SHORT COMMUNICATIONS

^{13}C NMR Study on the Specific Interaction of Cupric Ions with Polyacrylonitrile in Dimethylformamide

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Since 1951,[1] the interaction between polyacrylonitrile (PAN) and cuprous ions has attracted keen attention and was applied successfully, for a while, as a powerful dyeing method (i.e., cupper dyeing method) in PAN fiber industry. Here, cuprous ion was assumed to be first absorbed by PAN fibers, forming co-ordinate bonds with selected nitrile groups which were apparently arranged in a specific configuration, and the second reaction involved the formation of a salt between the dye anion and the weakly bound cuprous ion.[2,3] Another industrial application is the preparation of an electroconductive fiber from PAN in which PAN is treated with cupric ion, followed by a chemical reduction to copper or by the sulfurization to cupric sulfide.[4]

However, no direct experimental evidence has been presented to support the existence of co-ordinate bonds between copper cations and nitrile groups and this motivated strongly the present work.

Recently, we succeeded by ^{13}C NMR analysis in evaluating the triad and pentad tacticities of PAN samples, prepared by a redox initiator (hereafter referred to as R-PAN) and PAN samples, by γ-ray irradiation onto a urea–acrylonitrile canal complex (hereafter referred to as γ-PAN), and showed that the stereoregularities of R-PAN and γ-PAN can be well described by the Bernoulli and first-order Markov statistics,[5,6] respectively.

In this work, by using ^{13}C NMR technique we demonstrate the specific interaction of cupric ions with PAN having different stereoregularities dissolved in dimethylformamide (DMF).

A whole (unfractionated) R-PAN (the weight-average molecular weight M_w of 16.8×10^4), and a whole γ-PAN (M_w of 17.0×10^4), both employed in previous work,[5,6] were used. A 1:2 (volume) mixture of deuterated dimethylformamide (DMF) (DMF-d_7, E. Merk Inc., West Germany) and guaranteed grade DMF (Kishida Chem., Japan) was used as the solvent. Because of the good solubility in DMF cupric sulfate · 5 hydrates were used as the source of cupric ions. R- and γ-PAN were dissolved in the mixed solvent at a polymer concentration of 6.6 wt%. After ^{13}C NMR measurements for these solutions using an FT-NMR spectrometer (JEOL, FX-400), cupric ions were added step by step to each solution so that the cupric ion con-
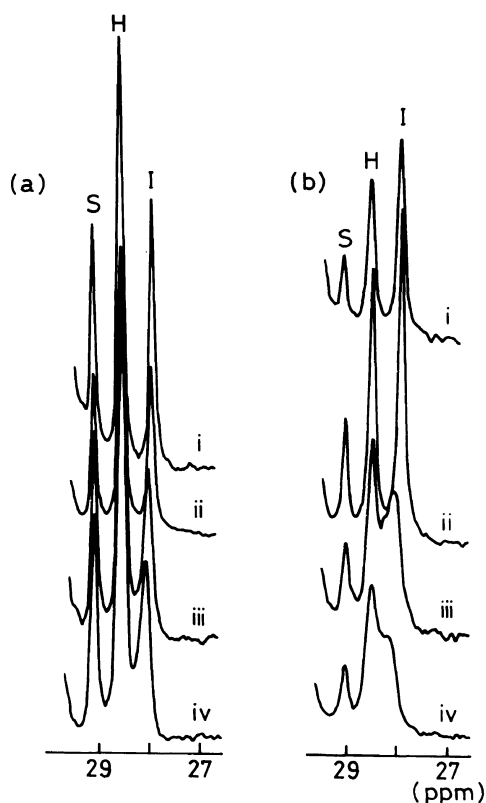
Figure 1. ^{13}C NMR spectra of the CH carbon region for R-PAN (a) and γ-PAN (b). Cupric ion concentration (i), 0%; (ii), 1/100 mol/CN residue of PAN; (iii), 1/20 mol/CN; (iv), 1/10 mol/CN.
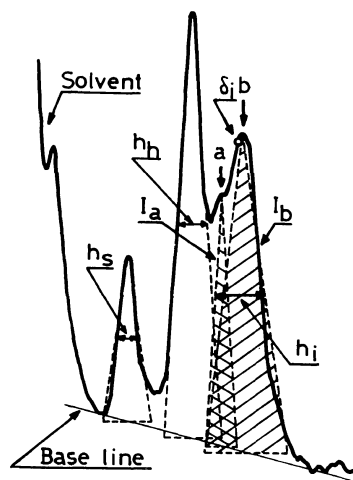

Figure 2. Illustration for determining the weight-averaged chemical shift and half value width for the triad I peak region of the NMR spectrum in Figure 1b (iii). a and b denote the chemical shift positions (in ppm) for the tops of the two approximated isosceles triangles, I_a and I_b denote the peak areas of the triangles, respectively.

centration was 1/100, 1/20, and 1/10 mol per cyano (CN) residue of dissolved PAN and for each solution, the ^{13}C NMR spectrum was again recorded. The NMR measurement was carried out under the following conditions: temperature, 80°C; repetition, 3 s; pulse width, 10 μs (45° pulse); number of pulse, 64 × 23. Chemical shift was determined using the TMS (0 ppm) as an internal reference.

Figure 1 shows ^{13}C NMR spectra of the CH carbon region of R-PAN (a) and γ-PAN (b). Cupric ion content increased from 0 to 1/10 mol/CN. Well separated three peaks for both R- and γ-PANs were already assigned to be isotactic (I), heterotactic (H), and syndiotactic (S) triads from higher magnetic field.[5] From the figure, it is quite obvious that for

both R- and γ-PAN samples, the peak responsible for the triad I dramatically decreases in the apparent intensity and considerably broadens concurrently with the addition of cupric ions. The broadening of the peaks for S and H triads by the addition of cupric ions was also observed but to a lesser extent. This means that cupric ions preferentially interact more strongly with the isotactic part of PAN than with the heterotactic and syndiotactic parts. A close inspection of the change in the I triad peak region for γ-PAN on addition of cupric ions revealed that the broadening of the peak was often accompanied by the appearance of a shoulder peak at the triad H peak side as shown in Figure 2. For these peaks, the weight-averaged value of chemical shift δ_i was roughly estimated from the chemical shift values (a and b ppm from lower magnetic field) for the tops and the peak areas (I_a and I_b) of the two approximated isosceles triangles (see Figure 2). Here, $\delta_i = b + I_a(a-b)/(I_a + I_b)$. The weight-averaged half value width h_i was determined as the half value width at the above δ_i ppm. Here, we assumed that the fractions of I,
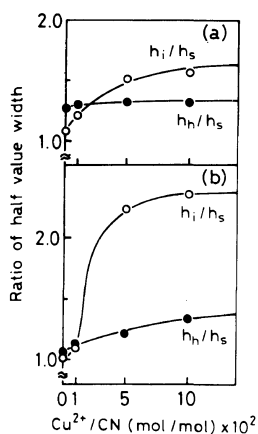
Figure 3. Change in the half value width of CH carbon peaks for R-PAN (a) and γ-PAN (b) as a function of cupric ion content. $\bigcirc$, h_i/h_s; $\bullet$, h_h/h_s.

H, and S triads remained unchanged on addition of cupric ions. This assumption seems reasonable by analogy of the experimentally confirmed constancy in the corresponding fractions for R-PAN where the I, H, and S triad peaks were well separated.

Figure 3 shows the effects of cupric ion concentration on the ratio of the half value width of CH carbon peaks for isotactic and heterotactic triads, h_i and h_h, to that for syndiotactic triad, h_s, of R-PAN (a) and γ-PAN (b). For both R- and γ-PANs, h_s was hardly effected by cupric ion concentration. The ratio h_i/h_s increased more significantly than h_h/h_s with an increase in cupric ion concentration. This tendency was much more obvious for γ-PAN than for R-PAN. These results strongly suggest that the continuous meso (m) sequence is preferable for the interaction of cupric ions with CN groups, since the m sequence block in γ-PAN is more abundant than in R-PAN.[6]

Figure 4 illustrates the change in the chemical shift of CH carbons responsible for the I, H, and S triads for R-PAN (a) and γ-PAN (b) with the addition of cupric ions. Obviously, in both cases, only the triad I peak significantly shifted toward the lower magnetic field as the cupric ion concentration increased. The H and S triad peaks were found practically unchang-
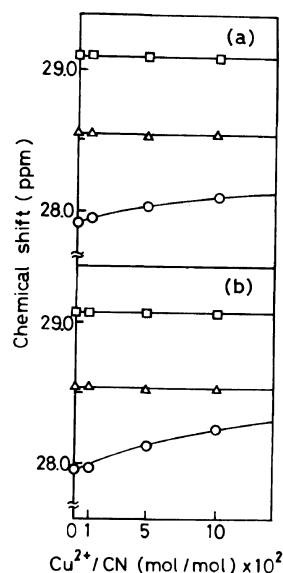

Figure 4. Change in chemical shifts of CH carbons for R-RAN (a) and γ-PAN (b). $\bigcirc$, I triad peak; $\triangle$, H triad peak; $\square$, S triad peak.

ed on addition of cupric ions. The lower magnetic field shift of triad I peak was much more conspicuous in γ-PAN than in R-PAN.

Figures 3 and 4 indicate that the changes in both the half value width and chemical shift of the triad I peak with the addition of cupric ions are larger in γ-PAN than in R-PAN. These facts might be related to the fact that the mmmm pentad fraction for γ-PAN is as much as 38%, but that for R-PAN, only 8%.[6] As noted in the previous work,[5] chemical shift of the CH carbon centered at the mm sequence can be relatively determined by the strong shielding effect $(-\varepsilon')$ of an induced magnetic field, an apparent deshielding effect (δ') caused by the disappearance of shielding effect in an isolated CN group and an apparent electron density increasing effect $(-\omega)$ caused by diminishing the electronegativity of CN group; all these effects result from the advent of the double bond nature brought about through the interaction of adjacent CN groups in the m sequence (m part might have an intermediate configuration between TT and TG). δ' was estimated to be very small (0.03—0.07 in
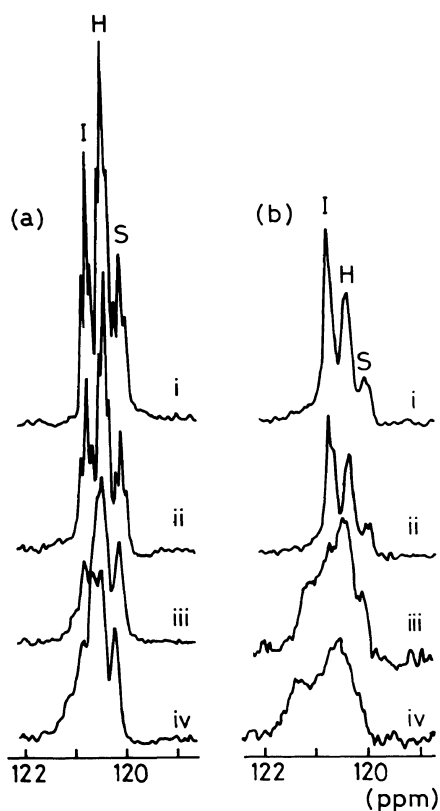
Figure 5. ^{13}C NMR spectra of the CN carbon region for R-PAN (a) and γ-PAN (b). Cupric ion concentration (i), 0%; (ii), 1/100 mol/CN; (iii), 1/20 mol/CN; (iv), 1/10 mol/CN.

^{13}C NMR spectra for CN carbon peak region also revealed a specific interaction between cupric ions and the CN carbon engaged in the triad I configuration, as shown in Figure 5. The lower three peaks for R-PAN represent 3 pentad sequences each having the triad I configuration (*i.e.*, mm sequence) at their center, and these peaks apparently decrease in the intensity as the cupric ion concentration increases (Figure 5(a)). For γ-PAN, an envelope peak (120.8 ppm) responsible for the triad I configuration becomes lower and broad as the cupric ion concentration increases. This broadening results in the appearance of two new peak envelopes in the lower magnetic field. This situation is the same as that of the triad I peak of R-PAN. The appearance of new envelopes in the lower magnetic field might be induced by a decrease in the electron density on CN carbons in continuous m sequences by specific interactions with cupric ions. Here, again the specific interactions of cupric ions with the triad I configuration part of PAN is obvious.

Since the pentad tacticity can be estimated from CN carbon peaks,[5,6] a more detailed study on the interactions between cupric ions and PAN molecules will be possible by analyzing the ^{13}C NMR CN carbon peaks.

ppm).[5] Then, if cupric ions specially interact with the m part, the most probable cause of the down field shift of the triad I peak might be the diminishing of ε' since ω can be considered not to be significantly influenced by the coordination of cupric ions on the π electrons of CN groups having double bond nature. This anticipation might explain the fact that the longer m part interacts more strongly with cupric ions than the shorter one.

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