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(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–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 sequen-
ces 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(dGC).poly(dGC)

![Graph](image_url)

**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).