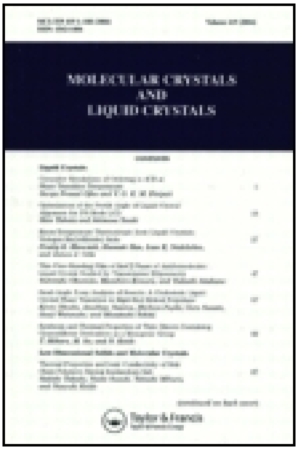

Molecular Crystals and Liquid Crystals

The Poly-A Interaction and Interfaces with Carbon Nanotubes

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The Poly-A Interaction and Interfaces with Carbon Nanotubes

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The interaction between a single and a double strand poly-A and single wall carbon nanotubes is studied with SEIRA, SERS, and AFM techniques. After the purification and separation, the sample of nanotube-poly-A contains 1–5 nanotubes covered by poly-A. According to SEIRA and SERS spectroscopy, poly-A in a single strand form preserves its initial conformation with numerous disorders and breaks in a single strand of poly-A at the carbon nanotube surface. After the adsorption on the nanotube surface, the double strand form of poly-A changes its conformation with a partial loss of the pairing between adenine bases. The main cites of the interaction of poly-A with nanotubes are adenine and phosphate groups.

Keywords: double strand; interaction; polyriboadenylic acid (poly-A); single strand; single wall carbon nanotubes (SWCNTs)

1. INTRODUCTION

The unique properties of fullerenes and carbon nanotubes (CNTs) in combination with biomolecules can lead to the creation of new types

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of adsorbents, drug delivery systems, novel materials for implants, miniature electronic and optical devices, sensors, etc. [1–10]. Biocompatibility, *in vivo* applications, and a high sensitivity of CNTs are some of their attractive features in this regard. In relation to that, the interaction of CNTs with nucleic acids (NAs) is of particular importance. The creation of new devices and new materials on the basis of NA-nanotube hybrids requires the full comprehension of their interaction mechanisms. Despite the numerous publications, any comprehension of the mechanism of interaction of CNTs and NAs has not been established up to date [11].

It is supposed [12] that the RNA-CNT hybrids have a number of potential advantages over the DNA-CNT ones for biomedical applications, such as: 1) RNA cannot be integrated into a host chromosome, so it is less mutagenic than DNA 2) modification of RNA has been shown to suppress a recognition by the mammalian immune system, and, therefore, RNA-wrapped CNTs may be a more effcient delivery system than DNA, and 3) RNA can be directly functional in cells, e.g., released RNA may act as interfering RNA (RNAi) to silence a target gene [13]. The last point is the most actual in modern biotechnology and medicine, and it is actively developed in the present time [13].

That is why here we study the CNT interaction and interfaces with 2 conformations of polyadenylic acid potassium salt (poly-A) in double and single strands that could be used as a model for different forms of nucleic acids.

2. METHODS AND MATERIALS

SWCNTs have been synthesized by arc discharge between two graphite electrodes in a He atmosphere at the Moscow Institute of Physics [14]. The nanotube content in the raw material was about 30–40 wt %. The contaminants are amorphous carbon, metallic catalyst particles, soot, etc. The material has been certified by high-resolution transmission electron microscopy and Raman scattering [14]. The length of SWCNTs was 1–2 µm, and the diameters are 0.9–1.6 nm with preferential fraction of 1.4–1.5 nm. The probe of SWCNTs was mixed with a poly A aqueous solution (0.25–0.5 mg/ml) (0.1–1 weight part of nanotubes to 1 weight part of poly-A) by an ultrasonic mixer Sonorex TK52 (60 W, 35 kHz) during 30 min (Fig. 1a) with a subsequent centrifugation under 30 000 turn/min min during 10–30 min. Poly-A was purchased from Fluka (Germany) and used without additional purification. The output of nanotubes during the process was 2–8%, the concentration of poly-A in different experiments was 10^{-3}–10^{-4} M, and the concentration of nanotubes

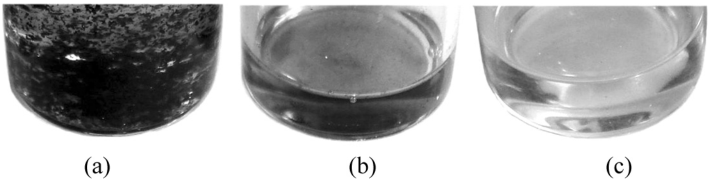

(a) (b) (c)

FIGURE 1 Image of the nanotube-poly-A solution: (a) before mixing in an ultrasonic mixer, (b) bottom and (c) top part of the solution after centrifugation.

was 10^{-4}–10^{-5} M as estimated according to [15]. This procedure separates nanotubes from a bundle for their further individual characterization and usage.

We have selected SWCNTs from the bundle with anionic surfactants (sodium dodecylsulfate, nucleic acids) and cationic forms (polyvinyl alcogol) and concluded about a possibility of the selection of nanotubes with nucleic acids in accordance with [8,16].

After the treatment, the inhomogeneous solution contained 3 parts of different densities. The upper and bottom parts contained a black dust with nanotubes and contaminations such as soot, metallic particles, etc., while the mid transparent part (Figs. 1b,c) contained a solution with isolated nanotubes. We remove the transparent part and divided it into 2 parts: more transparent (Fig. 1b) and less (Fig. 1c) transparent ones. A drop from the transparent part of the solution was then taken for Raman, AFM, and IR studies.

The characterization of individual nanotubes wrapped by poly-A, as well as the poly-A conformation on the separated nanotubes, was probed and enhanced with a conventional Klarite SERS support by Raman spectroscopy. The microscope experiment was done using a Via Raman Microscope (Renishaw) instrument with laser excitation at 785 nm with 0.3–60-mW power. The factor of enhancement in SERS experiments on the Klarite support was equal to 10^4–10^6 for different vibrations in comparison with a conventional Al support. The spot of the field for SERS study was taken as $1 \times 1\,\mu$. AFM microscopy with a Park Scientific Instrument Auto Probe LS was used to analyze the nanotube-poly-A interface. We have obtained images on a SWCNT in the contact mode with a silicon nitride ultrasharp tip (all images are obtained in air).

According to our Raman and AFM data, a sample of nanotubes mixed with a poly-A solution after the purification, ultra-sound treatment, and centrifugation, which was taken from the transparent part of the suspension, has 1–5 nanotubes in the bundle covered by poly-A.

But some samples have up to 10–15 nanotubes. So, the treatment we applied was not sufficient for the full separation of nanotubes from the bundle, however it gives a possibility for the better registration of the Raman signal from poly-A adsorbed on nanotubes as well for nanotubes selection. The pH of the solution was measured with a pH-150 M (Belorussia, Gomel) instrument with ±0.01 accuracy.

SEIRA (surface enhanced infrared absorption) spectroscopy was applied to study a conformation of poly-A at the SWCNT interface for an ensemble of SWCNT and poly-A molecules with of the use of a special SEIRA support fabricated in Kyiv [14]. The SEIRA application for the study of nanotubes gives a possibility to increase a sensitivity of IR spectroscopy by 3–10 times and enhances the absorbance of biological molecules adsorbed on the nanotube surface located on the rough gold surface (Fig. 2) [17]. A Bruker IFS-66 instrument with a reflection attachment (the incidence angle of 16.5°) was used for the registration of IR spectra in the reflectance mode in the region of 400–4000 cm^{-1}.

3. RESULTS AND DISSCUSION

3.1. Poly-A Structure

Poly-A has two ordered forms (Fig. 3): under neutral and alkaline pH, poly-A shows a single strand, and the transition in a double strand takes place at lower pH 6–5.25 in dependence on the ion concentration, temperature, etc. [18]. In our case under pH 5.25 and lower, adenine in poly-A is protonated on N1 sites. The formation of an H-bonded pair with other adenine with participation of N7 of one adenine and N10 of another molecule, as well as the aggregation of helices with the

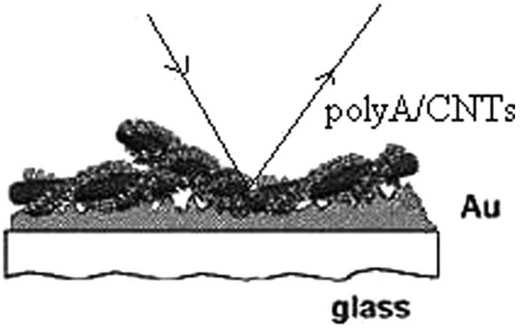


FIGURE 2 Geometry of the SEIRA experiment.

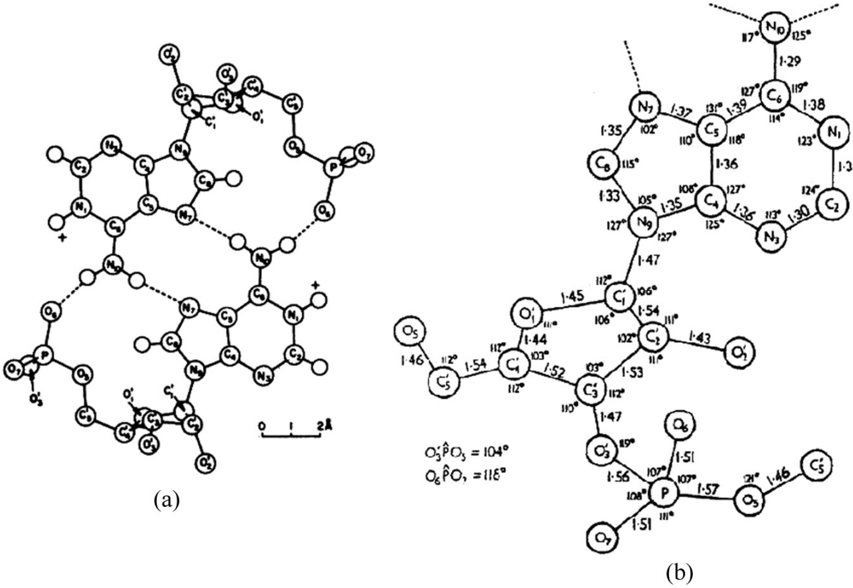


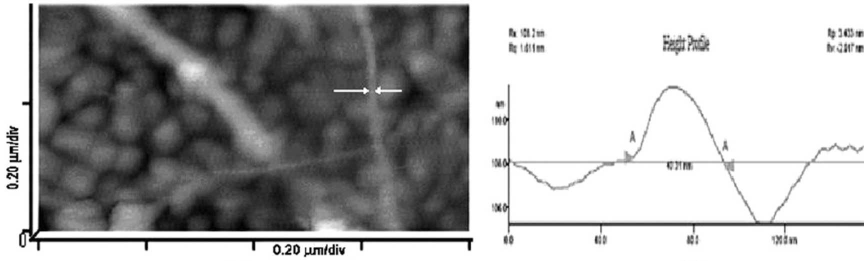
FIGURE 3 Structure of poly-A: (a) – double strand and (b) – single strand. (Rich, A., Davies, D. R., Crick, F. H., Watson, J. D. (1961) J. Mol. Biol.)

formation of double strand poly-A, occurs. The structure preserves in an aqueous solution, under cold temperatures, and under the fiber spinning. The stability of the helix form of poly-A is due to the dispersive, vertical stacking interaction for both ordered forms, as well as due to the formation of intramolecular interstrand and intrastrand H-bonds for the double strand of poly-A [19].

According to IR data [20] for a poly-A film under neutral pH, we can conclude that single strand poly-A can be additionally stabilized by the formation of H-bridges: $N_7 \ldots H_2O \ldots HNH$, $N_7 \ldots 2(H_2O) \ldots O_1P$ in the plane of the pair and $N_1 \ldots$H-O-H$\ldots N_1$, $N_3 \ldots$H-O-H$\ldots NH_2$ along the helix.

3.2. Characterization of Carbon Nanotubes

Visualization of separate nanotubes with poly-A was done using AFM imaging. According to AFM, the size of nanotubes after the separation was 4.3 nm (Figs. 4a,b) along the vertical axis and by 10 times larger, 40.31 nm, along the horizontal axis. It is known that any probe method, including AFM, does not give a real object image. An image is the product of both the object and probe effects. Due to the fact that the curvature of an AFM probe is much more than the size (diameter) of the object under study, we should expect the lateral size of the object



(a) (b)

FIGURE 4 AFM image (a) of CNTs and its cross section (b).

image being much larger than its real size. At the same time, the height of the object image meets the real size since the nanotube is a single object deposited on a flat surface and the AFM method is valid for height estimation without error. From the analyses obtained on supporting Klarite^{TM} Poly-A/SWCNTs system the real size of nanotubes cannot be estimated because of the gold surface roughness of the support itself. So, Figure 4b, shows that the nanotube height is equal to 4 nm, and its lateral size of 40 nm is estimated with large error. According to these data, we can suppose that 1 or 2 nanotubes have been separated from a bundle and registered by AFM.

The single wall carbon nanotubes are characterized by the so-called "breathing mode", the unique vibrational mode that is practically absent in other materials [21]. This vibrational mode is sensitive to a diameter of nanotubes, as well as to the density of states, and depends on the exciting light frequency. The linear dependence between the inverse diameter and a position of the breathing mode is expressed by the formula [22]

$$\nu(cm^{-1}) = \frac{223.75}{D_1(nm)} \tag{1}$$

that was obtained from *ab initio* calculations. In the most cases, the bundles of nanotubes are studied, so the Van der Waals forces between the nanotubes in a bundle take place and are determined by the diameter of nanotubes and the number of nanotubes in a bundle. That is why an additional constant appears in the formula or a coefficient in the term of fraction changes. Different formulas are applied by different authors to the calculation of the diameter of nanotubes;
work [23]:

$$\nu(cm^{-1}) = \frac{223.5}{D_3(nm)} + 12.5; \tag{2}$$

work [24]:

$$\nu(cm^{-1}) = \frac{224}{D_4(nm)} + 14; \tag{3}$$

work [25]:

$$\nu(cm^{-1}) = \frac{238}{(D_5(nm))^{0.93}}; \tag{4}$$

work [26]:

$$\nu(cm^{-1}) = \frac{248}{D_6(nm)}. \tag{5}$$

In [27], the formula is presented in following form:

$$\nu(cm^{-1}) = \frac{234}{D_2(nm)} + 10 \tag{6}$$

which is in good agreement with the data of electron microscopy.

We estimated a diameter of nanotubes in the initial fraction of nanotubes, as well in a solution, using the spectral parameters of breathing modes. The fitting of peaks for the breathing modes was done with the Opus 5.5 software package. The nanotubes have a number of "breathing modes" with frequencies of 136, 148, 156, 162, 169, and 177 cm^{-1} [11]. Using formulas (4) and (6), the diameter of nanotubes has been estimated (see Table 1). The diameter of an isolated single wall carbon nanotube wrapped by poly A (Fig. 5) has been estimated by formulas (1) and (5) which are suitable for the estimation of a diameter of isolated nanotubes (see Table 1). For isolated

TABLE 1 Diameter of CNTs

ν, cm^{-1} (for isolated CNTs)	–	–	157	159	160	178	221	236	260
D, nm, calculated with formula (1)	–	–	1.43	1.41	1.40	1.26	1.01	0.95	0.86
D, nm, calculated with formula (5)	–	–	1.58	1.56	1.55	1.39	1.12	1.05	0.95
ν, cm^{-1} (for bundles of CNTs)	136	148	156	162	169	177	219	233	264
D, nm, calculated with formula (4)	1.83	1.67	1.58	1.51	1.45	1.38	1.09	1.02	0.90
D, nm, calculated with formula (6)	1.85	1.69	1.60	1.54	1.47	1.40	1.12	1.05	0.92

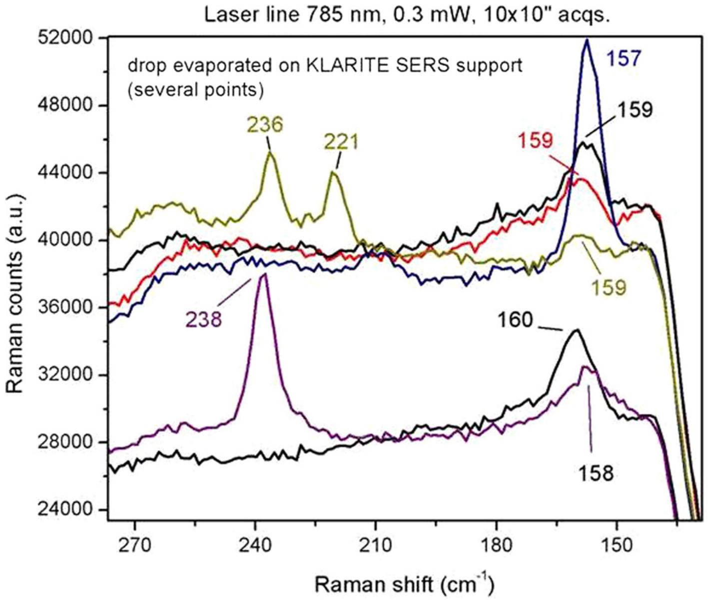


FIGURE 5 SERS of (1–3) isolated nanotubes in the region of ⟪breathing modes⟫.

nanotubes wrapped by poly-A, the frequencies of breathing modes are 157, 159, 160, 221, 236, and 238 cm^{-1}.

In addition to the breathing modes, the Raman spectra of carbon nanotubes have other characteristic features, namely G, D, and overtones of D, namely D^1 modes, with specific positions and half-widths that can be used as a passport for carbon nanotubes [28,29]. The Raman spectra of carbon nanotubes (Figs. 5 and 6) have characteristic features and differ from the Raman spectra of other carbon materials. [21,28,30].

3.3. Poly-A Conformation Under pH 4.92–6.47

The conformation of poly-A is determined by pH of a solution. Under pH 5.25–5.75, poly-A has the single strand form (Fig. 7). In our experiment, we worked with poly-A under pH 5.27 and 5.5. Under protonation from pH 5.27 to 4.62, poly-A transforms from the single strand form to the double strand one [18], and the marker bands of poly-A clearly indicate this. Here, we don't use a buffer solution due to the fact that this could fade the clearance of IR spectral features of a poly-A conformation.

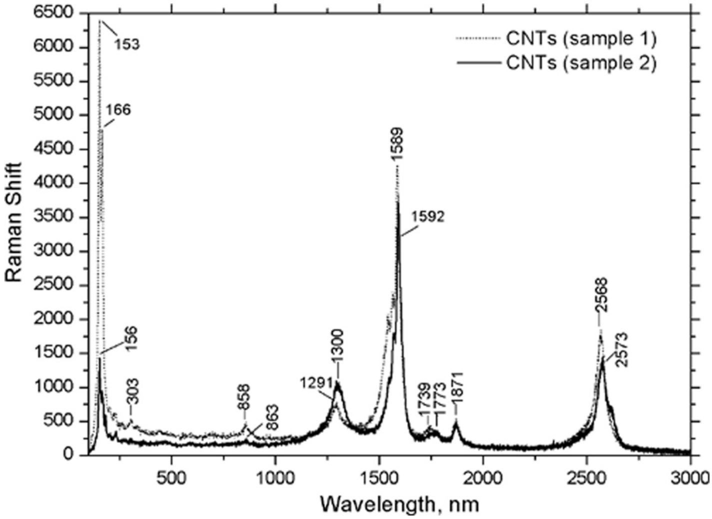
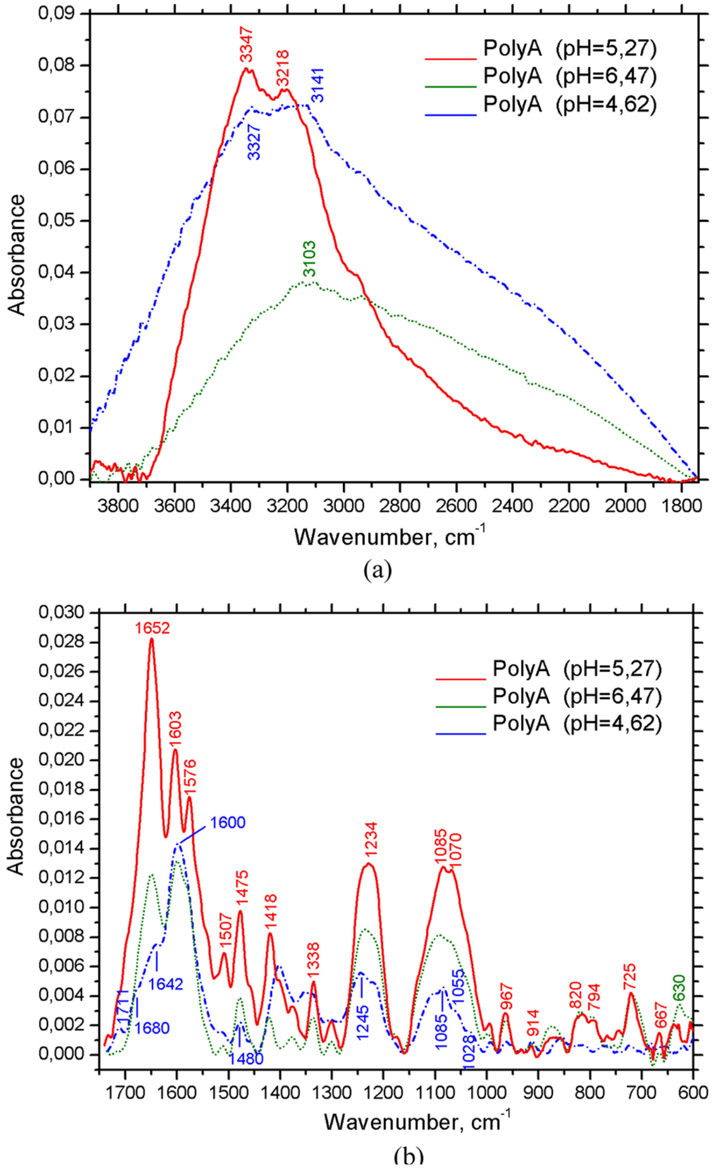


FIGURE 6 RS of initial fraction of nanotubes (1) and the dust bottom fraction of nanotubes after centrifugation (2).

3.4. Conformation of Poly-A Adsorbed on the Surface of Carbon Nanotubes

SERS (Fig. 8) and SEIRA (Fig. 9) data were used for the characterization of conformation changes of poly-A at the surfaces of carbon nanotubes. As a result of the interaction between poly-A and nanotubes, we have derived poly-A in the single strand conformation (pH = 5.5) [18,19]. With SERS spectroscopy, we registered numerous breaks and deformations of poly-A in the single strand conformation adsorbed on nanotubes; however, poly-A keeps its initial form. We registered the signal of poly-A adsorbed on an isolated nanotube (1–3) wrapped by poly-A at a concentration of 10^{-3}–10^{-4} M due to the use of a Klarite substrate and the enhancement of signals by about 10^4–10^5 times in comparison with an Al substrate. We got the separation of nanotubes by poly-A preferentially with a diameter close to 1 nm, meanwhile the diameter of nanotubes in the bundle was preferentially about 1.4 nm. The marker lines of poly-A at the nanotube surface observed in SERS spectra are as follows: 705, 725 (A), 795 (poly-A), (822 , 861, 920 – ribose phosphate), 1098 (phosphate), (1130, 1160, 1180, 1250, 1270, 1282 – ribose phosphate), 1329-(A), 1318, 1336 (A), 1557, 1577 cm^{-1}. In the case of poly-A adsorbed by the drop on metal (Al, Ag) surface, we have registered 3 strong bands only – 1334, 795, 725 cm^{-1}. These band



(a)

(b)

FIGURE 7 SEIRA spectra of poly-A in acid (pH = 4.92), neutral (pH = 5.27) and basic (pH = 6.47) solutions.

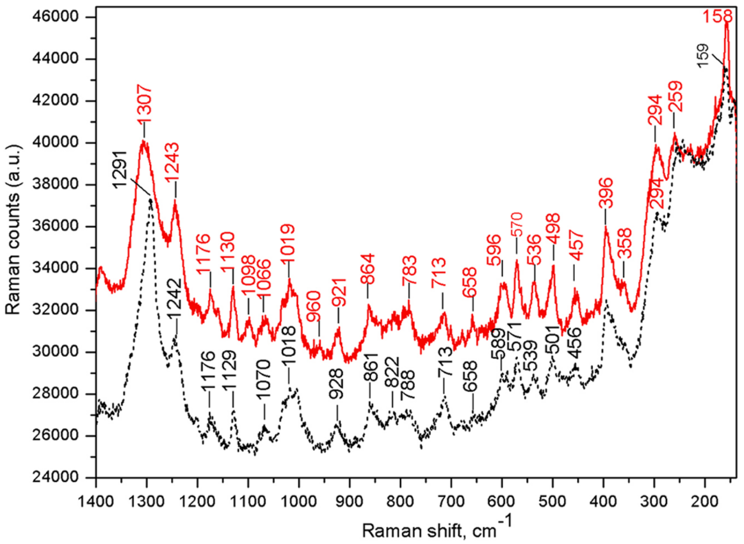


FIGURE 8 SERS of poly-A adsorbed on the carbon nanorube surface in the region of 1400–400 cm^{-1}.

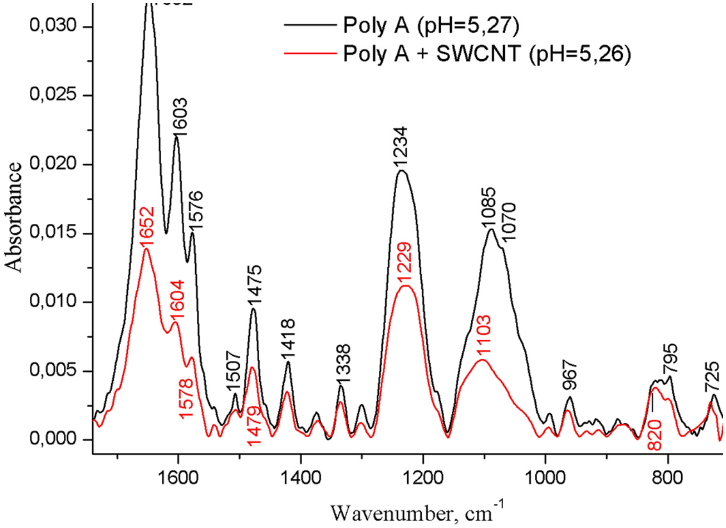


FIGURE 9 SEIRA spectra of poly-A and poly-A/CNTs in a neutral solution in the region of 1700–800 cm^{-1}.

positions can slightly change for different samples. In the case of the adsorption of poly-A on the nanotube surface, we have registered much more absorption bands, namely, all the bands that can be registered in a 10^{-2} M solution [8]. We are going to discuss it in more details in the frame of another paper.

Thus, poly-A in an ordered form has the vibration mode of a phosphodiester backbone centered near 815 cm^{-1}; in our case, we observed a shift of this band to 795 cm^{-1} for both samples: poly-A/metal surface and poly-A/SWCNT. This means that dried poly-A does partially loss an ordered form after the adsorption on the metal or nanotube surface. The position of the strong adenine band of poly-A adsorbed on a metal surface is the same as that for the ordered form, namely, 725 cm^{-1}; however a shift of this band to 717 cm^{-1} was observed in the poly-A/nanotube system. The last point could be an evidence of the interaction between the nanotube surface and adenine. The most interesting fact is a widening of the adenine band centered at 717 cm^{-1}, which is an additional evidence of the interaction between poly-A and nanotubes.

According to SEIRA data, we have not observed any changes in the spectra of poly-A on nanotubes for pH 5.27 in the region of bases vibrations at 1700–1500 cm^{-1}. However, we have observed strong changes in the phosphate vibration bands: phosphate symmetric vibration band shifts from 1085 cm^{-1} to 1103 cm^{-1} and phosphate asymmetric shifts from 1234 cm^{-1} to 1229 cm^{-1} after the adsorption of poly-A on nanotubes, as well as an increase of the sugar vibration bands by about 4 times. This suggests that the characteristic sites of the interaction of poly-A with nanotubes are adenine and phosphate groups. The pH of a poly-A solution (5.26) practically does not change after the addition of nanotubes (5.27).

The interaction of double strand poly-A with nanotubes lead to an increase in pH of the initial solution of poly-A from 4.62 to 4.7. The most drastic changes are observed in the region of the OH vibration band. We have observed a decrease in the water content in the poly-A/nanotube hybrid (Figs. 10, 11) more than by 10 times. Protonation of poly-A to 2.5 in the presence of nanotubes prevents the decomposition of poly-A.

The addition of nanotubes to poly-A prepared with pH 6.47 leads to a decrease in pH of the nanotube/poly-A complex down to 6.37. In this case, the conformation of poly-A adsorbed on the nanotube surface keeps the single strand form with minor changes (Fig. 12) and can be characterized as a partially ordered single strand form.

Thus, poly-A at the SWCNT interface, as follows from the data obtained for the ensemble of molecules, keeps the initial conformation

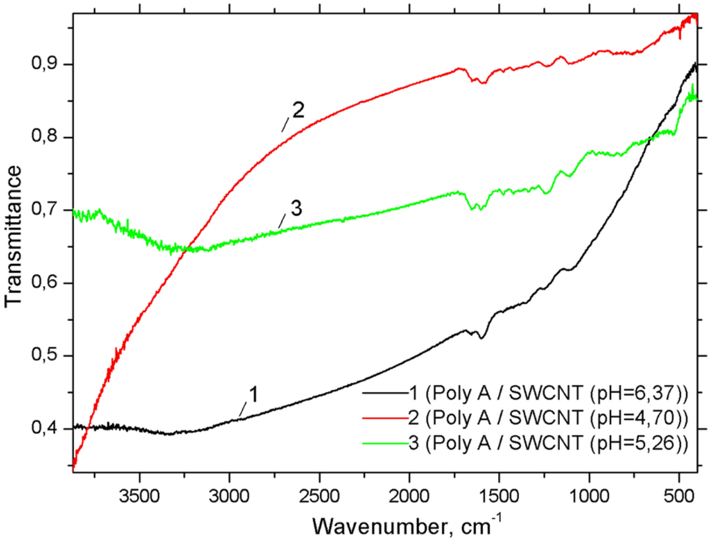


FIGURE 10 Comparative SEIRA spectra of poly-A/CNTs in the region of 4000–450 cm^{-1} in their initial form.

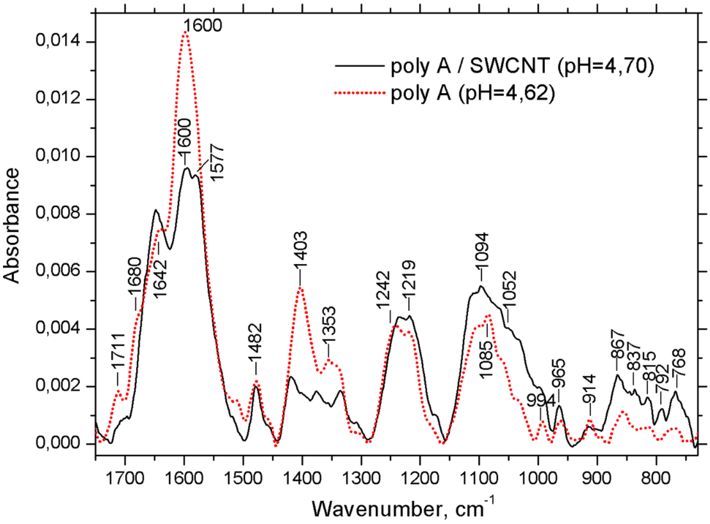


FIGURE 11 SEIRA spectra of the poly-A and poly-A/CNTS hybrid in an acid solution in the region of 1700–800 cm^{-1}.

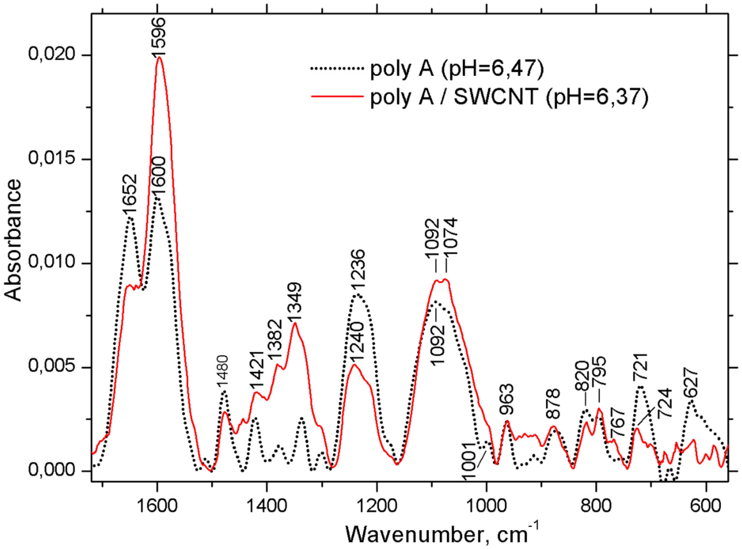


FIGURE 12 SEIRA spectra of the poly-A and poly-A/CNTS hybrid in a basic solution in the region of 1700–800 cm^{-1}.

with numerous changes, disorders, and breaks of the backbone, as follows from the data obtained for separate poly-A molecules.

4. CONCLUSIONS

- We have developed a technology of nanotube selection with poly-A. A nanotubes/poly-A complex solution stable during 3–6 months was obtained. The semiconducting nanotubes with a diameter of 1 nm were preferentially selected by poly-A, meanwhile a bundle mostly consists of nanotubes of 1.4–1.5 nm in diameter. The number of nanotubes in a selected sample was 1–5.
- We have registered the Raman signal from separated nanotubes wrapped by poly-A in the single strand form, as well as the numerous marker bands of poly-A indicating the presence of poly-A on the surface of nanotubes in their initial form. SEIRA data show that the conformation form of poly-A/nanotube in the assemble of isolated poly-A/nanotubes hybrids is practically non-changeable in comparison with poly-A in the condensed state.
- With SERS spectroscopy, we registered numerous breaks and deformations of poly-A in the single strand form adsorbed on single isolated (1–5) nanotubes; however, poly-A keeps its initial form. The

characteristic sites of the interaction of poly-A with nanotubes are adenine and phosphate groups. We have registered the signal of poly-A adsorbed on nanotubes with a poly-A concentration of 10^{-3}–10^{-4} M due to the usage of a Klarite substrate and the enhancement of signals by about 10^4–10^5 times in comparison with those for an Al substrate.

- Protonation of poly-A to pH 4.62 causes the transition of poly-A into the double strand form. The interaction of this form of poly-A with nanotubes leads to the deprotonation of the poly-A/nanotubes complex (pH 4.7). Nanotubes induce the breaks into a double strand in poly-A as well as a drastic decrease of the number of water molecules per nucleotides – more than by 10 times.
- The addition of nanotubes to poly-A prepared with pH 6.47 leads to a decrease in pH of the nanotube-poly-A complex to 6.37 and practically does not change its conformation.

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