*Scientific paper*

# Potentiometric and Conductometric Study of Aqueous Solutions of Lithium and Sodium Salts of Poly(thiophen-3-ylacetic acid)

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

## Abstract

The title polymer, PTAA, practically free of ester groups was obtained by oxidative polymerization of methyl thiophen-3-ylacetate and subsequent basic hydrolysis of primary polymer. Poly(thiophen-3-ylacetic acid) has been thoroughly characterized by NMR, IR, Raman, and UV/Vis spectroscopy. The polyacid behavior during neutralization titrations with lithium and sodium hydroxides, carried out under nitrogen atmosphere, has been studied by conductometry and potentiometry. Henderson-Hasselbach plots of potentiometric titration curves show a break point at pH around 6, where the curve slope drops from 1.8 (at lower pH) to a value from 1.05 to 1.3 (at higher pH values). The UV/Vis spectra monitored during back titration show: (i) monotonous decrease of both $\lambda_{\max}$ and $\varepsilon_{\max}$ as pH decreases, (ii) the presence of the isosbestic point at 401 nm that can be ascribed to conformational transition of PTAA chains, and (iii) absence of the isosbestic point at 392 nm reported previously by other authors.

**Keywords:** Ionic polymers, polyelectrolyte, polythiophene, titration curves, Henderson-Hasselbach plot, conformational transition

## 1. Introduction

Polyelectrolyte (PEL) is defined as a polymer composed of macromolecules in which a substantial portion of the monomeric units contain ionic or ionizable groups, or both.[1–2] As to properties, PELs significantly differ from non–ionic polymers, as well as from low–molecular–weight electrolytes.[3–12] In particular, electrolytic dissociation of PELs may be accompanied by conformational changes[13] of their chains that are most apparent in solutions of conjugated polyelectrolytes (CPEs), as they are directly observable through color (absorption as well as fluorescence) changes. PELs often exhibit ionic conductivity in the solid state but conjugated PELs can in addition exhibit electronic conductivity.[14] Chains of CPEs possess amphiphilic character giving them the capability of self–assembly, and the ability to interact specifically with other polyionic species such as nucleic acids and proteins.[15–20] CPEs are currently being tested as promising new materials for reducing the electron–injection barrier from high work–function metal electrodes into polymers in optoelectronic devices,[21–25] and as sensor materials for detection of ions,[26-30] biomolecules[31,32] and various organic molecules[31,32] operating on the basis of their UV/Vis (ultraviolet-visible), fluorescence, or redox responses. CPEs enable the layer–by–layer construction of a new type of polymer composite film consisting of alternating layers of cationic and anionic CPEs.[33–35] They are also used as favorable matrix materials for preparation of organic–inorganic composites with noble–metal plasmonic nanoparticles that can comprise hot spots greatly enhancing the local electrical field intensity.[36-40]

Properties of aqueous solutions of strong PELs (including CPEs) are dominated by repulsive Coulomb interactions between like–charged units of macropolyions (macromolecular polyions),[8–12] as well as by attractive Coulomb interactions between macropolyions and their counterions. The attractive interactions cause an accumulation of counterions in the close vicinity of the macropolyions.[41] On the other hand, small ions of the same charge sign as the macropolyions, so-called coions, are repelled by the macropolyions.

The overwhelming majority of studies on CPEs focus on the preparation, structure, and benchmark tests of the functional properties of these systems.[42–50] This also holds true for the poly(thiophen-3-ylacetic acid), PTAA, which is a CPE with weak acidic groups, the behavior of which is strongly influenced by the ionization equilibrium involving these groups. Vallat et al.[43,51] and Kim et al.[52–54] studied the acid-base titration behavior of aqueous solutions of PTAA simultaneously monitoring the UV/Vis spectra of the solutions. In addition to this, Vallat et al.[43,51] investigated completely neutralized PTAA, i.e., poly[sodium (thiophen-3-yl)acetate] denoted here as PTANa, by small angle neutron and X–ray scattering techniques. They obtained evidence of conformational transitions of PTAA chains during the acid-base titrations, and examined the effects of (i) the polymer concentration, (ii) polymer molecular weight, and (iii) NaCl added to solution (ionic strength effect) on the behavior of these solutions. Both teams reported increase in the slope of Henderson-Hasselbach plots in the presence of various concentrations of NaCl from values between 1.4 and 1.9 to values between 3 and 11.8, depending on salt concentration.[51–54] Interestingly, one of these groups reported a drop of the slope value from 2.0 to 1.1 for a cross-linked P3TAA.[54]

In this contribution we report results of extensive potentiometric and conductometric titrations of PTAA with NaOH, and LiOH, respectively. All the titrations were performed under the nitrogen atmosphere. To our best knowledge, no conductometric study of PTAA solutions has been published so far. The potentiometric titration results, presented in the form of the Henderson-Hasselbach plots, are analyzed and compared with the literature data. Differences from the titration results obtained by other authors are discussed in view of the differences in experimental details, such as sample preparation, dialysis, and others.

# 2. Experimental

## 2. 1. Polymer Synthesis and Characterization

The polymers studied were prepared in two batches by hydrolytic modification of poly(methyl thiophen-3-ylacetate), PTAMe that was synthesized by oxidative polymerization of methyl thiophen-3-ylacetate with $FeCl_3$ in chloroform using a procedure described elsewhere.[53] Poly(thiophen-3-ylacetic acid), PTAA, was obtained by the total alkaline hydrolysis of PTAMe. For details on polymer synthesis see "Supporting Information".

Basic characteristics of the first batch (batch 1) of PTAMe (later on hydrolyzed to obtain PTANa) used in the total hydrolysis of ester groups were as follows: number-average molar mass $M_n$ = 6.0 kDa, mass-average molar mass $M_w$ = 14.5 kDa, dispersity[55] $Đ$ = 2.4, number-average degree of polymerization $X_n \cong 39$. Since no degradation of polymer main chains was observed during the alkaline hydrolysis of PTAMe under slightly milder conditions than[43] we had applied, it is reasonable to assume that PTAA obtained by hydrolysis of PTAMe has retained the same degree of polymerization (i.e. $X_n \cong 39$). At this point it should be stressed that Vallat et al. compared[43] the relative molecular weight of their sample of PTAMe obtained by size-exclusion chromatography (SEC), based on polystyrene calibration, with the absolute molecular weight obtained from field-flow fractionation (FFF). According to their findings $M_w$(FFF) exceeded $M_w$(SEC) by a factor of approximately 1.7. Using this calibration (see "Supporting Information") for $M_w$ and the dispersity value $Đ$ = 2.4, our sample should have $M_n$ = 10.3 kDa, $M_w$ = 24.8 kDa and $X_n \cong 66$. The data for the second batch (batch 2) of PTAMe are: $M_n$ = 11.1 kDa, $M_w$ = 33.3 kDa, $Đ$ = 3.0, and $X_n \cong 72$.

Size-exclusion chromatography (SEC) analyses of polymers were performed using the HP 1100 instrument 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) calibrated with polystyrene (PS) standards (PL, Bristol, UK). Tetrahydrofuran (flow rate 0.7 mL/min) was used as a mobile phase. Apparent molecular weight averages relative to PS standards were obtained.

$^1$H and $^{13}$C NMR spectra were measured on a Varian $^{\text{UNITY}}$INOVA 400 instrument using polymer solutions in $CDCl_3$ (PTAMe) or $d_6$-DMSO (PTAA). The spectra were referenced to tetramethylsilane ($^1$H) and the solvent signals (77.00 ppm for $^{13}$C spectra in $CDCl_3$; 2.50 ppm for $^1$H 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 and with an FT Raman module (Nd:YAG laser 1064 nm) 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 in a 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.

## 2. 2. Preparation of Stock Solutions

PTAA/Na stock solution – mixed solution of PTAA and its sodium salt: dried sample of PTAA from the first batch was dispersed in triply distilled water under a nitrogen atmosphere and neutralized by titration with an aqueous solution of NaOH (0.0996 M). The solution that was turbid in the acidic pH range became completely clear at pH value of about 8.5. In order to obtain the maximal solubility of PTAA, the solution pH value was increased to 9.1 by adding an excess of the NaOH solution. To prevent possible formation of carbonate and hydrogen carbonate ions, the pH of the resulting polymer solution was decreased by titration with aqueous HCl (0.1 M) to pH = 5.1. The solution obtained in this way was filtered through a cellulose–nitrate 3.0 μm filter (Sartorius), poured into dialysis tubes (Spectra/Por 1; relative–molecular–mass cut-off: 6.0–8.0 kDa) and dialyzed against triply distilled water for about one month. During the dialysis pH of the solution decreased to a value around 3.75 due to the exchange of $Na^+$ with $H_3O^+$ ions from water. As a consequence partial precipitation of PTAA occurred in the dialysis tubes.[53] The solution became clear again upon adjusting its pH to 6.0 by adding an appropriate volume of the NaOH solution (via titration) under a nitrogen atmosphere. We took strict precautions against contamination of the solution with atmospheric $CO_2$ during the neutralization of PTAA to pH 6.0. Finally, the solution was successively filtered through cellulose–nitrate filters of porosity 3.0, 1.2, and 0.45 μm, and the filtrate stored in the dark at room temperature as the stock solution from which the solutions used later were prepared by weighing.

PTAA/Li stock solution – mixed solution of PTAA and its lithium salt – was prepared from the second batch of PTAMe using the same procedure as described above for preparation of PTAA/Na and LiOH instead of NaOH. The difference that should be mentioned here is that the molar–mass cut-off of dialyzing tubes used in dialysis against water was 3.5 kDa.

The composition of the stock solution (batch 1) was analyzed using (i) the potentiometric titration with NaOH solution (0.0996 M) to determine the concentration of free carboxylic groups, $c_{\mathrm{COOH}}$, and (ii) atomic absorption spectroscopy to determine the concentration of $Na^+$ counterions, $c_{\mathrm{Na+}}$. Neglecting the concentrations of $H_3O^+$ and $HO^-$ ions (pH values were around 6), the electroneutrality condition requires parity of concentrations $COO^-$ and $Na^+$ ions ($c_{\mathrm{COO-}} = c_{\mathrm{Na+}}$) in the stock solution. As PTAA is a weak polyacid, the degree of neutralization, $\alpha_n$, of PTAA can be calculated as $\alpha_n = c_{\mathrm{Na+}}/c_{\mathrm{COOX}}$, where $c_{\mathrm{COOX}}$ is the total concentration of carboxy groups given as $c_{\mathrm{COOX}} = c_{\mathrm{COOH}} + c_{\mathrm{COO-}}$. Because our PTAA samples were practically free of methyl-ester groups (see NMR spectra in the "Supporting Information"), $c_{\mathrm{COOX}}$ ($= c_{\mathrm{COO-}}/\alpha_n$) was equal to the concentration of monomeric units of the polymer in solution, $c_{\mathrm{pol}}$.

The concentration of the stock solution of PTAA/Li (sample from the second batch) was determined in the same way as that of the PTAA/Na solution (from the first batch) using LiOH solution (0.0901 M) as the titrant during the potentiometric titration. The atomic absorption spectroscopy was used to determine concentration of lithium counterions.

**Potentiometric Titrations** were performed at 25 °C using an MA 5740 pH meter (Iskra, Slovenia) and InLab®406 Mettler Toledo combined glass electrode with an incorporated gel-filled reference electrode. Before each measurement, the pH meter was calibrated using buffer solutions of pH 6.86, and 9.18; the electrode response slope was found to be 94.8% of the theoretical one. The magnetically stirred solution was kept under the nitrogen atmosphere during titration. The titrant ($CO_2$–free solution of 0.0996 M NaOH or 0.0901 M LiOH) was measured out using a 2 mL micro–burette (Gilmont) and the equivalence point (pH ≅ 8.9) was determined from the second derivative graph.

**Conductometric Acid-Base Titrations** were carried out at 25 °C using a 712 Metrohm conductometer. The stirred solution was titrated by Gilmont micro-burette under the nitrogen atmosphere.[56]

**Atomic Absorption Spectrometry** measurements were performed using an AAnalyst 600 (Perkin Elmer) instrument and standard solutions of sodium ions with $c_{\mathrm{Na+}}$ equal to 0.100, 0.200, 0.300, and 0.400 $\mathrm{mg_{Na+}/L}$. To determine $c_{\mathrm{Na+}}$ in the stock solution, the (stock) solution was diluted to match the concentration range of the standard solutions. Concentration of lithium ions in the stock solution of PTAA/Li was determined in a similar way.

**UV/Vis Absorption Spectra** 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 at 25 °C if not indicated otherwise.

## 3. Results and Discussion

Abbreviations for polymer systems studied in this paper are as follows (note that $\alpha_n$ 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 $NaOH_{(aq)}$ ($\alpha_n = 0.346$ in the case of our samples)

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

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

### 3. 1. Spectroscopic Characteristics of PTAA Samples

Comparison of $^1$H NMR spectra of our PTAMe and PTAA samples (see "Supporting Information") showed

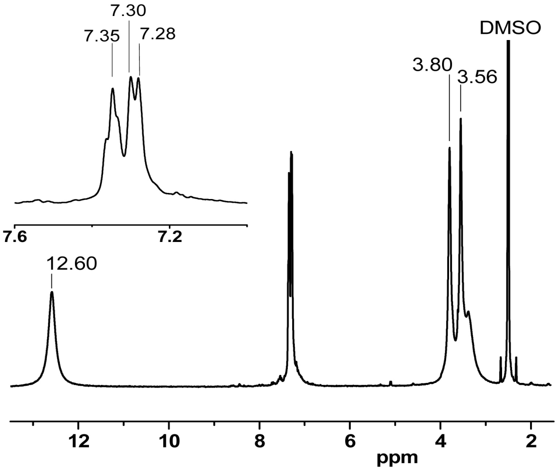

**Figure 1.** $^1$H NMR spectrum of PTAA (second batch).

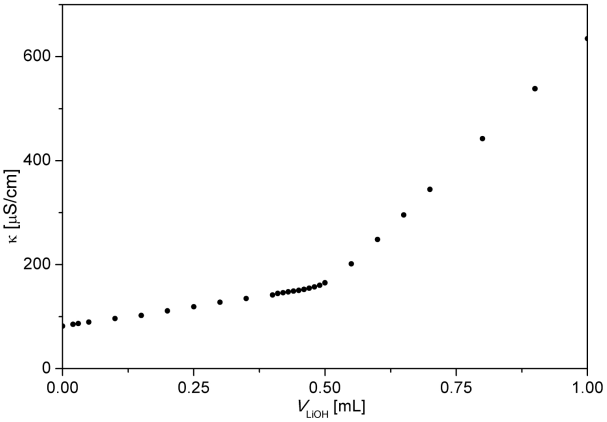

**Figure 2.** Conductometric titration curve obtained for the titration of PTAA solution (batch 2; initial $\alpha_n$ = 0.346 and initial $c_{PTAA/Li}$ = 0.0013 mol/L) with LiOH aqueous solution (0.0901 M); $\kappa$ is the specific conductivity of solution.

that the PTAA samples were almost free of -COOCH$_3$ groups. The $^1$H NMR spectrum of PTAA showed two signals of -CH$_2$- groups that could be assigned[57,58] to those included in the HT (3.80 ppm) and TT (3.55 ppm) sequences (H stands for head and T for tail of a monomeric unit). As the intensities of these signals were approximately equal, the content of HT sequences (i.e., the degree of regioregularity) of chains of the studied PTAA/Me and PTAA samples and their salts could be, within experimental error, ascertained to be around 50%. In other words, all samples studied can be regarded as regio-irregular polymers. The absence of the signal at 170.40 ppm in the $^{13}$C NMR spectrum of PTAA (see "Supporting Information") confirmed the practical (within the detection limits) absence of -COOCH$_3$ moieties in our PTAA samples. As compared with the spectrum of our samples (Figure 1), the $^1$H NMR spectra of PTAA and PTAMe published by Kim et al.[53] showed much less resolved signals of protons of -CH$_2$- groups as well as thiophene-rings.

The "Supporting Information" to this paper contains, in addition to the $^{13}$C NMR spectra already mentioned, the Raman and IR spectra of PTAA, the IR spectrum of PTAMe, the UV/Vis spectra of PTAA in DMF, DMSO and in the solid state, and the UV/Vis spectrum of PTAMe in DMSO.

## 3. 2. Conductometric Titrations

Polyelectrolytes containing carboxylic groups typically behave as weak polyacids. When such acids are weak enough their ionization can be provoked mainly by neutralization (i.e. by the addition of a strong base like an alkali hydroxide), and the degree of ionization can be assumed to be equal to the degree of neutralization. Furthermore, if the fraction of hydrophilic functional groups attached to polymer chains is not high enough, such a polyacid is usually only slightly soluble (or even insoluble) in water when the degree of neutralization is very low. This is true also for our PTAA solutions.

A conductometric titration curve shown in Figure 2 clearly proved that an increasing volume of the base (LiOH in this case) solution added continuously increased the degree of ionization of PTAA chains. The monotonous increase of the specific conductivity with the volume of added base confirms a linear increase of the degree of ionization if the degree of neutralization is increased. The equivalent volume could be determined very accurately: the result found ($V_{LiOH}$ = 0.5015 mL; $\alpha_n$ = 1.00) well agreed with the values obtained from the potentiometric titration and spectrophotometric determination.

## 3. 3. Neutralization Potentiometric Titration Curves

This method is one of the classical tools to characterize polyacids.[59,60] The shape of the titration curve can reveal not only the strength of the polyacid but also possible conformational changes accompanying its neutralization. The data can be analyzed using the Henderson-Hasselbach equation

$$\mathrm{pH} = \mathrm{p}K_a + n\log[\alpha_n/(1-\alpha_n)] \quad (1)$$

where p$K_a$ and $n$ denote constants that are typical for the given polymeric acid. In the absence of hydrophobic interactions, the parameter $n$ is closely related to the electrostatic repulsion between neighboring charged groups. Further, $n$ is characteristic of the polyacid type and does not show strong dependence on the polyacid molecular weight.[53,59]

Potentiometric titration curves of PTAA recorded for batches 1 and 2 are shown in Figure 3. The curve with solid circles (●) represents pH-change of solution during titration of PTAA with NaOH (0.0996 M; no NaCl added) as a function of degree of neutralization (more precisely: as a function of ratio of added volume of alkali hydroxide solution against equivalent volume $V_{MOH}/V_{MOH(equiv)}$). The curve with solid upward triangles (▲) belongs to the titration of PTAA, with LiOH (0.0901 M) in presence of neutral salt (1 M LiCl). The concentration of PTAA titrated with LiOH was around 30% lower than the one titrated with NaOH, but this fact does not have much influence on the shape of the titration curve.

The most notable difference between the curves is that the titration curve of PTAA with LiOH lies at considerably lower pH values than that of the titration with NaOH. This effect can be entirely attributed to the presence of LiCl that screens electrostatic forces among ions and so increases the apparent strength of the titrated polyacid. This phenomenon is routinely exploited for obtaining sharper equivalent points at potentiometric titration of weak polyacids.

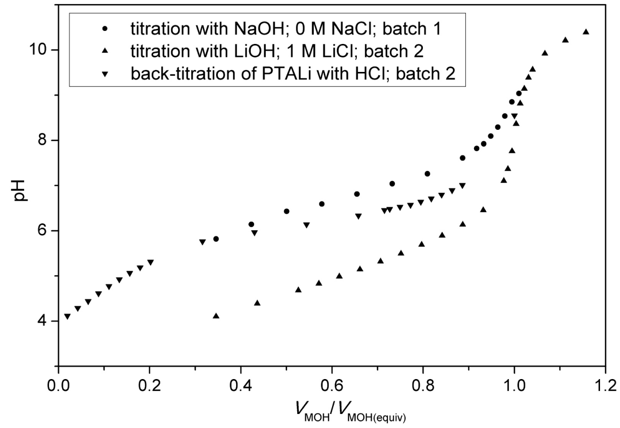

**Figure 3.** Comparison of potentiometric titration curves (obtained at 25 °C) recorded during: (a) titration of PTAA/Na ($\alpha_n$ = 0.346; batch 1) with 0.0996 M NaOH in water (solid circles ●); (b) titration of PTAA/Li ($\alpha_n$ = 0.346; batch 2) with 0.0901 M LiOH in 1 M LiCl (solid upward triangles ▲); (c) back titration of PTALi (batch 2) with 0.1 M HCl in water (solid downward triangles ▼). Samples (a) and (b) were dialyzed before titration while sample (c) was not dialyzed. The difference in concentration of the various samples was around 30%, with the mean value at 0.004 mol monomeric units of polymer/L.

Much more interesting is the difference between the third titration curve (solid downward triangles ▼) representing back titration of PTALi (batch 2 before dialysis) with 0.1 M HCl without neutral salt added, and the titration curve for PTAA/Na (solid circles ●). Although the concentration of the PTAA/Li solution was lower than that of the PTAA/Na, the pH value at the vicinity of 80% neutralization observed for the PTAA/Li solution is considerably lower than that observed for PTAA/Na solution. At present we do not have a plausible explanation for this phenomenon; nevertheless, a removal of the low-molar-mass fractions from PTAA/Na solution might be partially accounted for it.

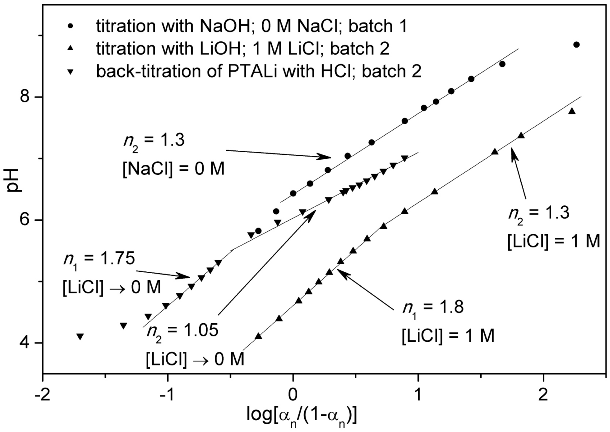

**Figure 4.** Plots of Henderson-Hasselbach equation applied to data from Figure 3 (for symbols see caption to Figure 3).

The results of potentiometric titrations presented in the form of the Henderson-Hasselbach plots are shown in Figure 4. As can be seen, the slope $n_2$ of curves belonging to both dialyzed samples above pH around 6 is equal to 1.3; mind that these curves are vertically displaced due to different strength of electrostatic screening in solutions (the presence and absence of salt, LiCl). There is a break on the curve PTAA/Li + LiCl solution at pH ≈ 6.0, below which the slope of the curve has increased to $n_1 \approx 1.8$. It is difficult to judge whether the same break occurs also on the curve for PTAA/Na because of absence of data in the region pH < 6.0 (notice that titration of PTAA/Na as well as PTAA/Li + LiCl solution started at $\alpha_n = 0.346$). It is however interesting that the slope of the PTAA/Li (without added LiCl) curve below pH of 5.5 also adopts the value $n_1 \approx 1.8$. This result was not found only by us but reported earlier for the Henderson-Hasselbach plot of the potentiometric titrations of PTAA samples at pH around 6.[53] For pH > 5.5, the slope of the curve for PTAA/Li (without added LiCl) attained the value $n_2 \approx 1.05$, which is slightly lower than $n_2$ values observed for PTAA/Na and PTAA/Li + LiCl solution at pH > 6. The discrepancy can be attributed to the eventual presence of the low-molar-mass fractions (oligoions) in non-dialyzed sample, for which the polyelectrolyte character is not well expressed; notice that about 40–50% of the PTAA solute had been washed out during the dialysis.

At this point we have to stress that the Henderson-Hasselbach plots of PTAA reported in previous studies have shown one difference compared to our results. While we have observed a drop in the slope from ≈1.8 to 1.3 or 1.05 at pH ≈ 6, Kim et al.[53] reported an increase in the slope from ≈1.8 to 3.8 at pH ≈ 6 for PTAA in aqueous NaCl (1.0 M) or even to 11.8 (in 0.2 M NaCl) and, in another study,[51] a break from ≈1.4 to ≈3 at pH ≈ 7. An increase in the slope when going from lower to higher values of log[$\alpha_n/(1-\alpha_n)$] has been speculated to be caused by the formation of intramolecular hydrogen bonds. This increase was shown to be suppressed by adding methanol into aqueous solution, and it was proposed that the added MeOH increases solvation of polythiophene chain backbone, which augments the main chain rotation and facilitates dissociation of protons.[53] On the other hand, Vallat et al.[51] suggested the transition among the hydrophobic and hydrophilic regime as the reason for the break-point at the Henderson-Hasselbach plot. The last explanation was based on changes of UV/Vis spectrum of PTAA during neutralization titration.

## 3. 4. UV/Vis Spectra Recorded During Titrations

Changes in conformation of PTAA chain can also be observed in the UV/Vis spectrum of the polymer; at least two studies exploiting such a possibility were published.[51,53] Let us focus on the back titration of PTALi with HCl aqueous solution. As can be seen from Figure 5 the acidic titration of PTALi is accompanied with both a continuous decrease in the molar absorption coefficient, $\varepsilon_{max}$, at the wavelength of the maximum of absorption band, $\lambda_{max}$ (at around 450 nm), and a decrease of $\lambda_{max}$. The same trend of $\varepsilon_{max}$ and similar values of $\lambda_{max}$ were observed also in the case of forth-and-back titration of PTANa.[51] In addition, forth-and-back titration of PTANa was claimed to be accompanied with the appearance of two isosbestic points (IP). Emergence of an isosbestic point (a wavelength, at which the measured absorbance of a sample does not change during titration) had been ascribed to two conformational transitions. The first IP ($\lambda \approx 392$ nm, reported for PTANa with $X_n = 45$, was ascribed to a conformational transition between densely collapsed and collapsed conformations ($\alpha_n \approx 0.5$) and the second IP at $\lambda \approx 401$ nm to the transition from collapsed to extended conformations ($\alpha_n \approx 0.81$).[51] Although some spectra shown in Figure 5 intersect at $\lambda \approx 401$ nm (those with $\alpha_n$ from 0.4 to 1.0) and, eventually, some of them also at $\lambda \approx 381$ nm ($\alpha_n$ from –0.2 to 0.1) it is difficult to confirm conclusively the existence of IP's directly from the UV/Vis spectra.

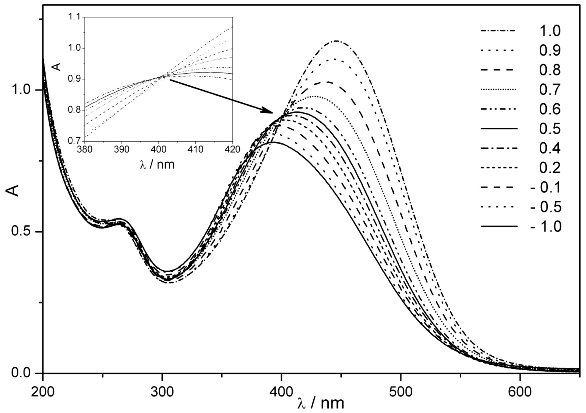

**Figure 5.** UV/Vis absorption spectra of four days old aqueous solution of non-dialyzed PTALi (batch 2) recorded during back titration with HCl. Spectra were recorded at different $\alpha_n$ (see legend inside the graph area) and are corrected for dilution. Negative values of $\alpha_n$ in this particular case denote relative excess of HCl. The inset shows intersections of spectra with $0.4 \le \alpha_n \le 1.0$ at $\lambda \approx 401$ nm. $T = 25$ °C, $c_{PTALi} \approx 1.1 \cdot 10^{-4}$ mol monomeric units/L.

An occurrence of IP is a direct consequence of superposition of spectra belonging to two different mutually related species (or conformations) coexisting in a solution. If the mole ratio between the species changes the superposed spectrum also changes but retains unchanged absorbance at IP's, where molar absorption coefficient of both species is equal. Hence the spectrum of an arbitrary mixture of such species can be obtained as a linear combination of the spectra belonging to solutions of two limiting compositions in the region in which IP occurs:

$$\varepsilon(\lambda,\alpha_n) = x_L(\alpha_n)\cdot\varepsilon(\lambda,\alpha_{nL}) + (1-x_L)\cdot\varepsilon(\lambda,\alpha_{nH}) \qquad (2)$$

where $\alpha_{nL}$ and $\alpha_{nH}$ are degrees of neutralization at lower and higher borders of the $\alpha_n$ region within which IP occurs, $x_L$ is the molar fraction of the solute forming mixture at given $\alpha_n$ while $\varepsilon(\lambda, \alpha_n)$, $\varepsilon(\lambda, \alpha_{nL})$, and $\varepsilon(\lambda, \alpha_{nH})$ are molar absorption coefficients of solutes at a given wavelength $\lambda$ and particular degree of neutralization. We have applied equation (2) to spectra shown in Figure 5 using absorbance instead of $\varepsilon$ and found that the spectra measured in the range of $\alpha_n$ from 0.4 to 1.0 are well reproduced by the linear combination of spectra obtained for $\alpha_n = 0.4$ and $\alpha_n = 1.0$. The result we obtained confirmed the existence of IP at $\lambda \approx 401$ nm that is most probably due to transition between extended and coiled chains.

# 4. Conclusions

The conductometric and potentiometric titrations reported in the present paper were carried out under nitrogen atmosphere on carefully purified and thoroughly characterized samples of practically completely hydrolyzed poly[(thiophen-3-yl)acetic acid] partly neutralized with NaOH and LiOH, respectively. The Henderson-Hasselbach plots for titrations of PTAA/Li and PTAA/Na have shown a break point at pH about 6, where the slope of the plot drops from ca 1.8 (for lower pH) to a value from 1.05 to 1.3 (for higher pH). This suggests different ability of COOH groups linked to PTAA chains to dissociate in more basic surroundings. In addition, our parallel UV/Vis spectroscopy monitoring of the neutralization titration of four days old (not dialyzed) aqueous solution of PTALi with HCl confirmed the existence of the isosbestic point at λ = 401 nm. On the other hand, this study did not confirm existence of the second IP at 392 nm, which has been reported in literature.[51]

Our results disagree with some observations of other groups, reporting an increase in the slope of the Henderson-

Hasselbach plots up to 3 or even up to 11.8 for linear PTAA chains.[51–54] On the other hand, our results are in accordance with the change of the slope from about 2.0 to 1.1, as reported for cross-linked PTAA.[54] There are some other discrepancies between published spectroscopic data and those published in this paper. Further, there are others inconsistencies among the data on PTAA-based systems available in literature. The discrepancies can partly be ascribed to possible differences in chemical structure of the samples studied by various groups, and partly also to the kinetic phenomena associated with slow conformational relaxation of PTAA type chains. A plausible analysis of these effects requires a more detailed study that will include also the effect of aging of measured solutions, which is beyond the scope of this paper. According to our experience great care has to be devoted to precise characterization of the samples studied, which may not be always the case in previous studies. The work along these lines is in progress and shall be presented in our subsequent contribution.

## 5. Acknowledgments

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Supporting Information Available: Text giving an experimental section (detailed synthetic procedure for PTAMe and PTAA), the FFF/SEC calibration diagram for determination of $M_w$, figures showing NMR, Raman, IR and UV/Vis spectra of some of the studied compounds. This material is available on the internet site of *Acta Chimica Slovenica*.

## 6. References

1. M. Baron, K. H. Hellwich, M. Hess, K. Horie, A. D. Jenkins, R. G. Jones, J. Kahovec, P. Kratochvíl, W. V. Metanomski, W. Mormann, R. F. T. Stepto, J. Vohlídal, E. S. Wilks, *Pure Appl. Chem.* **2009**, *81*, 1131–1186.
2. M. Hess, R. G. Jones, J. Kahovec, T. Kitayama, P. Kratochvíl, P. Kubisa, W. Mormann, R. F. T. Stepto, D. Tabak, J. Vohlídal, E. S. Wilks, *Pure Appl. Chem.* **2006**, *78*, 2067–2074.
3. H. Dautzenberg, W. Jaeger, J. Kötz, B. Philip, C. Seidel, D. Stscherbina, Polyelectrolytes: Formation, Characterization and Application*;* Hanser Publishers*,* Munich, Germany, **1994**.
4. M. Hara, Polyelectrolytes: Science and Technology*;* Marcel Dekker Inc.*,* New York, **1993**.
5. K. S. Schmitz, Macroions in Solution and Colloidal Suspension*;* VCH Publishers*,* New York, **1993**.
6. D. Hunkeler, C. Wandrey, *Chimia* **2001**, *55*, 223–227.
7. C. Holm, T. Hofmann, J. F. Joanny, K. Kremer, R. R. Netz, P. Reineker, C. Seidel, T. A. Vilgis, R. G. Winkler, in: M. Schmidt (Ed.): Polyelectrolytes with Defined Molecular Architecture II, Springer-Verlag, Berlin, Heidelberg, New York, **2004**, pp. 67–111.
8. G. S. Manning, *J. Chem. Phys.* **1969**, *51*, 924–933.
9. G. S. Manning, *J. Chem. Phys.* **1969**, *51*, 934–938.
10. A. Katchalsky, *Pure Appl. Chem.* **1971**, *26*, 327–373.
11. D. Dolar, in: E. Sélégny, M. Mandel and U. P. Strauss (Eds.): Polyelectrolytes, Reidel Publishing Co., Dordrecht, Holland, **1974**, pp. 97–113.
12. J. Blaul, M. Wittemann, M. Ballauff, M. Rehahn, *J. Phys. Chem. B* **2000**, *104*, 7077–7081.
13. A. Cesaro, S. Paoletti, S. Guidugli, J. C. Benegas, *Biophys. Chem.* **1991**, *39*, 9–16.
14. D. Bondarev, J. Zedník, I. Šloufová, A. Sharf, M. Procházka, J. Pfleger, J. Vohlídal, *J. Polym. Sci. Pol. Chem.* **2010**, *48*, 3073–3081.
15. A. V. Ambade, B. S. Sandanaraj, A. Klaikherd, S. Thayumanavan, *Polym. Int.* **2007**, *56*, 474–481.
16. H. A. Ho, M. Bera-Aberem, M. Leclerc, *Chem.-Eur. J.* **2005**, *11*, 1718–1724.
17. H. A. Ho, M. Leclerc, *J. Am. Chem. Soc.* **2003**, *125*, 4412–4413.
18. H. A. Ho, K. Dore, M. Boissinot, M. G. Bergeron, R. M. Tanguay, D. Boudreau, M. Leclerc, *J. Am. Chem. Soc.* **2005**, *127*, 12673–12676.
19. F. Xia, X. L. Zuo, R. Q. Yang, Y. Xiao, D. Kang, A. Vallee-Belisle, X. Gong, A. J. Heeger, K. W. Plaxco, *J. Am. Chem. Soc.* **2010**, *132*, 1252–1254.
20. Y. S. Wang, B. Liu, A. Mikhailovsky, G. C. Bazan, *Adv. Mater.* **2010**, *22*, 656–659.
21. J. H. Seo, A. Gutacker, B. Walker, S. N. Cho, A. Garcia, R. Q. Yang, T. Q. Nguyen, A. J. Heeger, G. C. Bazan, *J. Am. Chem. Soc.* **2009**, *131*, 18220–18221.
22. M. Elbing, A. Garcia, S. Urban, T. Q. Nguyen, G. C. Bazan, *Macromolecules* **2008**, *41*, 9146–9155.
23. R. Q. Yang, H. B. Wu, Y. Cao, G. C. Bazan, *J. Am. Chem. Soc.* **2006**, *128*, 14422–14423.
24. C. Hoven, R. Yang, A. Garcia, A. J. Heeger, T. Q. Nguyen, G. C. Bazan, *J. Am. Chem. Soc.* **2007**, *129*, 10976–10977.
25. H. B. Wu, F. Huang, Y. Q. Mo, W. Yang, D. L. Wang, J. B. Peng, Y. Cao, *Adv. Mater.* **2004**, *16*, 1826–1830.
26. M. H. Yu, F. He, Y. Tang, S. Wang, Y. H. Li, D. B. Zhu, *Macromol. Rapid Commun.* **2007**, *28*, 1333–1338.
27. A. Balamurugan, M. L. P. Reddy, M. Jayakannan, *J. Polym. Sci. Pol. Chem.* **2009**, *47*, 5144–5157.
28. J. Ritchie, A. Ruseckas, P. Andre, C. Munther, M. Van Ryssen, D. E. Vize, J. A. Crayston, I. D. W. Samuel, *Synth. Met.* **2009**, *159*, 583–588.
29. Y. Liu, K. Ogawa, K. S. Schanze, *J. Photochem. Photobiol., C* **2009**, *10*, 173–190.

30. J. Na, Y. S. Kim, W. H. Park, T. S. Lee, *J. Polym. Sci. Pol. Chem.* **2004**, *42*, 2444–2450.
31. T. Zhang, H. L. Fan, G. L. Liu, J. Jiang, J. G. Zhou, Q. H. Jin, *Chem. Commun.* **2008**, 5414–5416.
32. T. H. Kim, H. J. Kim, C. G. Kwak, W. H. Park, T. S. Lee, *J. Polym. Sci. Pol. Chem.* **2006**, *44*, 2059–2068.
33. J. R. Heflin, C. Figura, D. Marciu, Y. Liu, R. O. Claus, *Appl. Phys. Lett.* **1999**, *74*, 495–497.
34. L. Zhai, R. D. McCullough, *Adv. Mater.* **2002**, *14*, 901–905.
35. G. Decher, *Science* **1997**, *277*, 1232–1237.
36. R. P. Millen, M. L. A. Temperini, D. L. A. de Faria, D. N. Batchelder, *J. Raman Spectrosc.* **1999**, *30*, 1027–1033.
37. R. P. Millen, D. L. A. de Faria, M. L. A. Temperini, *Synth. Met.* **2006**, *156*, 459–465.
38. O. Dammer, B. Vlčková, M. Procházka, J. Sedláček, J. Vohlídal, J. Pfleger, *Phys. Chem. Chem. Phys.* **2009**, *11*, 5455–5461.
39. S. Kazim, J. Pfleger, M. Procházka, D. Bondarev, J. Vohlídal, *J. Colloid Interface Sci.* **2011**, *354*, 611–619.
40. S. Kazim, J. Pfleger, K. Halašová-Podhájecká, M. Procházka, D. Bondarev, J. Vohlídal, *Eur. Phys. J.-Appl. Phys* **2011**, *55*, Article Number: 23905.
41. J. R. Huizenga, P. F. Grieger, F. T. Wall, *J. Am. Chem. Soc.* **1950**, *72*, 2636–2642.
42. M. Bockstaller, W. Kohler, G. Wegner, G. Fytas, *Macromolecules* **2001**, *34*, 6353–6358.
43. P. Vallat, J.-M. Catala, M. Rawiso, F. Schosseler, *Macromolecules* **2007**, *40*, 3779–3783.
44. H. D. Burrows, M. J. Tapia, S. M. Fonseca, S. Pradhan, U. Scherf, C. L. Silva, A. C. C. Pais, A. J. M. Valente, K. Schillen, V. Alfredsson, A. M. Carnerup, M. Tomšič, A. Jamnik, *Langmuir* **2009**, *25*, 5545–5556.
45. D. L. Wang, J. Lal, D. Moses, G. C. Bazan, A. J. Heeger, *Chem. Phys. Lett.* **2001**, *348*, 411–415.
46. D. L. Wang, D. Moses, G. C. Bazan, A. J. Heeger, J. Lal, *J. Macromol. Sci., Chem.* **2001**, *38*, 1175–1189.
47. A. Kroeger, J. Belack, A. Larsen, G. Fytas, G. Wegner, *Macromolecules* **2006**, *39*, 7098–7106.
48. B. Guilleaume, J. Blaul, M. Wittemann, M. Rehahn, M. Ballauff, *J. Phys.-Condes. Matter* **2000**, *12*, A245–A251.
49. B. Guilleaume, J. Blaul, M. Ballauff, M. Wittemann, M. Rehahn, G. Goerigk, *Eur. Phys. J. E* **2002**, *8*, 299–309.
50. M. Patel, S. Rosenfeldt, M. Ballauff, N. Dingenouts, D. Pontoni, T. Narayanan, *Phys. Chem. Chem. Phys.* **2004**, *6*, 2962–2967.
51. P. Vallat, J.-M. Catala, M. Rawiso, F. Schosseler, *Europhys. Lett.* **2008**, *82*, 28009.
52. B.-S. Kim, H. Fukuoka, J. P. Gong, Y. Osada, *Eur. Polym. J.* **2001**, *37*, 2499–2503.
53. B.-S. Kim, L. Chen, J. Gong, Y. Osada, *Macromolecules* **1999**, *32*, 3964–3969.
54. L. Chen, B.-S. Kim, M. Nishino, J. P. Gong, Y. Osada, *Macromolecules* **2000**, *33*, 1232–1236.
55. R. G. Gilbert, M. Hess, A. D. Jenkins, R. G. Jones, P. Kratochvíl, R. F. T. Stepto, *Pure Appl. Chem.* **2009**, *81*, 351–353.«
56. M. Spiro, in: B. W. Rossiter and J. F. Hamilton (Eds.) Physical methods of chemistry. Vol. 2: Electrochemical methods, A Wiley-Interscience Publication, New York, **1986**, pp. 663–796.
57. G. Bidan, A. De Nicola, V. Enée, S. Guillerez, *Chem. Mater.* **1998**, *10*, 1052–1058.
58. T. Kirschbaum, C. A. Briehn, P. Bäuerle, *J. Chem. Soc.-Perkin Trans. 1* **2000**, 1211–1216.
59. A. Katchalsky, J. Gillis, *Rec. Trav. Chim. Pays-Bas* **1949**, *68*, 879–897.
60. P. Dubin, U. P. Strauss, *J. Phys. Chem.* **1973**, *77*, 1427–1431.

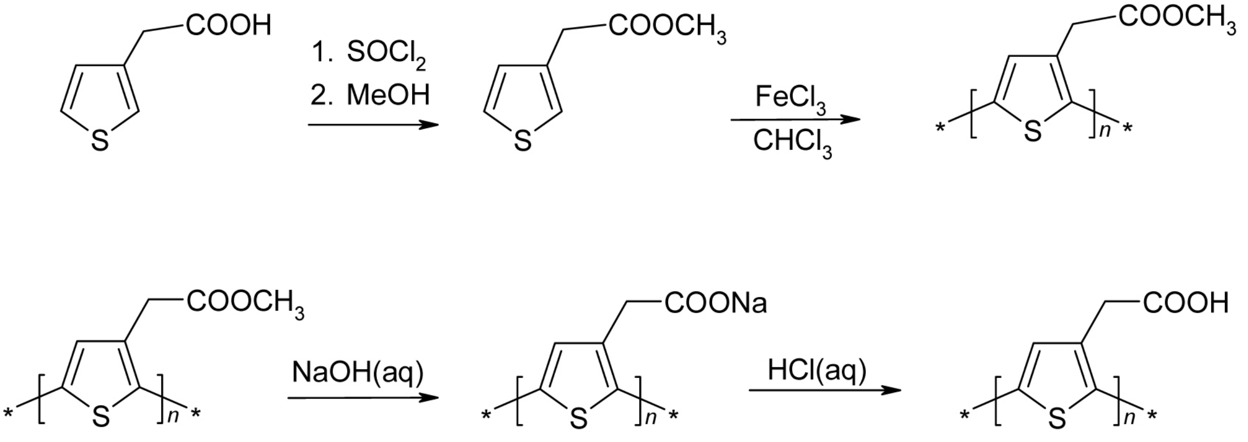
## Povzetek

Poli(tiofen-3-ilocetna kislina) (PTAA) je bila pripravljena z bazično hidrolizo poli(metiltiofen-3-il acetata), predhodno dobljenega z oksidativno polimerizacijo metiltiofen-3-il acetata. Pridobljena PTAA je bila analizirana z NMR, IR, Raman in UV/vidno spektroskopijo. Posneli in proučili smo konduktometrično in potenciometrično titracijsko krivuljo posneto pri nevtralizaciji PTAA z raztopinama litijevega in natrijevega hidroksida. Henderson-Hasselbachov diagram potenciometrične titracijske krivulje kaže prelom pri vrednosti pH 6, kjer se naklon premice z vrednosti 1,8 v kislem zniža na vrednosti med 1,05 in 1,3 v alkalnem. Med povratno (kislo) titracijo litijeve soli PTAA posneti UV/vidni absorpcijski spektri izkazujejo (i) monotono zniževanje $\lambda_{max}$ in $\varepsilon_{max}$, (ii) pojav izozbestične točke pri 401 nm kot posledice konformacijske spremembe polimera in (iii) odsotnost v literaturi zabeležene izozbestične točke pri 392 nm.

# Supporting Information

## 2. 1. Polymer Synthesis and Characterization

### Preparation and characterization of polymers



**Scheme 1.** Synthetic route for the synthesis of poly(thiophen-3-ylacetic acid).

**Methyl thiophen-3-ylacetate.** Thiophen-3-ylacetic acid (2.84 g, 20 mmol) was treated with thionyl chloride (11.8 g, 100 mmol) for 12 hours at 40 °C, then excessive thionyl chloride was removed by distillation and formed carboxylic acid chloride was slowly added to a large excess of methanol to obtain the desired methylester. Crude product was obtained by evaporating excessive methanol, washed with aqueous sodium bicarbonate, and several times with water, then dissolved in diethyl ether, dried with $MgSO_4$ and purified on alumina column. Isolated yield: 1.8 g (58%) of yellowish liquid. $^1$H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 7.72 (dd, 1H); 7.13 (dd, 1H); 7.04 (dd, 1H); 3.70 (m, 3H); 3.66 (m, 2H).

**Poly(methyl thiophen-3-ylacetate), PTAMe**

Batch 1: A solution of methyl thiophen-3-ylacetate in dry chloroform was slowly added to a suspension of $FeCl_3$ (4 molar equivalents) in dry chloroform at 0 °C (monomer concentration 0.125 mol/dm$^3$) and the reaction mixture was stirred for 3 h at 0 °C. Then the mixture was poured into water (200 mL), chloroform phase was collected and poured into ethanol/acetone mixture (1/1 v/v, 400 mL) to precipitate the product. Solid product was isolated by filtration, washed several times with water, then with methanol and dried.

First batch (used for preparation of PTAA); amount of methyl thiophen-3-ylacetate (5.85 g, 37.5 mmol); isolated yield: 3.7 g (64%) of brick-red solid, SEC: $M_n = 6000$; $M_w = 14500$.

**Poly(thiophen-3-ylacetic acid), PTAA.** PTAMe (3.3 g, batch 1) was treated with aqueous NaOH (2.5 M) at 100 °C for 36 hours and the modified polymer formed was isolated as described above. Isolated yield: 2.50 g (83%) of fine siena-brown solid.

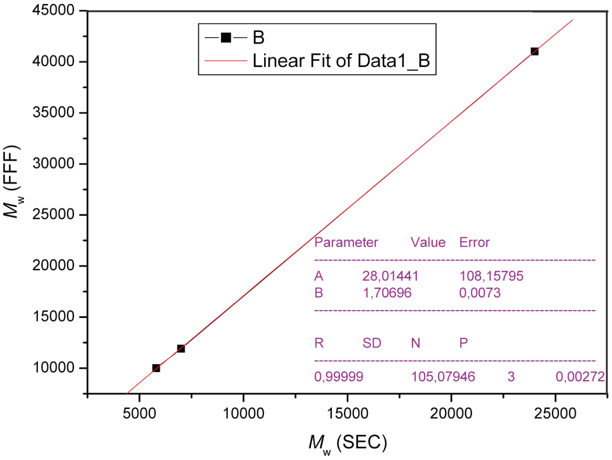


**Figure 1.** Relation between $M_w$ values of PTAMe obtained from FFF and SEC measurements, respectively (data from: Vallat, P.; Catala, J.-M.; Rawiso, M.; Schosseler, F. *Macromolecules* **2007**, *40*, 3779–3783).

$^1$H NMR (400 MHz, DMSO-$d_6$, 25 °C, ppm): 12.62 ppm (1H, -COOH); 7.35, 7.30, 7.28 (1H, thiophene rings of irregular chain); 3.8 (-$CH_2$- in HT sequences); 3.55 (-$CH_2$- in TT sequences). $^{13}$C NMR (400 MHz, DMSO-$d_6$, 25 °C, ppm): 171.31 (-COOH); 136.35; 136.08; 135.74; 134.437; 133.54; 132.82; 132.54; 131.80; 130.57; 129.09; 128.43; 127.05 (all carbon atoms of thiophene rings of regioirregular main chains); 34.41, 33.89 (-$CH_2$-).

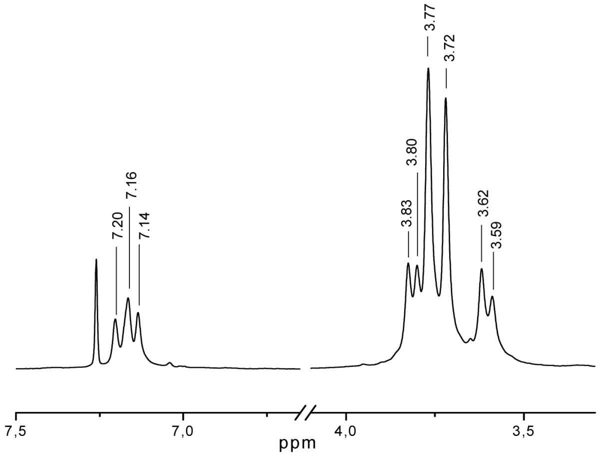


**Figure 2.** $^1$H NMR spectrum of PTAMe ($CDCl_3$).

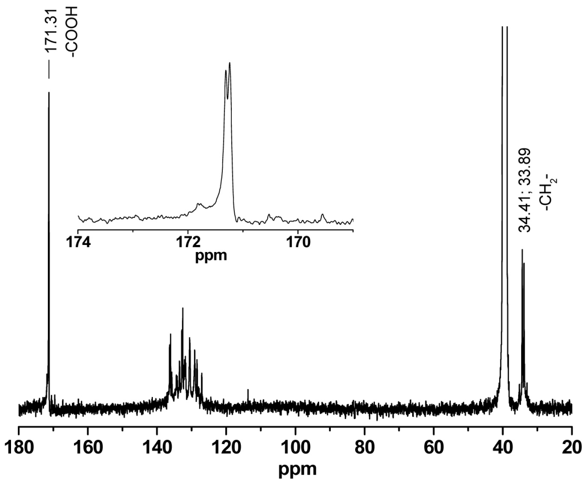


**Figure 3.** $^{13}$C NMR spectra of PTAA.

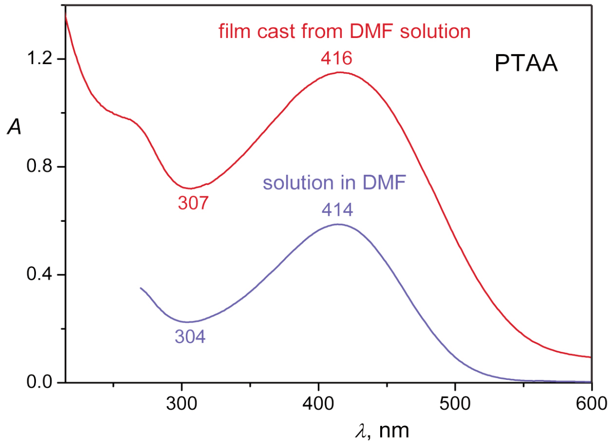


**Figure 4.** UV/vis spectrum of PTAA in DMF solution and in the solid state; measured at 20 °C

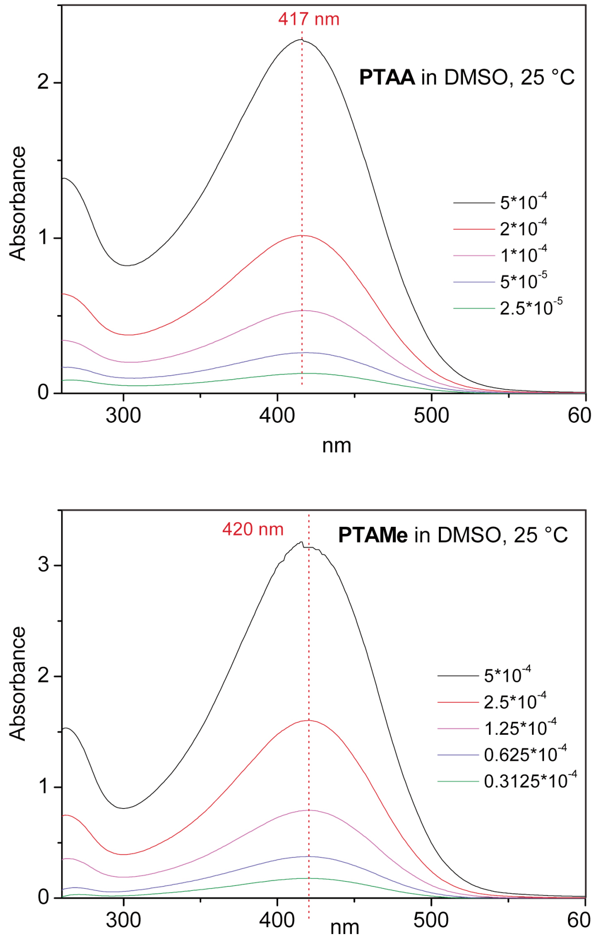


**Figure 5.** UV/vis absorption spectra of PTAA and PTAMe in DMSO at 25 °C.

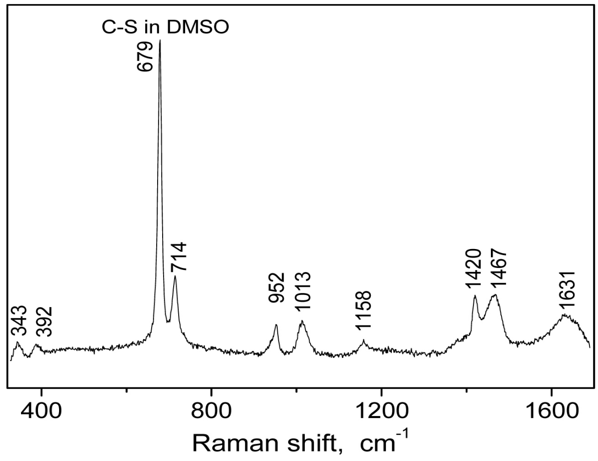


**Figure 6.** Raman spectrum of PTAA in DMSO; $c_{pol} = 1 \cdot 10^{-5}$ M; excitation at 532 nm.

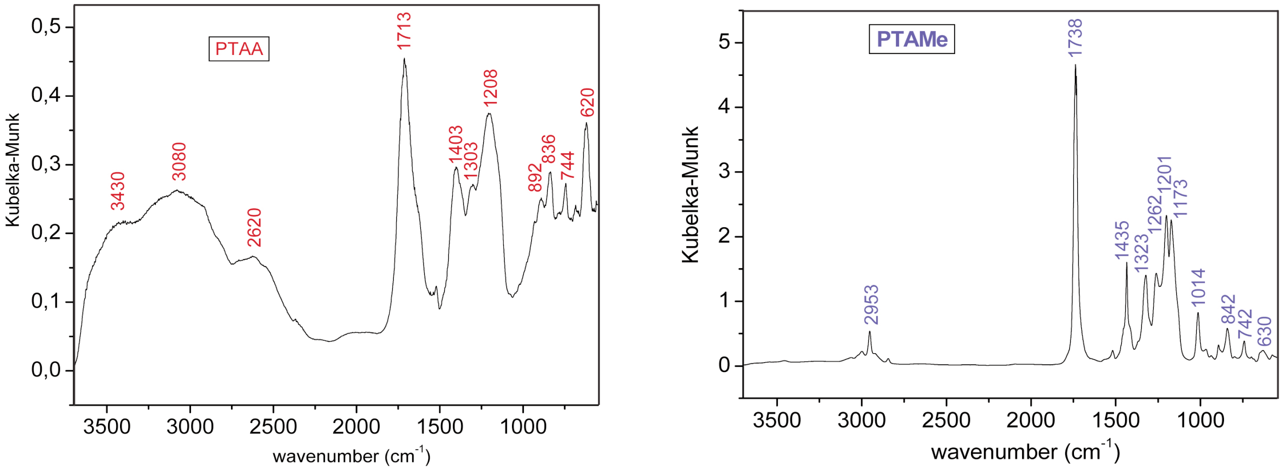


**Figure 7.** FTIR spectra of solid PTAA and PTAMe samples.