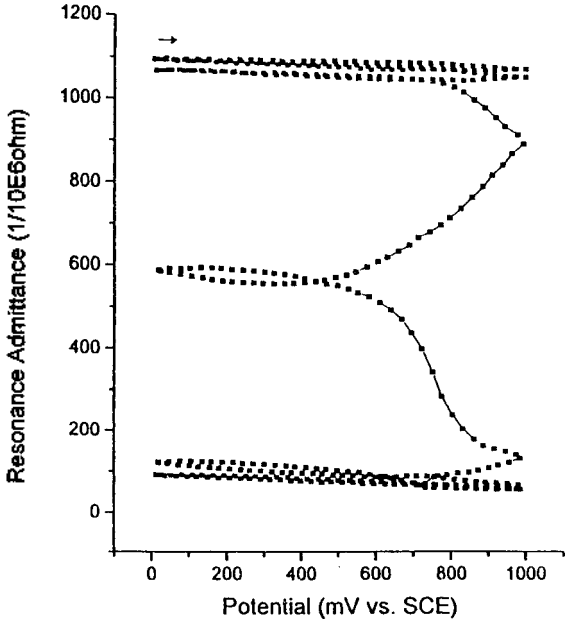

Figure 3. Change in resonance admittance observed during potential cycling in aqueous 0.2 M pyrrole (pH 7; 30 mM phosphate) and 0.1 M KBr solutions.

tion is shown in Figure 3, where resonant admittance shifts were plotted as the electrode potential was scanned cyclically. Sudden changes in resonant admittance are noticed between the nearly constant resonant admittance values observed during cyclic scans in the beginning and final stages. Similar changes in viscoelasticity of ppy were observed with longer scans when the potential scan was limited up to less positive potentials in the aqueous potassium bromide solution of pyrrole. For example, ten hours of continuous potential scans were required to observe the elastic to viscoelastic to elastic ppy films in the identical experiments except the potential window of zero to 0.65 V *vs* SCE. Thus three-stage evolution of viscoelasticity of ppy with films thicker is real in the presence of potassium bromide. We note that with platinum films deposited on mica by rf sputtering the three-stage evolution of platinum topography and crystallinity is evidenced for films of thickness between 20 and 1500 Å by scanning tunneling microscopy (STM).[9] We believe that the present EQCO results on ppy in the potassium bromide electrolyte are the first example showing the viscoelastic or structural evolution of conducting polymer films with thickness increased at the electrode/electrolyte interface. Further studies are in progress to investigate the viscoelastic property of ppy growing in different electrolyte media and to characterize the possible evolution of surface topography by STM.

In conclusions, we have established the cost-effective *in situ* electrochemical quartz crystal oscillator system to probe changes in viscoelastic property during electrodeposition and demonstrated that the viscoelastic property of ppy film prepared in aqueous potassium bromide solutions is fundamentally different from that in aqueous potassium nitrate solutions and that it significantly vary as film thickness increased.

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Conformational Studies on the DNA Oligomer d[(CG)$_3$TA(CG)$_3$] Duplex Induced by Hexaminecobalt(III) Chloride

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The B-Z transition illustrates that the conformational properties of DNA depend on the nature of the bases, the DNA sequences, and the solvent environment.[1] Z-DNA has been formed for some sequences which contain A·T as well as G·C basepairs.[2] However, the consecutive insertion of A·T basepairs into (dC-dG)$_n$ stretches in DNA oligomers strongly inhibits the formation of Z-form DNA. If two or more A·T basepairs, in an alternating purine-pyrimidine pattern, are inserted between stretches of alternating (dC-dG)$_n$, either the entire sequence may adopt a Z-DNA structure or only the (dC-dG)$_n$ stretches may do so. This depends on the solution conditions, the length of the (dC-dG)$_n$ stretches, and the number of A·T basepairs. For example, the oligomer duplex, d(CGCGTACGCG)$_2$, does not form a left-handed helix under any condition,[3] but the Z-?-Z junction is formed in the d[(br^5-CG)$_2$TTAA(br^5-CG)$_2$] duplex.[4] We have found that 2 mM Co(NH$_3$)$_6$Cl$_3$ converts the right-handed helix of the oligomer d(CG)$_5$ into a left-handed helix at room tempe-

rature (data not shown). However, the long d(C-G)$_n$ blocks are rarely found in native DNA5. In constrast to the rare occurence of d(C-G)$_n$ blocks, other alternating purine-purimidine sequences which have insertions of the A·T basepairs to the d(C-G)$_n$ block are widely found in native DNA.[6] Therefore, we have studied about the conformation of the DNA 14 mer d[(CG)$_3$TA(CG)$_3$]$_2$(TA 14 mer), using ^{1}H, ^{31}P NMR spectroscopy, and CD spectropolarimetry under Co-form condition. The sequence of the TA 14 mer is shown with the numbering system used:

```
 1 2 3 4 5 6 7 8 9 10 11 12 13 14
5'-CGCGCGTACGCGCG-3'
  . . . . . . . . . . . . . .
3'-GCGCGCATGCGCGC-5'
14 13 12 11 10 9 8 7 6 5 4 3 2 1
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The DNA oligomer d[(CG)$_3$TA(CG)$_3$] was synthesized on an Applied Biosystems 391 synthesizer using β-cyanoethyl phosphoramidites method. The synthesized oligonucleotide was purified by sephadex G-25 fine gel filtration column chromatography. The transition metal complex, hexaminecobalt (III) chloride($Co(NH_3)_6Cl_3$), was prepared by oxidizing a cobalt(II) chloride in concentrated ammonia solution.[7] All of the proton NMR experiments were carried out on 500 MHz and the phosphorus were at 202 MHz on Bruker AMX 500 spectrometer. The CD spectra were obtained on JASCO J720 spectropolarimeter and recorded from 230 to 310 nm.

The results of NMR and CD experiments indicate that the TA 14 mer maintains a B-DNA conformation at NaCl concentrations from 10 mM to 5 M at all temperatures(data not shown). Figure 1 shows the CD spectra of the B-form and the Co-form of the TA 14 mer at 40 ℃. The CD spectrum for the B-form of the TA 14 mer is characterized by a negative peak at 253 nm, a positive peak at 279 nm, and a zero point at 267 nm. While, in the Co-form, an inverted, red shifted CD spectrum is observed with a positive maximum at 275 nm, a zero point at 283 nm, and a negative peak at 295 nm. The inversion of the CD spectrum of the Co-form of the TA 14 mer is consistent with that the guanine residue adopts the *syn* conformation around the β-glycosidic bond forming Z-DNA.[8]

The conformational change of the Co-form of the TA 14 mer was studied as a function of temperature. The resulting spectra of the base and the T methyl proton resonances are shown in Figure 2. At 30 ℃, we can see easily that the Co-form of the TA 14 mer still has the B-conformation. As temperature is increased, the intensities of new methyl and base proton resonances get stronger, indicating a conversion to new conformation. At 50 ℃, there is apparent doubling of T7-Me resonance. This is consistent with near equal amounts of the B-DNA and new conformation in slow exchange on the NMR time scale. From the results of the temperature variation experiments, we find that the conformation of the Co-form of the TA 14mer is dependent upon the temperature. That is, this molecule is in the B-form at room temperature, but the Z-form might be favored at higher temperatures.

Segments of the NOESY spectra of the Co-form of the TA 14mer at 35 ℃ are shown in Figure 3. In this spectrum, the two strong intense crosspeaks (a) and (b) result from the close distance between the C-H5 and C H6 of the two conformation, B-form and new conformation. The crosspeak (e) must be intrabase interaction between the G-H8 and G-H1′ within the guanine residue. The NOESY spectrum shows the close proximity of G-H8 and G-H1′ in space which is consistent with guanine residues in the syn conformation around the β-gycosidic bond.[8] This is characteristic of Z-type structure. However, there is no crosspeak between H1′ and

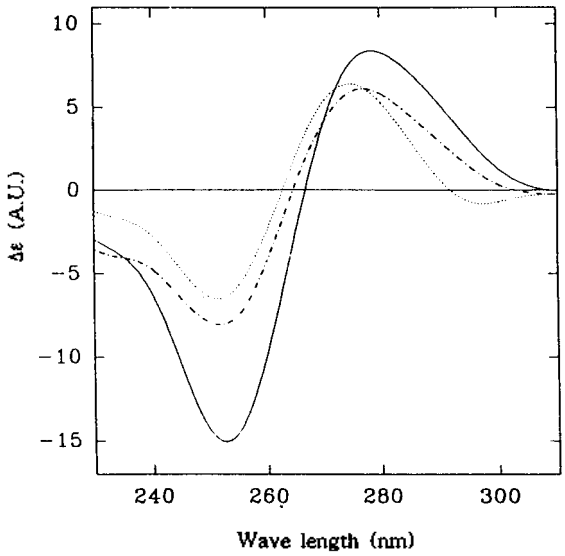

Figure 1. CD spectra of the B-form of the TA 14 mer (1.2 odu) in 0.3 mL aqueous solution, containing 10 mM phosphate buffer and 0.2 M NaCl, pH 7.0 at 20 ℃ (solid line), the Co-form of the TA 14 mer (1.2 odu) at 20 ℃ (dot and solid line) and the Co-form at 40 ℃ (dot line) in 0.3 mL aqueous solution, containing 20 mM NaCl and 2 mM $Co(NH_3)_6Cl_3$, pH 7.0.

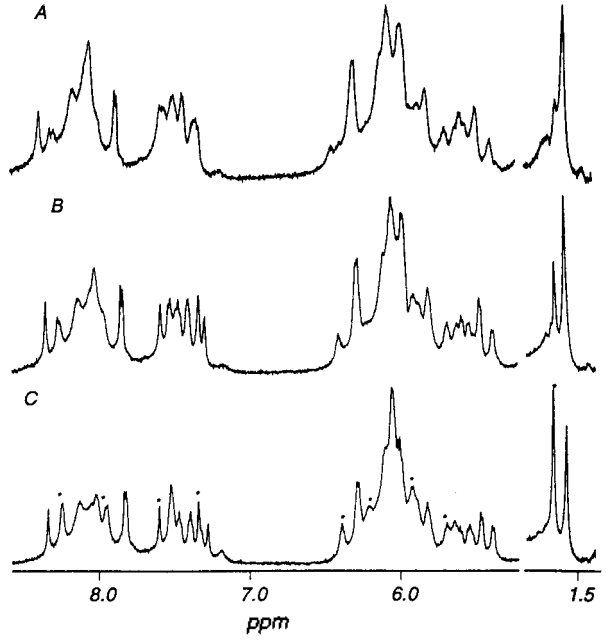

Figure 2. ^{1}H NMR spectra of the aromatic and the T methyl proton resonances of the Co-form of the TA 14 mer in 20 mM NaCl and 2 mM $Co(NH_3)_6Cl_3$, pH 7.0, D_2O at (A) 30 ℃, (B) 40 ℃, (C) 50 ℃. New resonances are marked by * in (C).

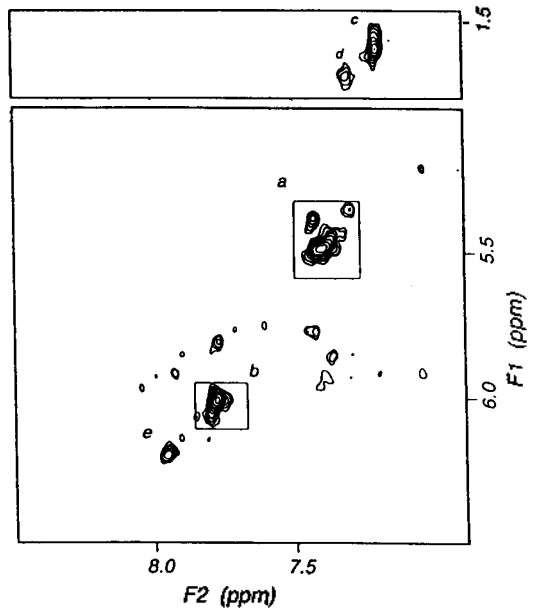

Figure 3. The corsspeak region between aromatic and sugar H1′ proton resonances of NOESY spectrum of Co-form of the TA 14 mer in D_2O at 35 ℃ and $\tau_m = 300$ ms. 512 t_1 values of 64 scans each were collected. the spectrum was zero-filled in t_1 and apodized with a squared sinebell phase shifted by 90° in both dimensions. (a) and (b) are overlapped crosspeaks between C-H5 and C-H6. (c) and (d) are crosspeaks between T-5Me and T-H6 of both B-form and Z-form. Samples are the same as Figure 2.

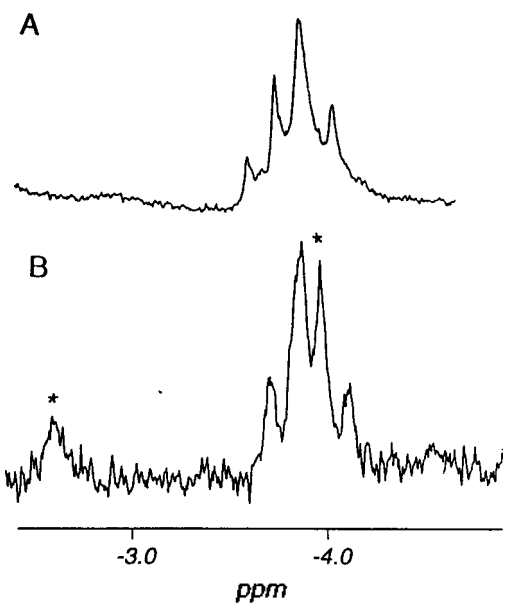

Figure 4. 202 MHz proton-decoupled ^{31}P NMR spectra of (A) B-form of the TA 14 mer in 10 mM phosphate buffer and 0.2 M NaCl, pH 7.0, D_2O at 25 ℃ and (B) the Co-form of the TA 14mer, which is the same as Figure 2, at 50 ℃. The experimet is carried out using the following conditions: 10000 scans, 90 flip angle, 1.5 sec aquisition time 16k data points. New resonances are marked by * in (B). Spectra are referenced relative to external TMP.

H8 proton in adenine residue, indicating that adenine residue has *anti* conformation around the β-gycosidic bond and the A·T basepairs are not in the Z-conformation.

^{31}P NMR spectra of the B-form and Co-form of the TA 14 mer at 50 ℃ are shown in Figure 4. The spectrum of Co-form of the TA 14 mer is markedly different from that of the B-form. The resonance at −3.9 ppm is likely due to the B-form, while, the new resonance which appears at −2.7 ppm is consistent with the phosphate in the Z-form. The relative integrated intensity of the downfield peak at −2.7 ppm to the upfield resonance between −3.7 and −4.2 ppm is approximately 1 : 8. In Figure 2C, comparison of two methyl intensities indicates that the amount of Z-form is about 50%. If the middle TpA were in Z-form at 50 ℃, we would expect this ratio to be 1 : 3. Thus, the conformation of the middle TpA step is not in Z-form. Therefore, it appears that while the two $d(CG)_3$ stretches of the TA 14 mer are in Z-form, the conformation of the middle TpA step is not the Z-form under Co-form conditions at 50 ℃. Thus, the overall conformation of the Z-form TA 14mer induced by hexaaminecobalt cation is likely to be a Z-Z junction.

In summary, the polyvalent cation hexaaminecobalt is needed at a concentration of 2 mM for the B-Z transition of this DNA oligomer although this transition is seen only at high temperatures. The Co-form of the TA 14 mer is not a normal Z-type structure. The conformation of the two $(CG)_3$ stretches is the Z-form but that of the middle TA step is not.

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