Conformational Transitions of Poly(dI-dC) in Aqueous Solution as Studied by Classical Raman Spectroscopy

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Abstract. Poly(dI-dC) in aqueous solution can undergo different equilibrium geometries which strongly depend on the salt nature and the concentration. These structures were studied by classical Raman spectroscopy (RS). Spectral changes depending on NaCl concentration and on the presence of Ni^{2+} ions were observed and interpreted on the basis of previously obtained results from resonance RS studies of poly(dI-dC) and classical RS studies for other alternating purine-pyrimidine polydeoxyribonucleotides, i.e. poly(dG-dC), poly(dA-dT) and poly(dA-dC)(dG-dT), which also showed B to Z conformational transitions upon varying the salt concentrations. It is shown that: i) The low-salt structure (0.1 mol/l NaCl) is in the pure canonical B conformation. ii) The high-salt (5 mol/l NaCl) Raman spectrum is similar to that obtained for the low-salt concentration. Thus the high-salt structure corresponds to the right-handed polymer with characteristic bands for both the B (predominant) and A conformations with some weak Z conformation markers which indicate a tendency for B to Z conformational transition of the polymer. iii) The addition of 9 \cdot 10^{-4} mol/l NiCl_{2} to the high-salt solution induces Z-conformation of the polymer.

Key words: Poly(dI-dC) — B and Z conformation — High-salt structure — Raman spectroscopy

Introduction

Poly(dI-dC) is a helical double-stranded alternating polynucleotide built with inosine and cytosine residues, which only form two hydrogen bonds per pair. This is in contrast with the three H-bonds/bp found in poly(dG-dC), owing to the lack of a 2-amino group in the inosine residues as compared to the guanine ones.

The conformation of this polymer has been studied by different spectroscopic
methods. Investigations of poly(dI-dC) by circular dichroism (CD) (Mitsui et al. 1970) revealed cytosine and inosine to form Watson-Crick base pairs. This result was confirmed by Mirau and Kearns (1984) in a study of the conformation of poly(dI-dC) in low-salt aqueous solution by one and two dimensional NMR. They also suggested that the conformation of poly(dI-dC) is similar to the B form of DNA. Sutherland and Griffin (1983) studied the conformation of this polymer by vacuum UV CD. They showed that the vacuum UV CD spectra of poly(dI-dC) are similar to the spectra of other nucleic acids with a right handed double helix in the structure. The structure of poly(dI-dC) in a low-salt solution was also determined by the classical Raman spectroscopy (RS) (Weidlich et al. 1990) as being B conformation. In a more recent CD study Vorlíčková and Sagi (1991) showed that the addition of a small amount of NiCl₂ to 5 mol/l NaCl solution of poly(dI-dC) was able to isomerize the polymer into the Z form. As was shown in the same study, the appearance of two very deep negative bands was characteristic for the high-salt structure of this polymer. This spectral feature is very similar to those observed for the so called “X-form” of poly(dA-dT) (Vorlíčková and Sagi 1991). In another study the same authors suggested an equilibrium structure for poly(dI-dC) between two right-handed conformations (B predominant) where the proportion depended on the salt concentration (Vorlíčková and Kypr 1985). In a study of deuterium exchange at C8-H group of hypoxanthine in poly(dI-dC) by Benevides and Thomas Jr. (1985), the authors showed that from the dynamic point of view the structure of the low-salt poly(dI-dC) seems to be a mixture of A and B forms, the so called B/A conformation, with the B form being predominant. Recently, we could show by resonance Raman spectroscopy (RRS), that the high-salt structure of poly(dI-dC) for which “X” conformation was proposed (Vorlíčková and Sagi 1991), had nearly the same base stacking geometry as that of the low-salt structure. Nevertheless, the chain conformational markers of the high-salt structure which is predominantly right-handed, present a mixture of features characteristic for B and A forms, with some very weak Z form markers (Miškovský et al. 1993). The most recent report in this field is a work by Wang and Keiderling (1993) where the authors interpreted the low-salt structure of poly(dI-dC) as B conformation, the high-salt one as a right-handed structure with some differences from the canonical B form, and the high-salt structure in the presence of 9 · 10⁻³ mol/l NiCl₂ as a left-handed structure.

In this work we present a classical Raman study of low-salt, high-salt and NiCl₂ containing high-salt solutions of poly(dI-dC). This study was prompted by the fact that the classical RS is more sensitive than RRS to vibrations of the conformationally sensitive sugar-phosphate backbone. The vibrations of phosphate chains provide good structural markers of the secondary structure of DNA. The most important markers are observed in the 600–1000 cm⁻¹ region, and they correspond to the sugar-phosphate vibrations of the DNA molecule.
Materials and Methods

Poly(dI-dC) samples (Sigma, 30 mg/ml) were used without further purification and prepared in $10^{-2}$ mol/l Tris buffer, pH 7.1, by adding 0.1 mol/l NaCl to the solution (B form), 5 mol/l NaCl (high-salt structure) or 5 mol/l NaCl plus $9 \cdot 10^{-3}$ mol/l NiCl$_2$ (Z form). To avoid possible precipitation the sample was prepared as a low concentration solution (about 1 mg/ml) and was later concentrated by slow evaporation using a vacuum centrifuge. The final concentration was approximately 30 mg/ml. In this preparation no clear precipitation was observed, but it could not be completely ruled out. Aqueous solutions of cytosine and inosine (Sigma) were prepared with the same buffers.

The Raman spectra of the polynucleotide solutions and the corresponding buffers were obtained in the 500–1750 cm$^{-1}$ range using a Jobin-Yvon HRD1 double monochromator. The 488 nm line (300 mW power at the sample) of a Spectra Physics BeamLok 2060/65 ion laser was used as the excitation wavelength. The presented spectra represent an average of 5 consecutive scans recorded at 1 cm$^{-1}$ steps. The accuracy of the band position is 2 cm$^{-1}$. The resulting spectra were smoothed by the fast Fourier transform method.

Results

The Raman spectra of poly(dI-dC) in 0.1 mol/l NaCl, 5 mol/l NaCl, and 5 mol/l NaCl plus $9 \cdot 10^{-3}$ mol/l NiCl$_2$ aqueous solutions are presented in Fig. 1. For an unambiguous assignment of the Raman bands of poly(dI-dC) and to rule out possible spectral changes caused by the local interactions of the hydrated nickel ions with the bases in aqueous solution, we also present the Raman spectra of inosine and cytosine (Figs. 2 and 3). They were obtained under the same conditions as those for poly(dI-dC). The frequencies of the Raman bands of poly(dI-dC) and their assignments are presented in Table 1.

Region 600–1000 cm$^{-1}$

This region mainly involves ring breathing vibrations sensitive to the nucleoside conformations (sugar puckering and sugar-base orientation) (Erfurth et al. 1975; Thomas Jr. and Benevides 1985).

One of the most important markers of the B to Z conformational transition in the altering polynucleotides is the breathing vibration of purine the frequency of which depends on the conformation of the sugar and on the glycosidic torsion angle (Benevides and Thomas Jr. 1983). This vibration of guanine in B form of poly(dG-dC) is localized at 680 cm$^{-1}$ and shifts to 625 cm$^{-1}$ in Z form of this polymer (Thamann et al. 1981; Benevides and Thomas Jr. 1983; Wartell et al. 1983). The same behavior of the guanine vibration can be seen in the B-Z transition of poly[d(A-C)].poly[d(G-T)] (Ridoux et al. 1987). The adenine vibration in the B-Z transition of poly[d(A-T)] has a similar behavior (Ridoux et al. 1988). These conformational transitions were induced by the high-salt concentration and by Ni$^{2+}$...
Figure 1. Classical Raman spectra of poly(dl-dC) in aqueous solutions, 10⁻⁴ mol/l Tris buffer (pH 7.1) under various conditions of ionic strength. A - 0.1 mol/l NaCl ("low-salt", B form), B - 5 mol/l NaCl ("high-salt" form), C - 5 mol/l NaCl plus 9·10⁻³ mol/l NiCl₂ (Z form).

ions. A change of the position of the band from 666 cm⁻¹ for B form to 622 cm⁻¹ of Z form of poly[d(A-T)], and from 682 cm⁻¹ for B form to 622 cm⁻¹ of Z form of poly[d(A-C)].poly[d(G-T)] has been observed under these conditions (Ridoux et al. 1987; 1988). For B form of poly[d(A-T)] and poly[d(A-C)].poly[d(G-T)] this form is interpreted as a breathing vibration of guanosine and/or adenosine in the C2' endo/anti geometry, and for Z form as a breathing vibration of guanosine and/or adenosine in the C3' endo/syn geometry. This interpretation is supported by a normal mode calculation of the adenine molecule, where the mode observed at 643 cm⁻¹ in the resonance Raman spectra was interpreted as being of a considerable ring-breathing nature (Dhaouadi et al. 1993). The band at 660 cm⁻¹ was observed in our spectrum of B form of poly(dH-dC) (Fig. 1). Two medium intensity bands at 652 and 620 cm⁻¹ appear in Z form. Since hypoxanthine belongs among the
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Figure 2. Classical Raman spectra of inosine in aqueous solutions, $10^{-2}$ mol/l Tris buffer (pH 7.1) under various conditions of ionic strength. A – 0.1 mol/l NaCl, B – 5 mol/l NaCl. C – 5 mol/l NaCl plus $9 \cdot 10^{-3}$ mol/l NiCl$_2$.

Purine bases we assumed a similar behavior of the hypoxanthine base as for adenine and/or guanine. This means that these two bands are assigned to a hypoxanthine breathing vibration as has been also found by the normal mode analysis of the hypoxanthine molecule (Uličný et al. 1994b). So, the band at 660 cm$^{-1}$ is interpreted as representing a vibration of inosine in the C2′ endo/anti conformation (B form), and the band at 620 cm$^{-1}$ is assigned to the same vibration of inosine in the C3′ endo/syn conformation (Z form). The band at 652 cm$^{-1}$ in our spectrum of poly(dI-dC) (Fig. 1C) shows that the Z form of poly(dI-dC) probably is not a pure canonical Z form.

A medium intensity band at 730 cm$^{-1}$ is observed for the B form structure of poly (dI-dC) (Fig. 1A). A corresponding band at 720 cm$^{-1}$ is observed in the spectrum of inosine (Fig. 2). The difference of 10 cm$^{-1}$ for this structurally sensitive
Figure 3. Classical Raman spectra of cytosine in aqueous solutions, $10^{-2}$ mol/l Tris buffer (pH 7.1) under various conditions of ionic strength. A - 0.1 mol/l NaCl, B - 5 mol/l NaCl, C - 5 mol/l NaCl plus $9 \cdot 10^{-3}$ mol/l NiCl$_2$.

band is caused by the different environment of free hypoxanthine, and hypoxanthine incorporated in the double stranded structure of poly(dI-dC). This band was also observed in the spectra of inosine by Medeiros and Thomas Jr. (1971a,b) and interpreted as breathing vibration of the hypoxanthine ring. The normal mode analysis made by Uličný at al. (1994a) suggests the association of this mode of vibration with the C1′O4′-N3C4-C1′N9C4 part of the inosine molecule. Thus the conformationally sensitive vibration of the hypoxantine ring is coupled with the sugar vibrations. In the previous RRS of this polymer we showed this band to be localized at 732 cm$^{-1}$ for B form, at 725 cm$^{-1}$ for Z form, and the 722 cm$^{-1}$ band for the high-salt form of poly(dI-dC) can be a good Z form marker (Miškovský et al. 1993). We observed a similar behavior for the band at 733 cm$^{-1}$ in the RR spectra of poly(dA-dT) (Miškovský et al. 1989a) and poly(rA-rU) (Tomková et al. 1994), and interpreted it as B-Z transition sensitive adenine breathing vibration.
<table>
<thead>
<tr>
<th>B-conformation</th>
<th>High-salt conformation</th>
<th>Z-conformation</th>
<th>Assignment</th>
<th>B→High salt change</th>
<th>B→Z change</th>
</tr>
</thead>
<tbody>
<tr>
<td>660 w</td>
<td>652 w, br</td>
<td>652 m, br</td>
<td>I: hypoxanthine ring breathing</td>
<td>I: downshift</td>
<td>I: intensity increase</td>
</tr>
<tr>
<td>730 m</td>
<td>730 m</td>
<td>730 m</td>
<td>I: C1'O4'-N3C4-C1'N9C4</td>
<td>no change</td>
<td>no change</td>
</tr>
<tr>
<td>792 vs</td>
<td>790 vs</td>
<td>792 vs</td>
<td>OPO symmetric stretch</td>
<td>no change</td>
<td>no change</td>
</tr>
<tr>
<td>834 sh</td>
<td>~822 sh</td>
<td>~826 sh</td>
<td>OPO antisymmetric stretch</td>
<td>OPO: downshift</td>
<td>OPO: downshift</td>
</tr>
<tr>
<td>1264 m</td>
<td>1236 m</td>
<td>1246 m</td>
<td>C: δC6H-C4N4'</td>
<td>C: doublet</td>
<td>C: doublet</td>
</tr>
<tr>
<td>1318 m</td>
<td>1318 m</td>
<td>1318 m</td>
<td>I: N7C8H-N9C8H-C8N7-N9C8</td>
<td>I: intensity decrease</td>
<td>no change</td>
</tr>
<tr>
<td>1340 m</td>
<td>1336 m</td>
<td>1336 m</td>
<td>I: hypoxanthine ring</td>
<td>I: downshift</td>
<td>I: intensity decrease</td>
</tr>
<tr>
<td>1382 w</td>
<td>1378 w</td>
<td>1384 m</td>
<td>I: NC2H-C2N3</td>
<td>I: downshift</td>
<td>I: intensity increase</td>
</tr>
<tr>
<td>1426 m</td>
<td>1414 w</td>
<td>1426 m</td>
<td>I: NC8H-N3C2H-N9C8-N1C2H</td>
<td>I: doublet, intensity decrease</td>
<td>I: intensity increase</td>
</tr>
<tr>
<td>1432 w</td>
<td>1432 w</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The position of this band is unchanged in the high-salt and Z form of the polymer (Fig. 1) (only a little change in relative intensities is observed), indicating the presence of B structure in the high-salt concentration solution as well as in the high-salt plus nickel solution of poly(dI-dC).

Another band with the same position for all of the three conformations of poly(dI-dC) is the cytosine 792 cm$^{-1}$ band (Fig. 1). This vibrational mode was observed in all the three spectra of cytosine (Fig. 2) at 788 cm$^{-1}$ but not in the spectra of inosine. Fodor et al. (1985) have observed this band and interpreted it as the N1R-C4N-C4C5C6 vibration at 782 cm$^{-1}$ in the RRS of dCMP (266 nm excitation wavelength). This band also contains the OPO symmetric stretch vibration (Benevides and Thomas Jr., 1983; Brown and Peticolas 1975) that is shifted towards the lower 760 cm$^{-1}$ frequency for Z form of the polymer (Fig. 1C). A similar behavior of this band was observed in a study of the B-Z transition of (dG-dC)$_n$-(dG-dC)$_n$ solution (Wartell et al., 1983) where a new band appeared at 750 cm$^{-1}$ in the Z form spectrum. The new bands at 742 cm$^{-1}$ and at 746 cm$^{-1}$ were also observed in the RR spectra of Z forms of poly[d(A-C)].poly[d(G-T)] (Ridoux et al., 1987) and poly[d(A-T)] (Ridoux et al., 1988), respectively. These conformationally sensitive bands are characteristic for Z form of the polymers, and have been assigned to the symmetric stretch vibration of the OPO group (Benevides and Thomas Jr., 1983). We can suggest on the basis of the above mentioned data that the presence of Ni$^{2+}$ ions in the high-salt solution of poly(dI-dC) leads to a conformation change of poly(dI-dC) to yield Z form (Fig. 1C).

One of the most important markers of the B-Z transition in the classical RS is the OPO antisymmetric stretch vibration that is localized at 830 ± 4 cm$^{-1}$ in B form spectrum, at 810 cm$^{-1}$ in Z form spectrum, and at 807 ± 3 cm$^{-1}$ in A conformation spectrum of DNA (Benevides and Thomas Jr., 1983). In our spectra this band was observed as a medium intensity shoulder at 834 cm$^{-1}$ for B form of poly(dI-dC) (Fig. 1A). When the transition to the high-salt or Z form occurred, the band shifted to lower frequencies (Fig. 1B and C). The differential Z minus B spectrum (Fig. 4) shows a positive band at 812 cm$^{-1}$. Similar shifts of the bands from 836 cm$^{-1}$ and 832 cm$^{-1}$ to 810 cm$^{-1}$ and 815 cm$^{-1}$ were observed in studies of poly[d(A-C)].poly[d(G-T)] (Ridoux et al., 1987) and poly[d(A-T)] (Ridoux et al., 1988). Observation of B to Z transition in poly(dG-dC).poly(dG-dC) solution (Thamann et al., 1981) showed a downshift of this vibration from 830 cm$^{-1}$ for B form to 810 cm$^{-1}$ for Z form structure. On the basis of the above, we can assume that in the presence of nickel poly(dI-dC) is in Z form (Fig. 1C). The spectrum of poly(dI-dC) in the high-salt form (Fig. 1B) shows a shoulder at 822 cm$^{-1}$ (Fig. 1B) that is the 4 cm$^{-1}$ downshift in comparison with the Z form of the polymer (Fig. 1C). Therefore, its position could indicate the presence of the A or Z form structure in the high-salt solution of poly(dI-dC).
Region 1000–1500 cm$^{-1}$

A band at 1264 cm$^{-1}$ is observed in the B form spectrum of poly(dI-dC) (Fig. 1A). This band was observed at 1250 cm$^{-1}$ in the RR spectra (256 nm excitation wavelength) of dCMP and assigned to the $\delta$C6H-C4N4' vibration of cytosine (Fodor et al. 1985). This vibration was also observed for B form of poly(dI-dC) at 1255 cm$^{-1}$ excited by 281 nm excitation wavelength (Miškovský et al. 1993) and at 1257 cm$^{-1}$ for B form of native DNA (Prescott et al. 1984). In transition from B to high-salt and Z form structures of poly(dI-dC), one can observe the appearance of a doublet at 1236 and 1256 cm$^{-1}$ in the high-salt form (Fig. 1B), and at 1246 and 1268 cm$^{-1}$ in Z form spectra (Fig. 1C) of poly(dI-dC). Similarly, in B to Z conformational transition of poly[d(A-T)].poly[d(G-C)], the band at 1251 cm$^{-1}$ for B form splits into a doublet with frequencies at 1245 cm$^{-1}$ and 1257 cm$^{-1}$ (Ridoux et al. 1987). The different behavior of this doublet for the high-salt and Z form of the polymer corresponds to different structures of poly(dI-dC) in 0.1 mol/l NaCl, 5 mol/l NaCl and 5 mol/l NaCl plus $9 \cdot 10^{-3}$ mol/l NiCl$_2$ solutions.

An interesting change was observed in transition from B to high-salt structure of poly(dI-dC). The band that was observed at 1318 cm$^{-1}$ in B form spectrum completely disappeared in the high-salt form (Fig. 1A and B). The position and the intensity of this band were unchanged for Z form as compared to B form. The corresponding band was observed at 1320 cm$^{-1}$ in the Raman spectrum of inosine (Fig. 2A). This band has been interpreted as a vibration of the hypoxanthine ring (Medeiros and Thomas Jr. 1971b). On the basis of their normal mode analyses Uličný et al. (1994a) assigned this mode mainly to the NC8-H bending motions of inosine. This interpretation indicates the presence of the sugar moiety in this vibration and thus it can be conformationally sensitive. However, the interpretation of possible structural changes of the high-salt structure of poly(dI-dC) reflecting this vibration is difficult. The reason for this is that local Ni$^{2+}$ interaction with N7 position of hypoxantine cannot be excluded that can lead to a change of the of poly(dI-dC) spectrum (Adam et al. 1986).

The inosine band at 1340 cm$^{-1}$ was observed in poly(dI-dC) B form spectrum (Fig. 1A). This band was observed at 1351 cm$^{-1}$ by Medeiros and Thomas Jr. (1971b) and assigned to hypoxantine ring vibration. The position of this band in the high-salt and Z form spectra is 1336 cm$^{-1}$. The study of B to Z transition in poly(dA-dC).poly(dG-dT) and in poly(dA-dT) by classical Raman spectroscopy (Ridoux et al. 1987, 1988) showed shifts of the adenine band from 1342 cm$^{-1}$ to 1328 cm$^{-1}$ and from 1342 cm$^{-1}$ to 1332 cm$^{-1}$, respectively. As we assume a similar behavior of identical purine modes for adenine and inosine, it can be concluded that the downshift of this band is characteristic for B to Z transition of poly(dI-dC). Also, it means that the high-salt form of the polymer contains some portion of the Z structure.
The band observed in the B form at 1382 cm\(^{-1}\) corresponds to inosine vibration (Brown et al. 1972; Small and Peticolas 1971). This band was interpreted on the basis of the normal mode analysis as NC2-C2N3 vibration of inosine (Uličný et al. 1994a). In transition to the high-salt form of poly(dI-dC) we can observe a weak decrease of the relative intensity and a downshift of this band to 1378 cm\(^{-1}\) (Fig. 1B). This change can be due to local interaction of Na\(^+\) ions with inosine since the same behavior of this band is observed in the high-salt and high-salt plus nickel spectra of inosine (Fig. 2). On the other hand, the intensity increase and the weak upshift of this band in the Z form spectrum of poly(dI-dC) (Fig. 1C) is caused by structural changes of the polymer. The same behavior of this band was observed in our previous RR study of B to Z transition of poly(dI-dC) (Miškovský et al. 1993).

Another interesting change is observed in B to high-salt transition of poly(dI-dC). The band observed for B form at 1426 cm\(^{-1}\) (Fig. 1A) is split into a doublet with frequencies at 1414 cm\(^{-1}\) and 1432 cm\(^{-1}\) in poly(dI-dC) high-salt form (Fig. 1B). This band corresponds to inosine vibration observed at 1420 cm\(^{-1}\) in the spectrum of inosine (Fig. 2A) and interpreted as NC8H-N3C2H-N9C8-N1C2H vibration (Uličný et al. 1994a). A shift of the adenine band from 1422 cm\(^{-1}\) to 1418 cm\(^{-1}\) accompanied by a relative intensity decrease was observed in a study of B to A transition of native DNA (Prescott et al. 1984). Thus we suppose the same behavior for the 1426 cm\(^{-1}\) inosine band that indicates the presence of A form in the high-salt structure in poly(dI-dC).

Discussion

Upon increasing NaCl concentration and adding a small amount of NiCl\(_2\) ions into the poly(dI-dC) solution changes occurred in the polymer conformation. In the present work these changes were studied by classical Raman spectroscopy and compared with classical RS results obtained previously for other Pu-Py alternating copolymers under the same variations of ionic strength. The spectral changes and their above proposed interpretations are summarized in Table 1.

The addition of 9·10\(^{-3}\) mol/l NiCl\(_2\) into the high-salt solution of poly(dI-dC) leads to B-Z conformational transition of the polymer. In particular, Z conformation is characterized by the following marker bands: a band at 620 cm\(^{-1}\) corresponding to inosine breathing mode coupled to sugar vibrations; OPO symmetric stretch vibration at 760 cm\(^{-1}\); OPO antisymmetric stretch vibration at 812 cm\(^{-1}\) (see the difference spectrum in Fig. 4), which appears in the spectrum of Z form of poly(dI-dC) as a shoulder at approximately 826 cm\(^{-1}\) (Fig. 1C); as well as a doublet at 1246 and 1268 cm\(^{-1}\) corresponding to cytosine δC6H-C4N1' vibration; and inosine band at 1336 cm\(^{-1}\). The bands at 652 cm\(^{-1}\) and at 730 cm\(^{-1}\) (characteristic of B form) suggest that this structure is not a pure canonical Z form.
as was observed by RR spectroscopy for a low concentrated sample of poly(dI-dC) (Miškovský et al. 1993). We suppose that this can be due to the high concentration of poly(dI-dC) in solution (Miškovský et al. 1989b).

According to our observations, the high-salt structure of poly(dI-dC) still is a right-handed structure with the following characteristic B and A conformation markers: i) B form: the spectrum is similar to that at low-salt with differences cited for A and Z form, particularly, no position change of inosine 730 cm$^{-1}$ vibration, ii) A form: downshift of OPO antisymmetric vibration from 834 cm$^{-1}$ to 822 cm$^{-1}$ (shoulder), downshift and an intensity decrease of 1426 cm$^{-1}$ band for B form at 1414 cm$^{-1}$ in the high-salt structure of the polymer. In addition, weak bands are observed in the high-salt spectrum typical of Z conformation, iii) Z form: downshift of OPO antisymmetric vibration from 834 cm$^{-1}$ to 826 cm$^{-1}$ (shoulder, which appears at 812 cm$^{-1}$ in the difference spectrum, Fig. 4), downshift of the 1340 cm$^{-1}$ band assigned to inosine vibration at 1336 cm$^{-1}$. It reflects a tendency for B to Z transition of poly(dI-dC).

In conclusion, we can confirm the interpretation of our previous results obtained in the resonance Raman study of this polymer (Miškovský et al. 1993). The high-salt structure of poly(dI-dC), CD spectra of which resemble that termed “X” form (Vorlíčková and Sagi 1991), is still a right-handed structure with the predominant B character that reflects some features typical of A conformation. This conclusion is coherent with our other studies of “X” form of various polynucleotides (Mojzeš et al. 1992; Tomková et al. 1995). These structures have been found to be right-handed and characterized by conformational markers of B and A conformations depending on the primary structure of the polymers. Here, the appearance of Z form markers in the high-salt form of poly(dI-dC) reflects the structural transition into Z form of the polymer.
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