) has attracted considerable attention because of its chemical stability, novel doping mechanism and the possibility for technical application as new electronic materials (1-3). However, little research effort has been devoted to the dynamic aspect of electrons of PAn so far. In our previous paper (4), the results of exploring the phase structure and electronic motion of PAn doped with HCl by means of varying-frequency proton NMR relaxation was presented. In this paper, we are to report the measurements of proton spin-lattice relaxation times as a function of the experimental NMR frequency for poly-o-toluidine doped with HClO₄ at room temperature.

The pristine poly-o-toluidine has a similar chain structure to PAn except carrying a methyl group with aromatic ring. Upon doping with protonic acid such as HCl and HClO₄, poly-o-toluidine becomes electrical conductive, but its conductivity is lower than that of doped PAn. At present, the conductivity of poly-o-toluidine can reach 10^{-2} S/cm (5), while that of PAn can be as high as 10 S/cm (1). Despite of this, poly-o-toluidine still deserves further studies for its higher toughness and solubility due to its

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lower intermolecular interaction and better flexibility compared with PAN.

EXPERIMENTAL

Poly-o-toluidine was synthesized by chemical oxidation of o-toluidine with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in aqueous HCl solution. The samples with different doping ratios were obtained by mixing the pristine poly-o-toluidine with aqueous solution of HClO_4 in different pH values. The doping ratio and conductivity of various samples are given in Table 1.

Table 1. The doping ratio (P) and conductivity (σ) of the various samples

Sample	5A	2A	0A
P*	—	23.5	36.1
σ , (S/cm)	5×10^{-11}	1×10^{-5}	1×10^{-2}

* $P = [\text{Cl/N}] \times 100\%$, Cl and N indicate the molar numbers of chlorine and nitrogen, respectively.

The powder samples were filled in 10 mm tubes for NMR measurement. Proton spin-lattice relaxation times were determined on a Bruker CXP 4-100 pulse NMR spectrometer. The repetition time was 1.5 S. T_1 measurements were performed using a 180° -t- 90° pulse sequence. t is the interval between successive pulse sequences.

RESULTS AND DISCUSSION

1. The recoveries of proton magnetization

Figure 1 shows the recoveries of magnetization of the various samples measured at 30 MHz and room temperature. The recovery of proton magnetization in sample 5A can be described by a single exponential function with a single spin-lattice relaxation time T_1 . But those in samples 2A and 0A can not be fitted by an exponential function and consist of at least two components with definitely distinguishable T_1 values, suggesting the existence of two relaxation processes; one yielding initial steeper recovery with a short T_1 , another giving rise to delayed recovery with a long T_1 . The appearance of two relaxation processes was interpreted in terms of " phase structure " usually used in polymer blend system, similar to the segregated " metallic island " model proposed by MacDiarmid (6). That is, they consist of two kinds of phase structures; one is the dispersing phase region containing more dopants, corresponding to a short T_1 caused by a lot of the

paramagnetism, the other is the continuous phase region with less dopants, corresponding to a long T_1 . So we think that the existence of two relaxation processes in HClO_4 -doped polytoluidine may be due to inhomogeneous distribution of dopants, which comes from the uneven doping.

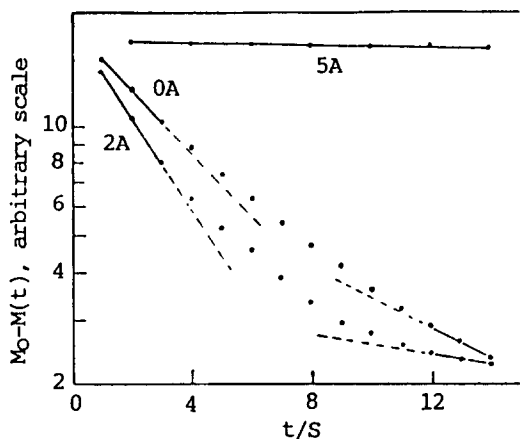


Fig. 1. The recoveries of magnetization at 30 MHz for various samples.

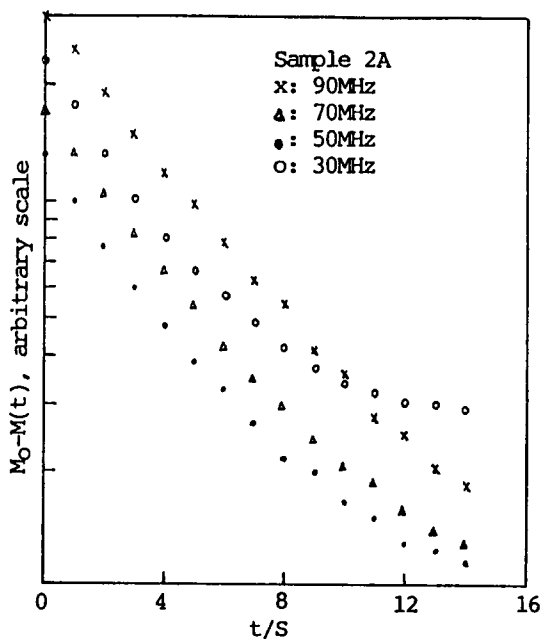


Fig. 2. The recoveries of magnetization of the sample 2A at different frequencies.

Figure 2 shows the recovery of magnetization in the sample 2A at different frequencies. As shown, the heterogeneity in phase structure of heavily doped polytoluidine displays even more obviously at low frequencies.

The similar inhomogeneities in phase structure have also been observed in some other conducting polymers such as HCl-doped PAn (4), SO_3 -doped poly(p-phenylene sulphide) (7), pyrolysates of polyacrylonitrile (8).

2. The doping ratio dependence of $(T_1)^{-1}$

The inverse spin-lattice relaxation time, $(T_1)^{-1}$, is a parameter characterizing the nuclear relaxation rate R . The $R [=(T_1)^{-1}]$ is just the slope of recovery of magnetization. It can be seen from Figure 1 that sample 2A has the highest nuclear relaxation rate among the three samples, and this means a complex dependence of R on doping ratio. The relationship between the nuclear relaxation rate in the phase region with short T_1 (hereafter referred as R_r) and doping ratio is shown in Figure 3. As shown, the R_r attains a maximum at about doping ratio of 23%. It is worth noticing that the dependence of R_r on doping ratio is far stronger in HClO_4 -doped polytoluidine than in HCl-doped PAn (4). The maximum of R_r is about 100 times as large as its minimum in the former while is about 15 times in the latter. The maximum of R vs. doping ratio was also been detected in some other conducting polymers like poly(p-phenylene sulphide) doped with SO_3 (7) and pyrolysed polyacrylonitrile (8).

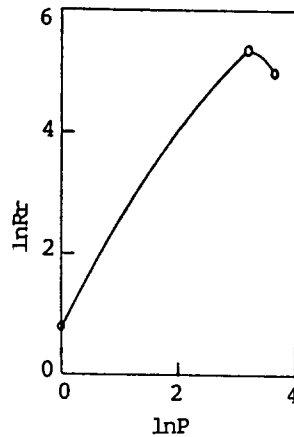


Fig. 3. Dependence of nuclear relaxation rate on doping ratio.

3. The frequency dependence of R_r

Proton spin-lattice relaxation rate in conducting polymers can be described as a function of the nuclear and electronic Larmor angle frequencies, ω_n and ω_e (7).

$$R = N_s \left[\frac{3}{5} d^2 f(\omega_n) + (a^2 + \frac{7}{5} d^2) f(\omega_e) \right] \quad (1)$$

where N_s expresses the effective number of electron spins which take part in the nuclear relaxation, a^2 and d^2 are the mean square of scalar and

dipolar parts of the hyperfine couplings, respectively; $f(\omega)$ is termed spectral density function and it is the frequency power spectrum of the fluctuating internal field at the position of protons. In this case that the nuclear relaxation is dominated by the interaction of nuclei with electrons, $f(\omega)$ reflects the electronic motion and depends sensitively on the dimensionality of the electronic motion. For one-dimension electronic motion (9).

$$f(\omega) = (2D_{\parallel}\omega)^{-1/2} + Q \quad (2)$$

where D_{\parallel} is the intrachain diffusive rate of electrons, Q is a constant reflecting the mode of electronic motion: Q is positive in the case that electronic motion can be explained by Heisenberg exchange and metallic conduction models and negative in the case of delocalization of electrons. In two and three dimension, $f(\omega) = (1/2\pi)(D_{\parallel}D_{\perp})^{-1/2}\ln(4\pi^2D_{\perp}/\omega)$ and $f(\omega) = \text{constant}$, respectively (8). D_{\perp} is the interchain diffusive or hopping rate of electrons.

The typical frequency dependence of R for HClO_4 -doped polytoluidine is depicted in Figure 4, in which R_s is the nuclear relaxation rate in the phase region with long T_1 . As shown, the R_r increased linearly with $f^{-1/2}$ at frequencies above 50 MHz while it trends to constant with decreasing frequency below 50 MHz. This indicates that electrons predominantly perform intrachain diffusive motion in the higher frequency range and at low frequencies interchain hopping of electrons appears. The crossover between the

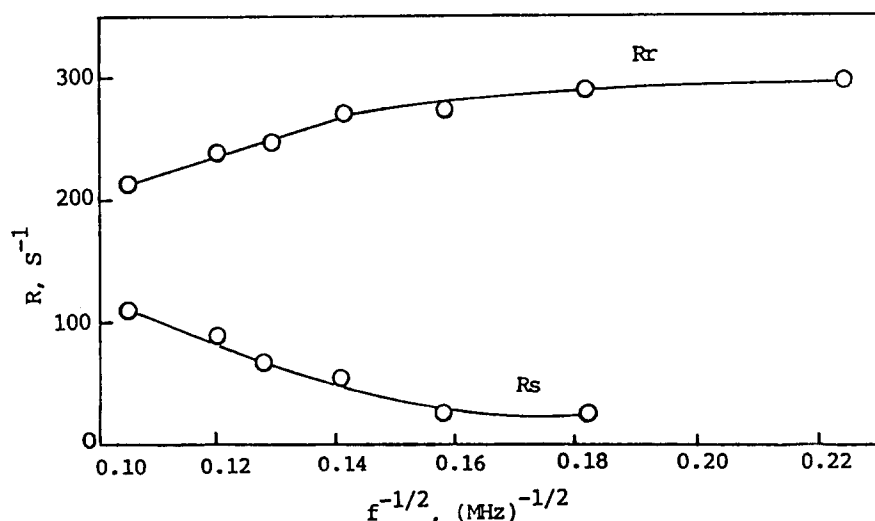


Fig. 4. R vs. $f^{-1/2}$ plots for the sample 2A.

interchain and intrachain motional regimes occurs at $\omega \approx D_{\perp}$ (10). So the interchain hopping rate for HClO_4 -doped polytoluidine is estimated to be of the order of 10^8 rad./S. From the slope of straight line parts of the R vs. $f^{-1/2}$ plots D_{\parallel} is estimated to be about 4×10^9 rad./S for sample 5A; 4×10^{10} rad./S for 2A and 6×10^{10} rad./S for 0A. $D_{\parallel} / D_{\perp}$ is about 10^2 , being similar to that of HCl-doped PAN (4). Both D_{\parallel} and D_{\perp} of HClO_4 -doped polytoluidine are of the same order of magnitude as those of PAN doped with HCl (4).

It can be seen from Figure 4 that the slope of R_s vs. $f^{-1/2}$ plot is negative, quite differing from the R_r . It seems to imply that there are some complex relaxation mechanism to work in the long- T_1 phase region.

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REFERENCES

1. J.C. Chiang and A.G. MacDiarmid, *Synth. Met.*, 13, 193 (1986).
2. G.E. Wnek, *Synth. Met.*, 15, 213 (1986).
3. A.G. MacDiarmid, J.C. Chiang, A.F. Richter and A.J. Epstein, *Synth. Met.*, 18, 285 (1987).
4. Saoru Ni, Jinsong Tang and Fosong Wang, manuscript in preparation.
5. Lixiang Wang and Fosong Wang, *Acta Polymerica Sinica* (in press).
6. M. Angelopoulos, A. Ray and A.G. MacDiarmid, *Synth. Met.*, 21, 21 (1987).
7. S. Kazama, *Synth. Met.*, 16, 77 (1986).
8. S. Kazama, T. Hashimoto and A. Takake, *Synth. Met.*, 14, 153 (1986).
9. F. Devreux, *Phys. Rev. B*, 25, 6609 (1982).
10. M. Nechtschein, F. Devreux, R.L. Greene, T.C. Clarke and G.B. Street, *Phys. Rev. Lett.*, 44, 356 (1980).