PROTONATED POLYNUCLEOTIDE STRUCTURES*

15. Metastable Protonated Polydeoxyribonucleotides**

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ABSTRACT. The CD spectra of three polydeoxyribonucleotide complexes, poly(dG–C), poly(dG–C), poly(dA–G), poly(dA–G), poly(dT–C) and poly(dT–G) have been studied as a function of pH at 25°C. Only poly(dA–G).poly(dT–C) showed large hysteresis, analogous to that observed for poly(dG).poly(dC), while the alternating pur–pin–pyr containing polymers reversible titration curves exhibited. The hysteretic form R of poly(dA–G).poly(dT–C) is metastable at neutrality and reverts spontaneously and irreversibly to the neutral form N upon heating to about 60°C. A whole titration cycle to pH 2.5 and back to neutrality has to be performed in order to obtain the metastable form R again.

ABBREVIATION. CD = circular dichroism.

I. INTRODUCTION

In the preceding paper [1] protonation hysteresis phenomena in the system poly(dG).poly(dC) were described. It was of evident interest, if alternating polydeoxyribonucleotides or other sequences would also show hysteresis. In this paper the titration results on G–C and A–T containing polymers are presented. Only the all-purine.all-pyrimidine polymers show hysteresis, while the alternating polynucleotides do not.

II. MATERIALS AND METHODS

Poly(dGC).poly(dGC) was an experimental lot from Boehringer (Mannheim, Germany) and

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was kindly given by Dr. K. Wulff. Poly(dA-G).poly(dT-C) and poly(dA-C).poly(dT-G) were prepared by a standard method using *E. coli* DNA polymerase I [2].

The spectroscopic and titration measurements were performed as described in the previous paper [1].

III. RESULTS AND DISCUSSION

The observation of the exceptionally large hysteresis observed with poly(dG).poly(dC) prompted us to examine other polydeoxyribonucleotides. The analogous, alternating G–C polymer, poly

![Graph](image.png)

**Fig. 1.** (a) CD spectra of poly(dG–C).poly(dG–C) in 0.15 N NaCl at 25° at pH 6.3 (N), pH 3.0 (I), pH 2.4 (A), back titration to pH 7.6 (R). – (b) CD spectra of poly(dA–G).poly(dT–C) in 0.15 M NaCl at 25° at pH 7.5 (N), pH 5.0 (I), pH 2.4 (A), back titration to pH 7.1 (R). – (c) CD spectra of poly(dA–C).poly(dT–G) in 0.15 M NaCl at 25° at pH 7.0 (N), pH 4.0 (I), pH 2.8 (A), back titration to pH 7.2 (A).