

Scientific paper

UV/Vis Study of the Alkali Salts of Poly(thiophen-3-ylacetic acid) in Water

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Received: 22-02-2012

Dedicated to Prof. Dr. Gorazd Vesnaver on the occasion of his 70th birthday

Abstract

UV/Vis spectroscopic investigation of aqueous solutions of regio-irregular poly(thiophen-3-ylacetic acid) (PTAA) with and without methyl-ester groups in the presence of sodium and lithium ions as counterions is presented. The samples were carefully purified and characterized with respect to molar mass and the amount of –COOH groups present. We examined how the UV/Vis spectra of solution change with aging of PTAA solution, polymer concentration, addition of low molecular weight salt, temperature, and some other parameters. We show that results crucially depend on whether the spectra are taken for freshly prepared or mature solutions. We demonstrate the validity of the Beer-Lambert law for PTANa, PTAA/Na, and PTAA/Li (aged solution), and violation of this law for PTANa/Me (fresh) solutions in water; the latter system is instead found to exhibit an isosbetic point at 402 nm. We prove that UV/Vis spectra of polythiophene derivatives in water depend on the “age” (time after dissolution) of the solution. The inconsistencies among the spectroscopic data found in literature, as also the discrepancies with our own measurements on PTAA-based systems are discussed.

Keywords: Polyelectrolytes, polythiophenes, conformational transition, UV/Vis spectroscopy, aging, conformational relaxation

1. Introduction

Polyelectrolytes belong to an important class of functional polymers^{1,2} that attract lots of attention due to numerous applications in technology (ion exchangers, emulsifiers, flocculants, drug reducers, oil recovery, specialty coatings, etc.), as well as in science (genomics, interactions with nucleic acids and proteins, self-assembling systems, etc.). Polyelectrolytes with conjugated main chains,³ the so-called conjugated polyelectrolytes (CPEs) exhibit, in addition to what is mentioned above, strong application potential in the fields of optoelectronics and sensors.^{4–9} Properties of aqueous solutions of polyelectrolytes (including CPEs) are affected by Coulomb interactions between macropolyions and their counterions. In the case of weak polyelectrolytes such as poly(thiophen-3-ylacetic acid), PTAA, the polymer chain conformation and ther-

modynamics of solution are both strongly influenced by the ionization equilibriums involving weak acid groups. Despite the interest coming from industry and science, detailed studies of solutions of weak CPEs are rare.^{6,10–18} As far as PTAA is concerned, their aqueous solutions were investigated by Vallat^{11,19} and Kim with co-workers.^{20–22} These authors examined behavior of PTAA during the acid-base titration, and recorded UV/Vis spectra under various experimental conditions. Vallat et al.^{11,19} also investigated solutions of sodium salt of PTAA (further denoted as PTANa) utilizing the small-angle neutron and X-ray scattering techniques. They examined the effects of polymer concentration, and ionic strength, providing evidence for conformational transitions of PTAA chains during the acid-base titration.

PTAA is a representative CPE of macromolecules with fully conjugated backbone. The degree of delocaliza-

tion of electrons in a conjugated backbone depends on the extent of overlap of neighboring π -bonds that is strongly influenced by the substituents attached to the backbone. Therefore, any change affecting conformation of PTAA chains, is reflected in the UV/Vis absorption spectrum of the polymer. Few studies of PTAA solutions, exploiting this effect, have been published already.^{19,21} During our recent study (see the preceding paper in this series²³) we noticed substantial differences between the UV/Vis spectra of PTAA solutions examined in various published papers.^{19–22} In addition, we also observed some differences between the literature and our own results. The preceding study²³ revealed significant differences between Henderson-Hasselbach plots, obtained by us and those published by other authors. This frustrates reliable interpretations and/or theoretical analysis of measured thermodynamic and transport data. In addition, the literature data cannot be rigorously analyzed, because many important details on the polymer preparation and characterization, such as monitoring of the aging of solutions, are missing. Furthermore, some of the published results were obtained on solutions that were not dialyzed (or at least, dialysis is not mentioned in experimental part), which is contrary to the standard practice established in the field of polyelectrolyte characterization.

We recognized in due time that UV/Vis spectra of PTAA and its salts change with time. For this reason we decided to undertake an extensive spectroscopic study, based on carefully purified solutions and well defined PTAA samples. The influence of the following parameters: (i) age of solution (time dependence of spectra after dissolution), (ii) degree of PTAA neutralization, (iii) PTAA concentration, (iv) effect of addition of low molecular weight salt, (v) influence of the nature of counterion, and (vi) temperature, were examined. In addition, the effect of the presence of methyl ester groups in PTAA chains (incompletely hydrolyzed precursor of PTAA) has been examined. These results were critically compared with already published data.

2. Experimental

2.1. Polymers

Poly(thiophen-3-ylacetic acid), PTAA, was prepared by oxidative polymerization of methyl (thiophen-3-yl)acetate with FeCl_3 to give methyl ester of PTAA (PTAMe) that was consecutively basically hydrolyzed to give polyacid PTAA, using the procedures described earlier.^{21,23} Two batches of PTAA (identical with those used in Ref. 23) prepared from two different batches of PTAMe were used: batch 1 ($X_n \cong 39$; $\bar{D} = 2.4$) was used for preparation of sodium salts PTAA/Na and PTANa (PTAA partly and completely neutralized with NaOH, respectively) and batch 2 ($X_n \cong 43$; $\bar{D} = 3.0$) for preparation of corresponding lithium salts; PTAA/Li and PTALi ($X_n \cong$ stands for apparent

number-average degree of polymerization and \bar{D} for dispersity²⁴ of PTAA). Spectroscopic characteristics are given in “Supporting Information” to the previous paper.²³ Note that a complete hydrolysis of PTAMe to PTAA salt was achieved after 48 hours of treating PTAMe with the hydroxide.

Poly[(thiophen-3-ylacetic acid)-co-(methyl thiophen-3-ylacetate)], PTAA/Me. This formal copolymer sample is, actually, not a copolymer but a modified homopolymer: incompletely hydrolyzed PTAMe. PTAA/Me was prepared from PTAMe (0.7 g, batch 3) that was treated with aqueous NaOH (2.5 M) at 100 °C for 16 hours. The reacted solution was poured into aqueous HCl (1M), precipitated polymer isolated by filtration, washed several times with water, methanol, and diethylether, and finally dried in vacuum. Isolated yield was: 200 mg (31%) of fine sienna-brown solid. ¹H NMR (400 MHz, DMSO-*d*₆, 25 °C, ppm): 12.62 (1H, –COOH); 7.35, 7.30, 7.28 (1H, thiophene rings of irregular chain); 3.8 and 3.55 (2 H, CH₂ in PTAA units); 3.90, 3.67 and 3.63 (5H, –CH₂– and –CH₃ in PTAMe units). ¹³C NMR (400 MHz, DMSO-*d*₆, 25 °C, ppm): 171.42 (–COOH); 170.40 (–COOCH₃); 136.21; 135.74; 134.58; 134.37; 133.50; 132.88; 132.10; 131.88; 130.67; 129.22; 128.55 (all carbon atoms of thiophene rings of regio-irregular main chains); 51.96 (–OCH₃); 34.41, 33.89 (–CH₂–). The ¹³C NMR spectrum is shown in Fig. 1. The ¹H NMR spectrum of PTAA/Me in DMSO-*d*₆ is shown in Fig. 1 in “Supporting Information” to this paper.

The content of –COOH groups in PTAA/Me (i.e., the degree of hydrolysis of parent polymer PTAMe) as ascertained from intensities of (i) ¹³C NMR signals of –COOH and –COO(CH₃) groups, and (ii) ¹H NMR signals of –CH₂– groups of PTAA units and –CH₂– and –CH₃ groups of PTAMe units, was estimated to be ~70%. This value is in agreement with the estimate ($\geq 60\%$) obtained from the ratio of the titrated –COOH groups and the total number of carboxylic groups, as obtained from the mass of the sample. Hence PTAA/Me may be formally regarded as poly[(thiophen-3-ylacetic acid)-co-(methyl thiophen-3-ylacetate)] (2:1).

2.2. Measurements

Molar mass characteristics were determined for precursor polymers (PTAMe) using HP 1100 chromatograph equipped with a diode array UV/Vis detector and a series of three SEC columns (PL mixed-A, mixed-B and mixed-C, Polymer Laboratories, Bristol). Tetrahydrofuran (flow rate 0.7 mL/min) was used as a mobile phase calibrated with polystyrene (PS) standards (PL, Bristol, UK). Apparent molar mass averages relative to PS standards are reported.

NMR spectra were measured on a Varian UNITYINOVA 400 instrument using polymer solutions in CDCl₃ (PTAMe) or

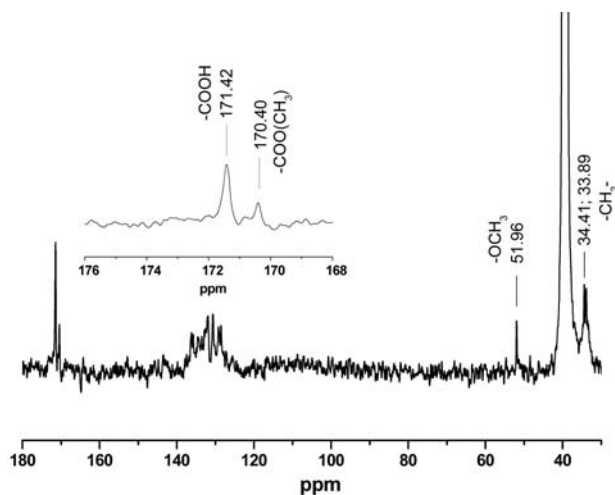


Figure 1. ^{13}C NMR spectrum of PTAA/Me recorded in $\text{DMSO-}d_6$ (400 MHz, 25 °C).

d_6 -DMSO (PTAA). The spectra were referenced to tetramethylsilane (^1H) and the solvent signals (77.00 ppm for ^{13}C spectra in CDCl_3 ; 2.50 ppm for ^1H and 39.50 ppm for ^{13}C spectra in d_6 -DMSO).

Infrared spectra were recorded on a Nicolet Magna 760 FTIR instrument equipped with an Inspector IR Microscope using the diffuse reflectance technique (128 scans at a resolution of 4 cm^{-1}) and undiluted as well as KBr-diluted samples.

Raman Spectra were measured on PTAA solution in DMSO at room temperature using a Raman spectrometer equipped with a Jobin-Yvon-Spex 270M (1800 gr/mm grating) monochromator and CCD detector (Princeton Instruments). Excitation at 532.5 nm (average laser power at the sample in a cuvette was about 100 mW) and an accumulation time of 150 s were used.

UV/Vis absorption spectra aqueous solutions of the studied polymers were recorded on a Varian Cary 100 UV/Vis spectrophotometer using quartz cuvettes with optical paths of 1.0, 0.5, 0.2, 0.1, and 0.025 cm, and for temperatures from 5 to 40 °C (in steps of 5 °C). The UV/Vis absorption spectra of PTAA/Me were recorded by Varian Cary 50 UV/Vis spectrophotometer at temperature around 22 °C.

2. 3. Preparation of Stock Solutions

Preparation of stock solutions of partially neutralized sodium (PTAA/Na) and lithium (PTAA/Li) salt of PTAA, as well as determination of their concentrations by potentiometric neutralization titration and flame atomic absorption spectroscopy, is in detail described in our preceding work.²³ Stock solution of sodium salt

of PTAA/Me (PTANa/Me) is prepared by dispersing weighed amount of dry PTAA/Me in known volume of triply distilled water. PTAA/Me is not soluble in pure water, but it became soluble during the titration with 0.1 M NaOH. Dissolution of PTAA/Me in water is a very slow process, so the titration took three days. In vicinity of the equivalent point pH value of the solution became unstable; it dropped overnight for few tenths of the pH unit. This prevented us to determine the concentration of carboxylic groups with the accuracy better than $\pm 5\%$. No dialysis of the PTANa/Me sample was performed.

3. Results

Abbreviations for polythiophenes used throughout this paper are as follows (α_n stands for the degree of neutralization of a polymeric acid):

PTAA – poly(thiophen-3-yl acetic acid)

PTANa – sodium salt of PTAA, i.e., completely neutralized PTAA ($\alpha_n = 1$)

PTALi – lithium salt of PTAA, i.e., completely neutralized PTAA ($\alpha_n = 1$)

PTAA/Na – PTAA partially neutralized with $\text{NaOH}_{(\text{aq})}$ ($\alpha_n = 0.346$ in the case of our samples)

PTAA/Li – with $\text{LiOH}_{(\text{aq})}$ partially neutralized PTAA ($\alpha_n = 0.346$ in the case of our samples)

PTAMe – poly(methyl thiophen-3-ylacetate), the precursor for preparation of PTAA

PTAA/Me – incompletely, about two-thirds hydrolyzed PTAMe, formally a copolymer poly[TAA-*co*-TAMe](2:1)

PTANa/Me – sodium salt of PTAA/Me (all comprised COOH groups neutralized by NaOH).

3. 1. Aging (Ripening) of PTALi in Aqueous Solution

To obtain evidence about possible processes following the dissolution of ionized polymer chains, we have monitored the UV/Vis spectrum of PTALi for 100 days after its preparation. Of course, this study had to be done on a non-dialyzed PTALi sample. During this experiment the studied PTALi solution was kept at room temperature. A slow but continuous change of the spectrum of the solution with time was observed (Fig. 2). During the relaxation, the absorption band of PTA^- polyanions broadened toward both sides, its maximum (characterized by its wavelength λ_{max}) shifted from 450 nm (identical with λ_{max} observed by Kim et al.²¹ for PTANa) to 415 nm, and the band intensity (i.e., its molar absorption coefficient, ϵ_{max}) decreased by 40%.

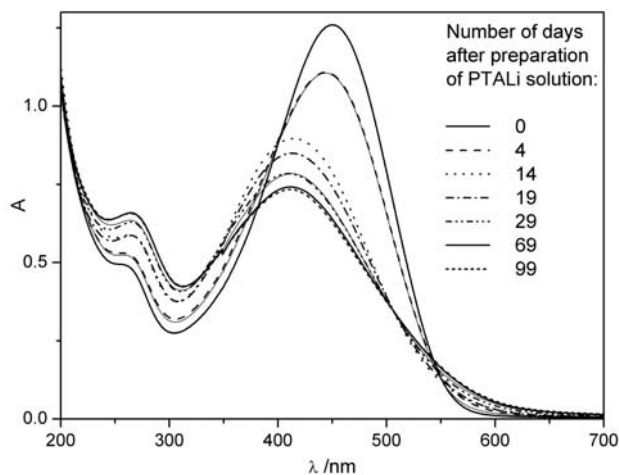


Figure 2. UV/Vis spectrum of PTALi solution in water (A is absorbance), monitored as a function of time after preparation (effect of aging) at 25 °C. The aqueous solution of PTALi sample was not dialyzed, and was kept from the moment of preparation at room temperature.

The overall relaxation process proceeded in two stages. The first stage took from 10 to 14 days and it was characterized by almost complete blue shift of λ_{\max} to the final position, principal decrease of ϵ_{\max} , and the spectra intersections at λ about 400 nm, and 545 nm. Interestingly, the intersection at 400 nm coincides with position of the isosbestic point (IP) observed during the back (i.e., acidic) titration of PTANa with HCl by Vallat et al.¹⁹ In addition, the spectrum of 4 days old solution can be very well reproduced by a linear combination of spectra of the fresh and the 14 days old solutions. This means that we can interpret the intersections at 400 nm and 545 nm as IPs.

In the second stage of relaxation (this one lasted ~ 90 days) mainly a decrease of ϵ_{\max} and further band broadening was observed while λ_{\max} remained practically unchanged. Unlike the spectra of the first stage of relaxation, the second-stage spectra intersect at $\lambda \approx 340$ nm and 507 nm. Excellent reproduction of the spectrum measured on the day 29, by the linear combination of the spectra obtained on the days 14 and 99, proved that both these intersects can be regarded as IPs. It should be stressed that these two isosbestic points have not been reported in literature so far.

3. 2. Time Dependence of UV/Vis Titrations of PTAA/Li(aq) and PTALi(aq)

Two kinds of experiments were carried out for this purpose. In the first series of experiments we examined the effect of the age (4, 14, and 29 days) of the PTAA/Li solution on the UV/Vis spectra taken during its acidic titration. As can be seen (Figure 3) the spectra taken during titrations of 14 and 29 days old solutions did not exhibit IP at 401 nm that was observed for the titration of 4 days old

solution (see Ref. 23, Fig. 5). This proves that the transition underlying occurrence of this IP had been accomplished during the sample aging before titration. Further it is seen that the longer the solution was aged before titration, the lower the value of ϵ_{\max} at the end of titration was found. This reflects the effect of the solution aging on the value of ϵ_{\max} ; i.e., the overall decrease in ϵ_{\max} observed was contributed by both acidification and aging of the studied solutions. The fact that the final value of λ_{\max} exhibited fluctuation: λ_{\max} (age): 393 nm (4 days); 392 nm (14 days); 396 nm (29 days) most probably reflects the experimental uncertainty.

The second series of experiments dealt with basic UV/Vis titration of dialyzed, well mature (82 days old) aqueous solutions of PTAA/Li (batch 2, pH = 6, $\alpha_n =$

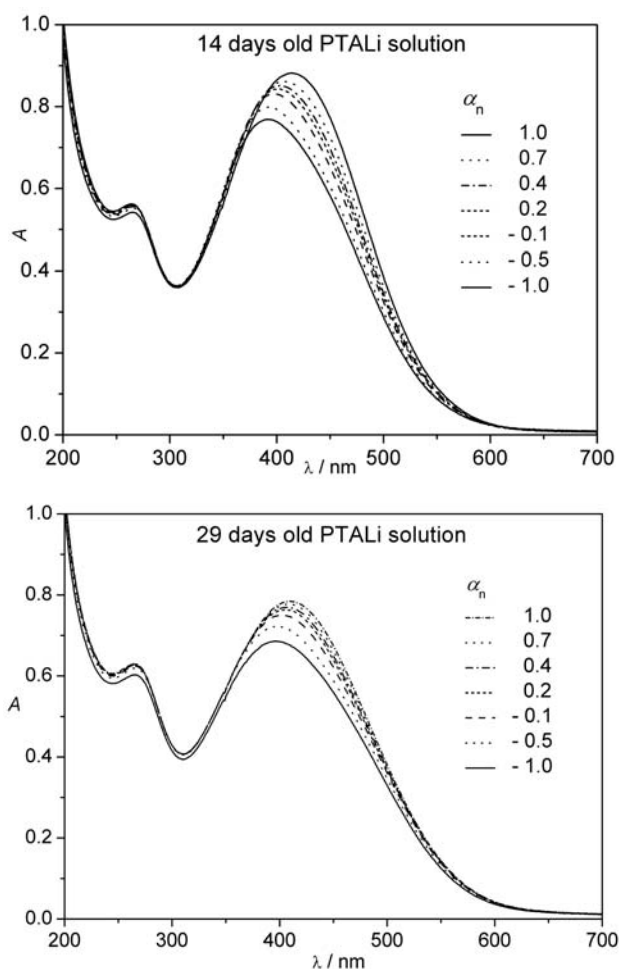


Figure 3. a) UV/Vis absorption spectra of fourteen days old aqueous solution of non-dialyzed PTALi (batch 2), recorded during back titration with HCl. Spectra were recorded at different α_n (the legend is shown inside the graph area) and are corrected for dilution. Negative values of α_n denote relative excess of HCl. $T = 25$ °C, $c_{\text{PTALi}} \approx 1.1 \cdot 10^{-4}$ mol of monomeric units/L. From the time of preparation the solution was kept at room temperature. See Fig. 5 in Ref. 23 for comparison (back titration of four days old PTALi solution). b) The same as for a) but for 29 days old solution of PTALi in water.

0.35). The titration (completed within one hour) with 0.1 M LiOH (Fig. 4a) exhibited the following features:

- (i) After adding LiOH in the amount corresponding to neutralization of all $-\text{COOH}$ groups, λ_{max} appeared at 420 nm in contrast to the value $\lambda_{\text{max}} = 450$ nm found for freshly prepared, non-dialyzed PTALi solution.
- (ii) λ_{max} appeared at 463 nm upon adding LiOH in a high excess: $\alpha_{\text{n,theor}} \approx 2$ or more (see inset in Fig. 4a). The value $\lambda_{\text{max}} = 463$ nm should be regarded as a true value pertaining to completely ionized PTAA. Taking into account that spectrophotometric titration was performed rather quickly (in less than 1 hour) we suspect that appearance of maximum at 463 nm upon an addition of substantial excess of LiOH (and not already at $\alpha_{\text{n,theor}} = 1$) is related to kinetically driven processes.

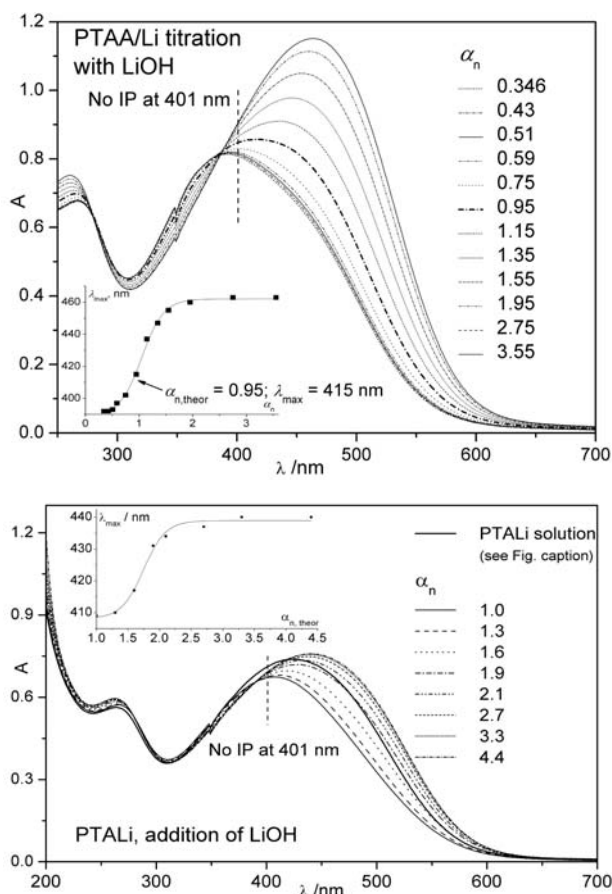


Figure 4. a) UV/Vis absorption spectra of PTAA/Li (dialyzed sample from batch 2) recorded ($T = 25$ °C) during neutralization with LiOH. Values of α_{n} exceeding 1 denote relative excess of LiOH. PTAA was dissolved in water for 82 days; almost all this time PTAA was in the form of partially neutralized Li salt of PTAA ($\text{pH} \approx 5 - 6$), and was kept at room temperature. The small wiggle at 350 nm is caused by the exchange of spectrophotometric lamps. b) The same as for a), but for the sample of PTALi, obtained from PTAA/Li solution after precipitation with HCl and redissolution with LiOH. Redissolved PTALi was aged in aqueous solution for 81 days.

- (iii) No IP at 401 nm was detected but the spectra intersections at ≈ 390 nm were observed. Because Vallat et al. observed IP at ≈ 390 nm during forth-and-back titration of PTAA¹⁹ we examined the possibility to reproduce measured spectra by a linear combination of spectra belonging to $\alpha_{\text{n}} = 0.346$, and $\alpha_{\text{n}} = 3.55$. Our attempt failed: in other words, we have not been able to construct the spectrum from the individual spectra belonging to the above values of α_{n} . This means that there is no real IP at 390 nm.

The UV/Vis titrations of 82 days old solution of PTAA/Li with NaOH and CsOH show the same features as titration of PTAA/Li with LiOH (Fig 4a): appearance of a probable IP at ≈ 384 nm, similar intensities of spectra, and similar values of λ_{max} (see “Supporting Information” for further details).

For comparison, UV/Vis spectra were measured also during addition of LiOH to already mature solution of PTALi. This solution was obtained after precipitation of PTAA/Li with HCl and subsequent redissolving of PTAA precipitate (not dried) with LiOH. The obtained PTALi solution was matured for 81 days at room temperature. The titration (better said: overtitration) of ripe PTALi solution with 0.1 M LiOH showed the following features (Fig 4b):

- (i) λ_{max} of starting PTALi solution (≈ 410 nm) was raised up to value of ≈ 440 nm upon the addition of three-fold surplus of LiOH (see inset in Fig. 4b). This value is notably lower in comparison to that obtained during overtitration of mature solution of PTAA/Li (≈ 463 nm). Also, an increase of the absorption band at λ_{max} , ϵ_{max} , is significantly lower in comparison to the titration of mature solution of PTAA/Li.

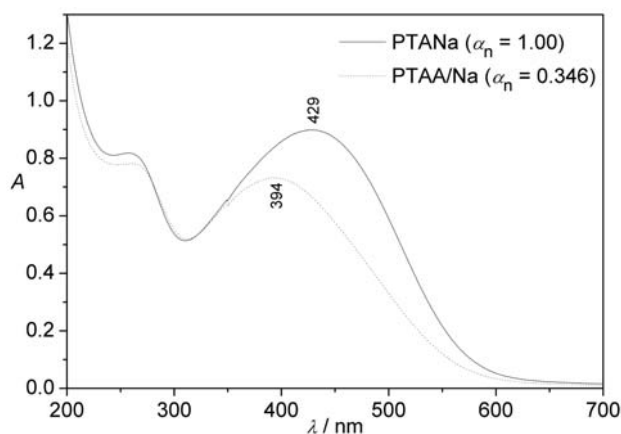


Figure 5. Comparison of UV/Vis spectra (A is absorbance) of mature solutions (≈ 110 days) of PTANa ($\alpha_{\text{n}} = 1$) and PTAA/Na ($\alpha_{\text{n}} = 0.346$) recorded at identical total $c_{\text{pol}} = 1.275 \cdot 10^{-4}$ mol/L in a cuvette of optical path length 1.000 cm at 25.0 °C. The small wiggle at 350 nm is caused by the exchange of spectrophotometric lamps. PTAA/Na was dissolved in water for almost four months. PTANa was obtained from PTAA/Na (batch 1) by adding NaOH.

(ii) Again, no IP at 401 nm was detected during over-titration of mature solution.

At the present we do not have satisfactory explanation for such a different behavior between mature solutions of PTAA/Li and PTALi during addition of LiOH. We may only speculate that faster relaxation observed in the case of PTALi solution is a result of the hydrophilic character¹⁹ of PTALi while more hydrophobic nature of PTAA/Li prevents full solvation (and consequent stabilization) of polymer molecules with water molecules.

It should be noted that in the first study,²¹ where UV/Vis spectra of PTAA were recorded during neutralization with NaOH, authors explicitly stated that no IP was found during the titration. This observation is concordant with our experience from titrations of ripe (≈ 110 days) solution of PTAA/Na with NaOH_(aq) (Fig. 5). The same holds true for slightly less old solutions of PTAA/Li (82 days) and PTALi (81 days), but not for freshly prepared PTAA solution, and neither with the results of Vallat et al.¹⁹ The differences among average molar masses of samples used in experiments are considered to be small, and probably cannot explain these effects. Unfortunately, no information about the “age” of the solution, and very little details about the solution preparation are given in the PTAA studies published so far. Closer inspection of Figs. 3a, 3b, 4a, 4b, and 5 reveals that absorbance (and thus molar absorption coefficients) of PTAA of various degrees of neutralization in (relatively) ripe solutions are very much the same around the local minima at $\lambda \approx 310$ nm. This fact makes UV/Vis spectrophotometry a good candidate for determination of the PTAA concentration in water.

3. 3. Concentration Dependence of UV/Vis Spectra of PTAA

PTAA chains are in principle amphiphilic in their nature and they can undergo aggregation in solution, which might somewhat invalidate the Beer-Lambert law. Optical spectra plotted as ϵ_λ (molar absorption coefficient at wavelength λ) vs λ (Figure 6) show that the Beer-Lambert law was not fulfilled completely for PTAA/Li solutions aged for 40 days and covering more than two decades of c_{pol} . Greatest deviations (up to 8%) occurred at $\lambda \approx 450$ nm, whereas the lowest ones (below 1.5%) around the local minimum at $\lambda \approx 310$ nm. In addition, λ_{max} decreased during dilution (see inset in Fig. 6).

Compared to spectra of PTAA/Li, the spectra of more mature (110 days) PTAA/Na solutions better obeyed the Beer-Lambert law, they showed constant $\lambda_{\text{max}} = 393$ nm (the same as the most diluted Li analogue) and increased value of ϵ_{310} (4045 vs 3670 L mol⁻¹ cm⁻¹). All these differences are consistent with different “ripeness” (40 vs 110 days) of the solutions (Fig. 2).

It should be mentioned here that the value of ϵ_{310} is

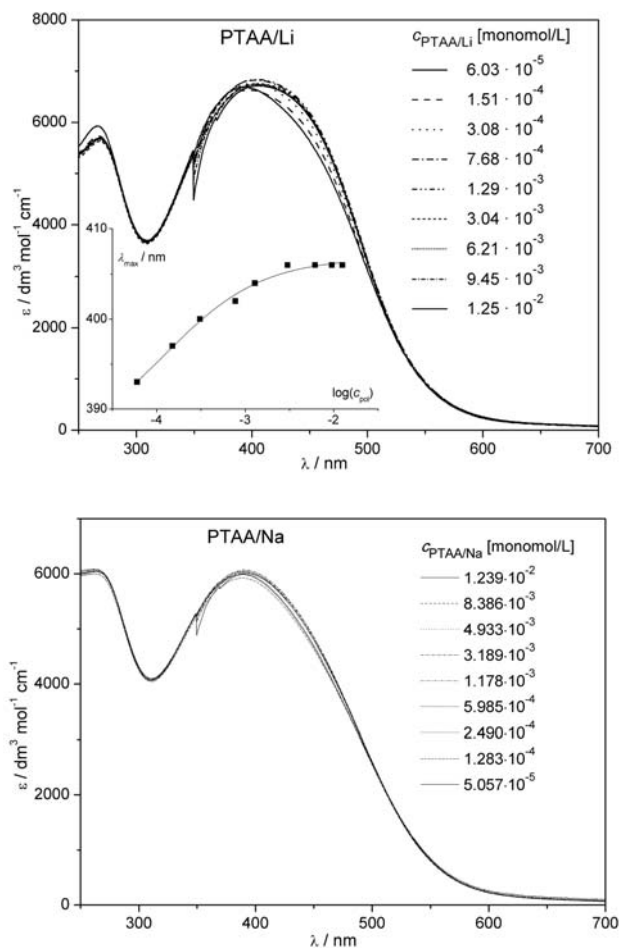


Figure 6. Test of validity of Beer-Lambert law for the aqueous solutions of PTAA/Li (batch 2; aged for ≈ 40 days) and PTAA/Na (batch 1; aged for ≈ 110 days) at 25 °C. The wiggle at 350 nm is caused by the exchange of spectrophotometric lamps.

practically independent α_n for a mature solution as far as its $\alpha_n < 1.0$, but high enough to prevent phase separation. Regardless the difference of ca 10%, both here determined values of ϵ_{310} are considerably higher than the value readout from the Fig. 1 of Ref. 19 (≈ 2000 L mol⁻¹ cm⁻¹). This finding suggests that experiments reported in Ref. 19 were performed on freshly prepared solution (see Fig. 2).

Interesting results were obtained with partially ($\approx 70\%$) hydrolyzed and with NaOH fully neutralized PTAME, i.e. PTANa/Me. This sample was not dialyzed and spectra were recorded for freshly prepared solution. The dilution of PTANa/Me solution from $c_{\text{pol}} \approx 1.96 \cdot 10^{-3}$ M to about 50-times lower c_{pol} was accompanied by a decrease in both λ_{max} and ϵ_{max} (Fig. 7) and appearance of IP at $\lambda \approx 402$ nm (the same position as in the case of aging of PTALi solution or acidobasic titrations of freshly prepared PTAA-based solutions). As a result, the Beer-Lambert law is not valid for fresh solutions of PTANa/Me.

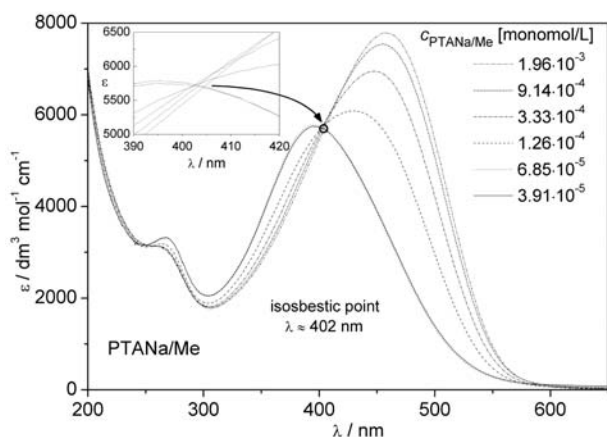


Figure 7. Test of validity of Beer-Lambert law for freshly prepared aqueous solution of PTANa/Me (batch 3) at room temperature. The degree of hydrolysis of methoxy groups is around 0.70 while the hydrolyzed groups are completely neutralized. The legend inside the graph area is showing polymer concentration c_{pol} (expressed in moles of monomeric units in one litre) belonging to the particular spectrum. The inset is enlarged region where the spectra intersect.

3. 4. Effect of Ionic Strength

Addition of NaCl to ripe PTANa solution (batch 1) induces a blue shift of λ_{max} (up to about 15 nm) and a decrease in ϵ_{max} (up to about 12%; see Fig. 8a). It is well known that an increase in the ionic strength of a solution weakens both repulsive and attractive electrostatic interactions among the charged moieties present in the solution. Hence shielding of repulsions among -COO^- groups should increase the population of less extended (more coiled), entropically favorable conformations of macropolymers, with lower extent of delocalization of the valence electrons. The corresponding increase in the band-gap energy explains the observed blue shift of λ_{max} .

The spectrum of PTAA/Na solution (unlike to that of PTANa) exhibits a slight but reproducible red shift of λ_{max} up to about 2 nm upon addition of NaCl (Fig. 8b). This shift is accompanied with a regular decrease of absorbance in the whole UV/Vis region can be a consequence of aggregation and/or phase separation occurring in solution upon adding NaCl. The red shift is believed to occur »due to the increased rigidity of the chains in the aggregates and possibly the onset of some crystallization inside the aggregates«,¹⁹ while the observed regular decrease of absorbance may be actually the outcome of increased light scattering occurring when phase separation takes place. Indeed, the solution of PTAA/Na is becoming more and more turbid upon addition of NaCl.

3. 5. The Specific Ion Effect

As it was shown in work of McCollough et al.²⁵ spectra of regioregular water-soluble polythiophenes (to be more specific: poly[3-(thiophen-3-yl)propionic acid]) depend on the nature of counterions present in solution. He observed a

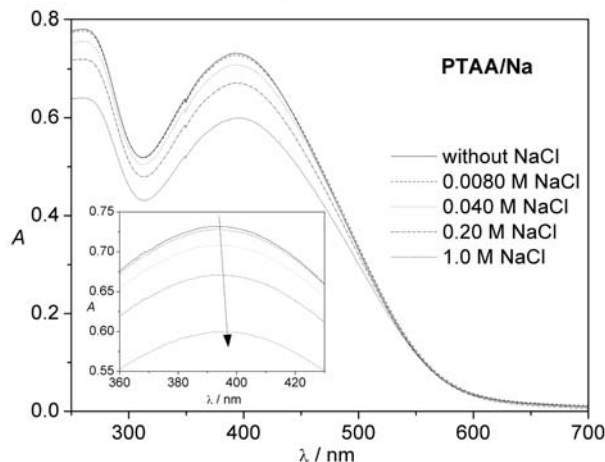
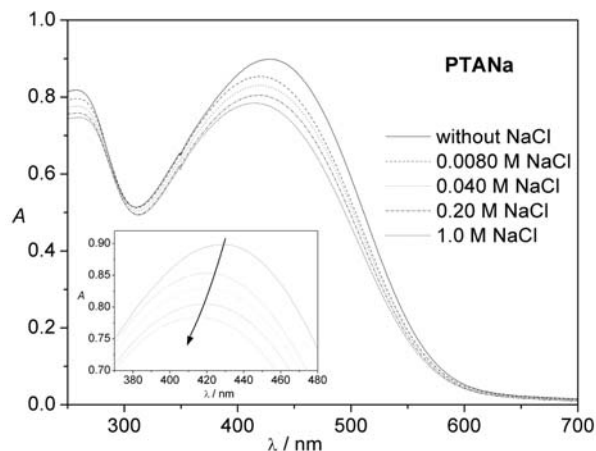


Figure 8. UV/Vis spectra (A is absorbance) of aqueous solutions of PTANa (8a-left) and PTAA/Na (8b-right) as a function of the concentration of NaCl. An increase in the ionic strength decreases the molar absorption coefficient, ϵ_{max} , $c_{\text{pol}} = 1.275 \cdot 10^{-4}$ mol/L, optical path length 1 cm, others as for Fig. 5.

shift of λ_{max} for about 40 nm when going from Li^+ to Cs^+ counterions.²⁵ Similar experiment was performed by us but with two differences: (i) our sample of PTAA was regio-irregular, and (ii) different alkali (Li^+ , Na^+ , and Cs^+) counterions (in the form of alkali hydroxide) were gradually added into ripe solution of PTAA partially (PTAA/Li; $\alpha_n = 0.346$) neutralized with LiOH. The evolution of spectra during neutralization titration (see Fig. 4a – case of adding LiOH to PTAA/Li and Fig. 2 in “Supporting Information” – case of adding NaOH and CsOH) shows no distinct differences among solutions with these three counterions. The origins of the specific effect mentioned by McCollough et al.,²⁵ and an absence of it shown by us deserves a separate study.

3. 6. Temperature Dependence of the UV/Vis Spectra

One of the interesting findings related to UV/Vis spectra of PTAA-based polymers is their dependence on temperature. As shown above, the spectra obtained for

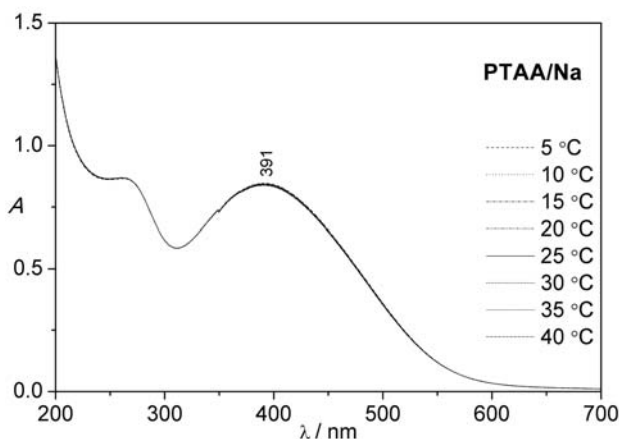


Figure 9a. Temperature dependence of the UV/Vis absorption spectrum of PTAA/Na ($\alpha_n = 0.29$; pH < 6); $c_{\text{pol}} = 1.4 \cdot 10^{-4}$ M; $\lambda_{\text{max}} = 391$ nm.

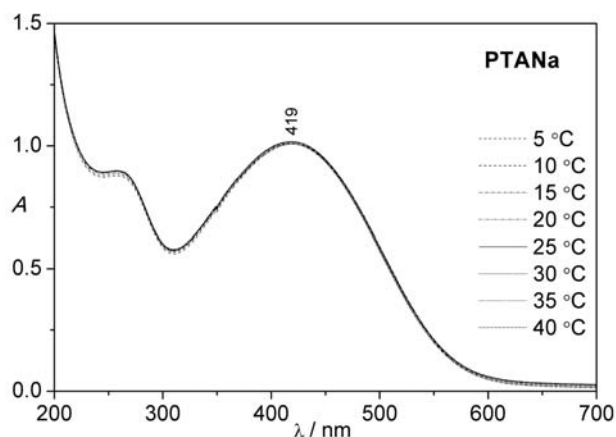


Figure 9b. Temperature dependence of the UV/Vis absorption spectrum of PTANa ($\alpha_n = 1.00$); $c_{\text{pol}} = 1.4 \cdot 10^{-4}$ M; $\lambda_{\text{max}} = 419$ nm.

freshly prepared solutions can be very sensitive to both the degree of neutralization and ripening, so one would expect that they might depend also on the temperature variation. Indeed, as shown by Kim et al., spectra of PTAA partially neutralized with NaOH and recorded at low α_n (pH \approx 5.2) show modest increase of λ_{max} with temperature (from \approx 398 nm at \approx 22 °C to \approx 407 nm at \approx 88 °C), while the decrease of λ_{max} with temperature obtained at higher values of α_n (at pH of 6.3 and 11.1) is more pronounced (from \approx 451 nm at \approx 22 °C to \approx 426 nm at \approx 91 °C²¹).

Our temperature dependence study of the UV/Vis spectra was limited to temperature range between 5 and 40 °C. We determined the spectra of dialyzed (cut off 6–8 kDa) and ripe samples of PTAA/Na ($\alpha_n = 0.29$; batch 1) and PTANa. No change of spectra with temperature has been observed under these conditions (Figs. 9a and 9b). Beside the fact that our samples were not sensitive to the temperature variation, one should also notice that our values of λ_{max} are notably smaller than those obtained by Kim et al.²¹ We suspect that temperature dependence, re-

ported in Ref. 21, was studied on freshly prepared solution. Unfortunately, no information on such details is provided in Ref. 21.

4. Discussion

The fact that characteristics of polymer solutions may change with time is known from literature.²⁶ Thus it is often advisable to allow polymer solution to ripe for a proper time, before measurements and/or processing takes place. Aging of polymer solutions usually receives little or no attention by scientists,^{27,28} with an exception of the polymer degradation studies.^{29–32} Typical CPE molecule is constituted of a hydrophobic main chain and ionic and/or pendent groups capable to ionize, which implies a delicate competition between electrostatic and hydrophobic interaction in aqueous solution. Such a competition may result in slow changes in conformations of chains and their supramolecular structure, accompanied with changes in the degree of dissociation of ionizable groups, which should finally lead to an equilibrium state. Hence a non-reactive aging effect should actually be classified as a relaxation process.

4. 1. UV/Vis Spectra

The spectrum of PTANa (Fig. 5) taken in aqueous solution shows a broad band of π - π^* transitions in the main chains centered at the wavelength $\lambda_{\text{max}} = 429$ nm with the molar absorption coefficient $\epsilon_{429} = 7050$ dm³ cm⁻¹ mol⁻¹, while that of PTAA/Na is characterized by $\lambda_{\text{max}} = 394$ nm and $\epsilon_{395} = 6150$ dm³ cm⁻¹ mol⁻¹. High λ_{max} of PTANa chains should be ascribed to the repulsion of $-\text{COO}^-$ groups, making the conformations with coplanar thiophene rings preferable to the distorted ones, so increasing the extent of delocalization of π -electrons along the PTA⁻ main chains. Spectra of PTANa and PTAA/Na in ripe solutions practically overlap in the region of λ from 280 to 340 nm, showing a local minimum at $\lambda = 311$ nm, with $\epsilon_{311} = 4045$ dm³ cm⁻¹ mol⁻¹. As the overlap is independent of α_n , the optical absorption at 311 nm can be used for determination of the concentration of a solution of PTAA/Na in ripe solutions of any value of α_n . A similar overlap of the spectra is seen in the paper of Vallat et al. (Fig. 1 in Ref. 19) for PTAA/Na samples of various α_n , but the value of ϵ in the region around 305 nm (as read from the published figure) is ca. 2000 dm³ cm⁻¹ mol⁻¹, i.e., a half of the value observed in our work. Maybe accidentally, their value of ϵ is equal to that we observed for the incompletely hydrolyzed sample of PTANa/Me in freshly prepared solution, the local absorption minimum of which occurs at ca. 306 nm.

We noticed that the UV/Vis spectrum of PTAA containing stock solution showed an attribute that can be called “time-increasing stability”: the longer the time that

elapsed from preparation of the solution, the higher the volume of alkali hydroxide solution was needed to observe the change of the spectrum typical of partially neutralized PTAA to the spectrum typical of fully neutralized PTAA. On the other hand, a notable difference in the shape of the spectra prepared from the same batch of PTAA sample, but at different times can be observed (Fig. 2). The deviations discussed most probably originate from very slow equilibration of the conformations of polymer chains. One possible reason for the slowness of conformational transitions, suggested in other context also by Kim et al.,²¹ could be a stabilization by intramolecular hydrogen bonds between carboxyl side groups²⁵ (see Fig. 3 of the “Supporting Information”). This hypothesis is supported by the close similarity of the spectra of PTAA (pure acidic form) in DMF solution ($\lambda_{\text{max}} = 414$ nm) and in the solid state ($\lambda_{\text{max}} = 414$ nm; Fig. 4 in “Supporting Information” to the previous study²³). Others polythiophenes such as poly(3-hexylthiophene)³³ and cationic polythiophene polyelectrolytes^{34,35} show a red shift of the main optical absorption band of about 100 nm or even more when transferred from solution to the solid state. This shift is generally ascribed to the stacking of thiophene rings in the solid state. The absence of any red shift of this kind in the case of PTAA shows that ring stacking does not take place in the case of this polymer, which can be explained simply by the strong intrachain H-bond interactions hindering conformational transitions. In addition, the UV/Vis spectrum of a ripe aqueous solution of PTAA/Na (Fig. 9a) does not show a notable change if the temperature is varied from 5 °C to 40 °C over a few hours, which also proves the high conformational stability of chains resulting from intrachain H-bonds. The UV/Vis spectrum of PTANa solution also exhibits a high stability in the same temperature region. In this case, however, the stability is obviously ensured by electrostatic repulsions of $-\text{COO}^-$ anions (see below).

4. 2. Isosbestic Points

While the optical spectra of PTANa and PTAA/Na as PTAA/Li (see Fig. 6) in ripe solutions obey the Beer-Lambert law rather well, the spectrum of a freshly prepared aqueous solution of PTANa/Me does not. The spectrum shows an increase in both λ_{max} (from 396 nm to 458 nm) and the corresponding ϵ_{max} (from about 6450 to roughly 8850 $\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$), if c_{pol} is increased from $5 \cdot 10^{-5}$ to ca 10^{-3} mol/L (Fig. 7). At $c_{\text{pol}} < 7 \cdot 10^{-5}$ mol/L the spectra obey the Beer-Lambert law. A pronounced reversible change in the spectrum induced exclusively by a change in the concentration of the measured solution almost always stems from intermolecular interactions. Hence we speculate that besides hydrolysis of $-\text{COO}^-$ also the aggregation of PTAA/Me chains into nano-sized micellar clusters (which is driven by the hydrophobic interactions of monomeric units with the methyl-ester group) could be responsible for the observed spectroscopic behavior of PTANa/Me solutions.

The above spectra of PTANa/Me suggest the existence of an isosbestic point (IP) at $\lambda = 402$ nm ($\epsilon_{402} = 6350 \text{ dm}^3 \text{cm}^{-1} \text{mol}^{-1}$). The IP is defined as the wavelength (or frequency, wave number, or photon energy) at which the total absorbance of the sample does not change during a chemical or physical change of the sample³⁶ provided that the number of absorbing species in solution is conserved. The last condition is assured by plotting the spectra using ϵ_{λ} vs. λ coordinates. The detail shown in the inset of Fig. 7 indicates that the ϵ_{λ} vs. λ curves do not cross at exactly the same point; however, this can be ascribed also to experimental error. Interestingly, Vallat et al.¹⁹ observed an IP at almost the same wavelength ($\lambda = 401$ nm) during the titration of PTAA (declared to be free of methyl-ester groups) with NaOH. They ascribed this IP to the conformational change of an “extended-to-collapsed” polyanionic chain, related to the transition between hydrophilic and hydrophobic regime. In addition, they observed a second IP at $\lambda = 392$ nm and ascribed it to the “collapsed-densely collapsed” chain transition. On the other hand, Kim and Osada et al.^{20–22} did not report the existence of any IP during titration of PTAA, just as we did not observe any IP during our experiments with ripe solutions of PTAA.

5. Conclusions

We obtained new results for the UV/Vis spectra of PTAA-based aqueous systems. We demonstrated the validity of the Beer-Lambert law for PTANa, PTAA/Na, and PTAA/Li, and its violation for PTANa/Me solutions in water; the latter system was instead found to exhibit an isosbestic point at 402 nm. On the other hand, we observe isosbestic point at $\lambda = 401$ nm, but only during the acid-basic titrations of freshly prepared PTAA solutions, while this IP was clearly absent during the titration of ripe PTAA solutions. The UV/Vis spectra presented here do not indicate π -stacking of thiophene rings as observed for some other polythiophenes.

In this study we showed that UV/Vis spectra of polythiophene derivatives in water strongly depend on the “age” of solution, i.e. the time spent after dissolution. This effect was for PTAA not known before, and is rarely mentioned in studies of aqueous polyelectrolyte solutions at all. There are discrepancies between the published spectroscopic data, and those obtained in this work, as well as among the data on PTAA-based systems available in literature. They can be attributed to the slowness of conformational relaxation of PTAA/Na chains. Alternatively, they can in part be ascribed to certain differences in the chemical structure of the samples studied by various groups.

Due to sensitivity of UV/Vis spectra of conjugated polymers to subtle differences in polymer structure, the UV/Vis measurements should be performed under well defined conditions, and on the sample with well documen-

ted “history”. Only such an approach enables reliable comparison of results obtained by different Laboratories.

6. Acknowledgments

The study was supported by the Slovenian Research Agency (P1-0103-0201 and J1-0103-4148), the Czech Science Foundation (P108/12/1143) and the Ministry of Education of the Czech Republic (MSM0021620857). D. B. acknowledges the support of the Grant Agency of Charles University (project 166410). We thank Professor M. Veber¹ for advice, Mrs. J. Furlan¹ and Mrs. Z. Držaj¹ from the Laboratory of Analytical Chemistry for performing the atomic absorption analysis and to Prof. P. Nachtigall² for DFT calculations concerning the conformations of PTAA chains with intramolecular hydrogen bonds. G. H. was supported by the Slovenian Research Agency Grant for Young Researchers (2011–2015).

Supporting Information Available: ¹H NMR spectrum of partially hydrolyzed PTAA (PTAA/Me), UV/Vis spectra obtained during neutralization of PTAA/Li with NaOH and CsOH, figures of structures of conformers, showing hydrogen bonds between the –COOH groups of neighboring units, and a survey table, containing compilation of the UV/Vis spectroscopic data obtained by different research groups. This material is available on the internet site of *Acta Chimica Slovenica*.

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Povzetek

V delu so predstavljene raziskave UV/vidnega absorpcijskega spektra vodnih raztopin nezaestrene in deloma zaestrene poli(tiofen-3-ilocetne kisline) (PTAA) v prisotnosti natrijevih in litijevih protiionov. Merjeni vzorci so bili skrbno očiščeni in opredeljeni glede na njihovo molsko maso in vsebnost –COOH skupin. Raziskali smo, kako se UV/vidni spektri raztopin spreminjajo s staranjem raztopine, s koncentracijo polimera, z dodatkom enostavne soli, s temperaturo in z vplivi še nekaterih drugih parametrov. Pokazali smo, da Beer-Lambertov zakon razmeroma dobro velja v starih raztopinah PTANa, PTAA/Na in PTAA/Li, medtem ko je oblika absorpcijskega spektra sveže raztopine PTANa/Me močno odvisna od koncentracije ter izkazuje izozbestično točko pri 402 nm. Izidi raziskav kažejo, da so UV/vidni spektri vodnih raztopin politiofenskih derivatov znatno odvisni od starosti raztopine. Predstavljena so neskladja med spektroskopskimi podatki, objavljenimi v literaturi, in rezultati naših meritev, kakor tudi možni vzroki teh neskladij.

Supporting Information

References quoted in this Supporting Information (SI) are related to the list of references at the end of this material.

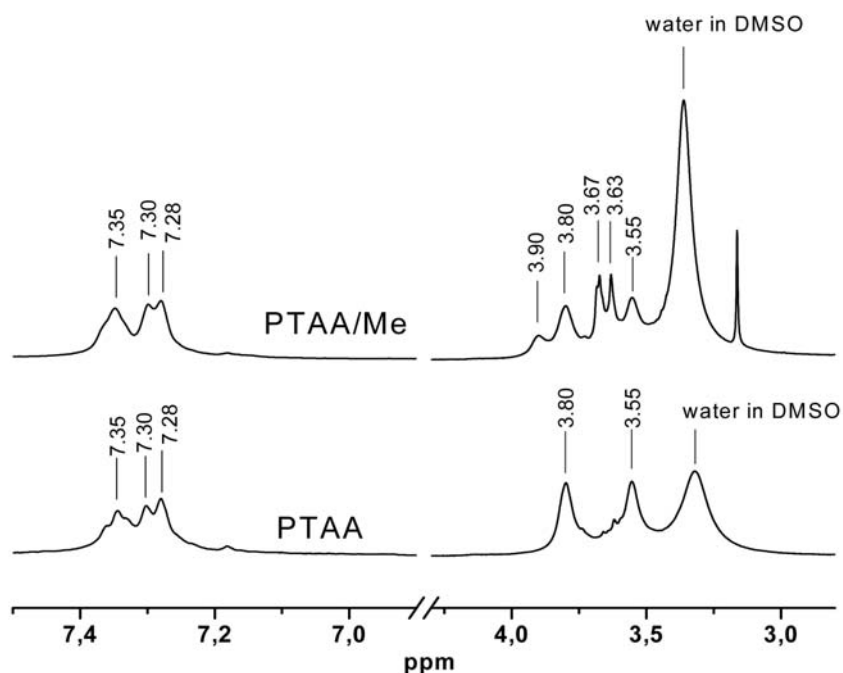


Figure 1. ^1H NMR spectra of partially (PTAA/Me) and fully hydrolyzed PTAA in $\text{DMSO-}d_6$.

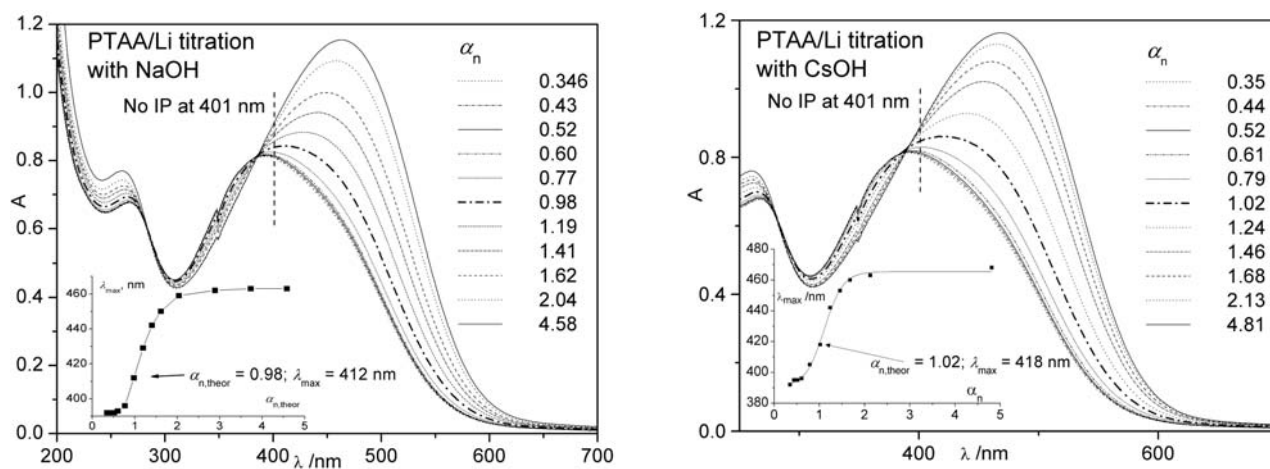


Figure 2. a) UV/Vis absorption spectra of PTAA/Li (dialyzed sample from batch 2) recorded during neutralization with NaOH (additions of 0.1 M NaOH). PTAA was dissolved in water for 82 days; almost all this time PTAA was in the form of partially neutralized Li salt of PTAA ($\text{pH} \approx 5\text{--}6$), and was kept at room temperature. $T = 25^\circ\text{C}$. The small wiggle at 350 nm is caused by the exchange of spectrophotometric lamps. b) The same as for a) but for neutralization with CsOH (additions of 0.1 M CsOH).

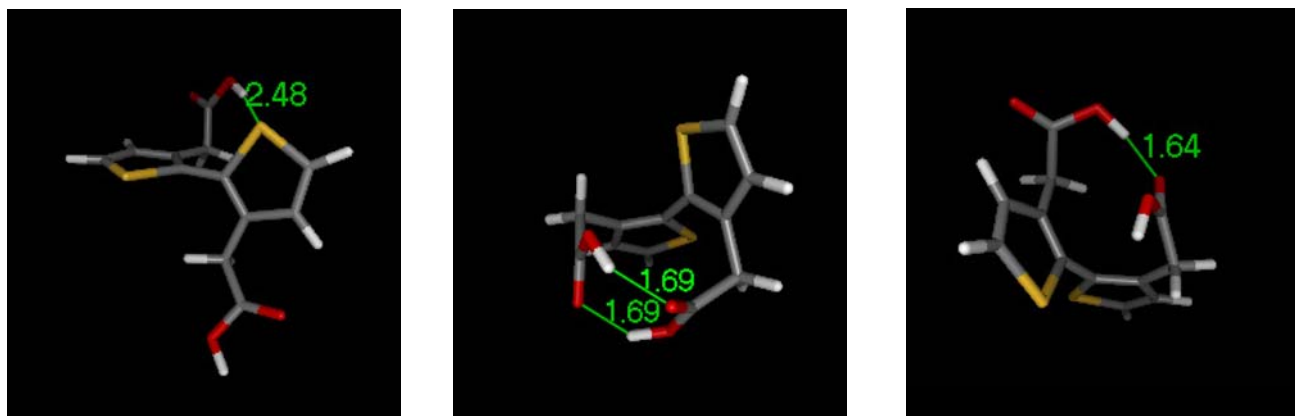


Figure 3. Examples of hydrogen bonds: up – between –COOH groups located on neighboring head-to-head connected monomeric units of a PTAA chain; bottom – between a –COOH group and sulfur atom in neighboring thiophene ring. Geometry optimization of various conformers was obtained with the B3LYP exchange-correlation functional^{2,3}, employing 6-31G(d,p) basis set as implemented in Gaussian 03⁴ program suite.

Table 1. Survey of the UV/Vis spectroscopic data on PTAA-type polymers found by us and published in literature.

polymer type	this paper $X_n = 39$ ^{SEC-PS} (66 ^{SEC} calibration – Vallat ¹)	Vallat et al. $X_n = 45$ and 125	Kim, Osada et al.
	λ_{\max} (nm) / ϵ_{\max} (dm ³ cm ⁻¹ mol ⁻¹) reference(s) (for aqueous solutions if not stated else)		
PTANa	419–429 / 7 050 pH 8–9	435 / 6 600 ¹ , Support 440 ⁵ , Fig. 2, $X_n = 125$ 512 ⁶ , regioregular pH 9, $X_n = 120$	450 ⁷ , Fig. 7, pH 11, drop with T to 425 at 95 °C 427 ± 2 ⁷ , pH 7, phosphate buffer 440 ± 2 ⁸ , Fig. 5, pH 6 – 11, $X_n = 35$ ^{SEC-PS} 432 ⁸ , Fig. 6, pH 7 drop with T to 410 at 100 °C 450 ⁹ , Fig. 10, pH 6.3 and 11.1; 1 M NaCl drop to 425 at 95 °C 445 ⁹ , Fig. 10, pH 6.3 to 11.1; 1 M NaCl 440 ⁹ , Fig. 10, pH 6.3 to 11.1; 0.2 M NaCl 385 ¹⁰ , Fig. 3, $c_{\text{pol}} = 10^{-4}$ M, pH 7.2
PTAA/Na	394 / 5 740, pH 6	412 / 5 000 ⁵ , pH 6	
PTAA	414, in DMF 415–419 / 5200, DMSO 416, in the solid state	399 / 4 800 ⁵ , pH < 5	408 ⁷ , Fig. 5, 411 ⁷ , Fig. 8, in DMSO 420–413 ⁷ , Fig. 5, rise in c_{pol} , DMSO + 25% H ₂ O 413 ± 2 ⁷ , Fig. 5, DMF and DMSO + 20% H ₂ O 430 ⁷ , Fig. 8, DMF/DMSO 2:1 to 7:1 398 ⁷ , Fig. 8, H ₂ O/DMSO 7:1

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