

Short communication

Chromism and molecular weight of polyaniline derivatives

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ABSTRACT

The striking solvatochromic shift observed in polyaniline derivatives correlates with two solvent polarity scales, donor number (DN) and hydrogen bond acceptor scale (Taft's β -scale). The large shift is caused by conformational changes in solution that result in dramatic differences in relative molecular weight values obtained by gel permeation chromatography (MW_{GPC}) in different solvents. For example, for poly-*o*-toluidine base in the emeraldine oxidation state, a low transition energy solvent like NMP (excitonic transition, λ_{max} 608 nm) yields a very high molecular weight value ($M_w \sim 15,000 \text{ g mol}^{-1}$) whereas a high transition energy solvent like CHCl_3 (excitonic transition, λ_{max} 570 nm) yields an absurdly low value ($M_w \sim 650 \text{ g mol}^{-1}$). An absolute molecular weight value, $M_w \sim 4700 \text{ g mol}^{-1}$, was obtained for the first time using laser light scattering (MW_{LS}) suggesting that CHCl_3 promotes a highly coiled chain conformation whereas NMP promotes a more expanded, rod-like conformation. A similar trend is observed for poly-*o*-toluidine base in the fully oxidized pernigraniline oxidation state (Pierels transition). This suggests that even though the Pierels and excitonic transitions have different molecular origins their conformation driven solvatochromic shifts trend in a similar fashion which is different from thermochromic trends reported in previous studies.

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1. Introduction

The polyanilines constitute a large family of ring- and nitrogen substituted polymers that exhibit electrical conductivity in the range 10^{-10} to 10^3 S/cm depending on doping level and backbone functionalization [1]. The parent polyaniline in the insulating emeraldine base form is soluble in dipolar aprotic solvents (NMP, DMPU, DMF) enabling a wide range of spectroscopic studies including film/fiber processing [2]. Ring alkyl- and alkoxy substituted polyanilines are soluble in a wider range of organic solvents and display interesting thermo- and solvatochromism similar to other conducting polymers like polythiophene [3–5]. Both phenomena are believed to be caused by a change in polymer conformation (rod-coil) although confirmatory evidence is lacking due to variety of factors. For example, laser light scattering, the most direct method used to obtain information on polymer size, shape, etc., could not be used because polyaniline solutions are intensely colored and absorb at wavelengths used in traditional laser light scattering instruments (514 and 633 nm laser). Membrane osmometry

has recently been used to measure the absolute molecular weight (MW) of parent polyaniline (but not for polyaniline derivatives) although this method does not provide direct information of chain conformation [6]. Indirect evidence for solution driven changes in polymer conformation can be obtained using size exclusion chromatography (SEC) but there are very few reports using multiple solvents [7]. When using SEC to measure the MW of polyaniline one frequently observes a bimodal distribution corresponding to high and low MW fractions [8,9]. Even in solvents where a unimodal peak is observed MW values range widely, e.g., from 41,000 to 8000 g mol^{-1} for poly-*o*-toluidine base (emeraldine) depending on the synthetic method [10].

In this study, we describe surprisingly large differences in relative MW values obtained using different solvents in SEC, MW_{SEC} , and correlate this to conformation driven solvatochromic shifts in absorption maxima in solution. We have also obtained the absolute MW values for polyaniline derivatives for the first time using laser light scattering (MW_{LS}) [11] and show that the conventional analysis of what are considered “good solvents” and “poor solvents” based solely on solvatochromic shifts may need to be re-evaluated.

2. Experimental

*Synthesis of poly-*o*-toluidine in the emeraldine oxidation state:* To a magnetically stirred solution of *o*-toluidine (2.0 ml, 0.019 mol)

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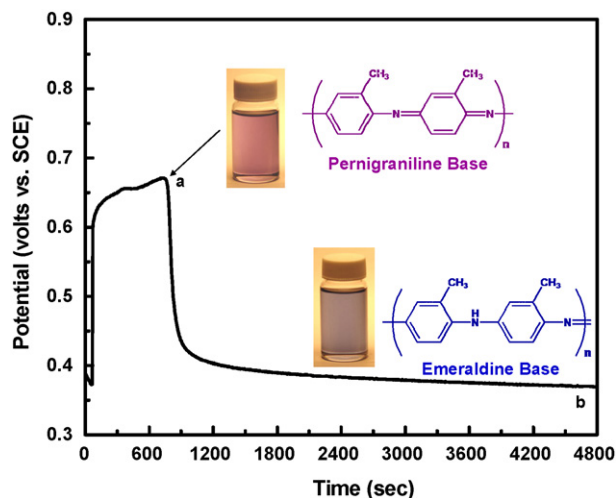


Fig. 1. Potential-time profile of chemical oxidative polymerization of *o*-toluidine in aqueous 1.0 M HCl using peroxydisulfate oxidant at 21 °C. Reaction quenched in aqueous 0.1 M NH_4OH at point “a” to isolate pernigraniline base and at point “b” to isolate emeraldine base.

dissolved in 30 ml aqueous 1.0 M HCl was added ammonium peroxydisulfate (1.15 g, 0.005 mol) dissolved in 20 ml aqueous 1.0 M HCl. The open circuit potential of the reaction was monitored continuously with time (Fig. 1) using previously established setup for potential-time profiling (Pt wire electrode, saturated calomel electrode (SCE) reference) [11]. The potential increases from 0.36 V and reaches a plateau at 0.67 V, when the bulk of the poly-*o*-toluidine in the pernigraniline oxidation state (pernigraniline salt, PS) is formed. The potential then drops from 0.67 to 0.4 V over a period of 2–3 min, consistent with the reduction of pernigraniline salt (PS) to emeraldine salt (ES) by excess monomer in solution, which is oxidized to *o*-toluidine radical cation. The reaction is allowed to proceed for 90 min to ensure coupling of ES chains to freshly formed *o*-toluidine radical cations. The bright-green precipitate of ES is suction filtered in air, washed with deionized water (10×50 ml), and acetonitrile (10×50 ml), and air dried in the filter funnel for 10 min. The free-flowing powder is then placed in an Erlenmeyer flask that was filled to the brim with aqueous 0.1 M ammonium hydroxide (1 L) and the top was covered with parafilm to exclude air. The contents of the flask are stirred for 24 h to ensure complete conversion of ES to emeraldine base (EB). The black/blue precipitate of EB is suction filtered in air, washed with water (10×50 ml), acetonitrile (10×50 ml), air dried in the filter funnel for 10 min and then dried under dynamic vacuum oven for 24 h.

Synthesis of poly-*o*-toluidine in the pernigraniline oxidation state: The reaction described above was quenched in excess aqueous base when the potential was still high. For example, the potential increases from an initial value of 0.36 V and reaches a plateau at 0.67 V, when the bulk of the pernigraniline (PS) is formed. The potential then decreases slightly, i.e., to 0.665 V (Fig. 1, point ‘a’), signaling the completion of formation of the pernigraniline oxidation state. At this point the contents of the reaction flask are poured rapidly into 2 L aqueous 0.2 M NH_4OH that was pre-cooled to 0 °C. The resulting black-violet precipitate of pernigraniline base (PB) was quickly suction filtered and washed with excess cold (0 °C) deionized water (10×50 ml), followed by acetonitrile (10×50 ml), and dried under dynamic vacuum.

3. Results and discussion

Poly-*o*-toluidine base synthesized in the emeraldine and pernigraniline oxidation states described above display pronounced solvatochromism [12]. The emeraldine base form is intensely col-

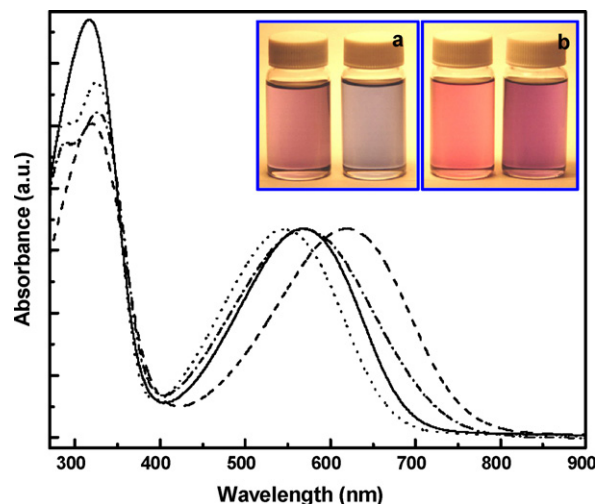


Fig. 2. Electronic absorption spectra of poly-*o*-toluidine base. Pernigraniline oxidation state in CHCl_3 (dotted line) and NMP/LiBF₄ (dot-dash line). Emeraldine oxidation state in CHCl_3 (solid line) and NMP/LiBF₄ (dashed line). Inset: images of emeraldine (a), and pernigraniline (b) in CHCl_3 (left vial) and NMP/LiBF₄ (right vial).

ored in solution and is characterized by a broad excitonic transition in the 525–675 nm range (Fig. 2). The λ_{max} spans a range of ~62 nm depending on the solvent, e.g., CH_2Cl_2 (λ_{max} 560 nm, violet-red) vs. 1-methyl-2-pyrrolidinone (NMP)/LiBF₄ (λ_{max} 622 nm, navy blue).

Size exclusion chromatography was used to evaluate the role of solvent-driven conformational changes in the large solvatochromic shift observed. Relative MW_{SEC} values were obtained in different solvents using narrow distribution polystyrene standards as the reference (Table 1). Although we expected to see some solvent-driven differences, the experimentally obtained values are dramatically different, e.g., $15,170 \text{ g mol}^{-1}$ for NMP/LiBF₄ vs. $\sim 655 \text{ g mol}^{-1}$ for CHCl_3 (Table 1)! The values in CHCl_3 are at the lower detection limit of the column, $\sim 500 \text{ g mol}^{-1}$. It is to be noted that poly-*o*-toluidine base is completely soluble in both solvents and so what we are observing is fully representative of the polymer. From the polydispersity index (PDI) the calculated number of toluidine repeat units ranges from ~63 for NMP/LiBF₄ and an absurdly low value of ~3 for CHCl_3 . Laser light scattering was used to determine which of these two values is closer to the absolute MW.

Using a developmental 3-angle static light scattering instrument equipped with a 785 nm laser light source the absolute molecular weight M_w [11], of poly-*o*-toluidine base (emeraldine) was found to be 4732 g mol^{-1} in CHCl_3 and 4690 g mol^{-1} in NMP/LiBF₄ (Table 2). Values for refractive index increment, dn/dc , were obtained using a differential refractometer also equipped with a 785 nm laser light source. This first report of the absolute MW of a ring-substituted polyaniline derivative is facilitated by the use of a 785 nm laser light source, where poly-*o*-toluidine does not absorb. In contrast, most commercial laser light scattering instruments use ~514 or ~632 nm laser light source where both emeraldine and pernigraniline oxidation states of poly-*o*-toluidine base have strong absorption. As

Table 1

Relative molecular weight of poly-*o*-toluidine base using size exclusion chromatography, MW_{SEC} .

Solvent (oxidation state)	λ_{max} (nm)	M_w	M_n	N^a
NMP/LiBF ₄ (emeraldine)	620	15,170	6596	~63
CHCl_3 (emeraldine)	570	655	309	~3
NMP/LiBF ₄ (pernigraniline)	555	11,399	3901	37
CHCl_3 (pernigraniline)	534	N/A ^b	N/A ^b	–

^a Number of repeat units = $M_n/105$ (toluidine repeat unit).

^b Peaks below the lower limit of the column ($<500 \text{ g mol}^{-1}$).

Table 2
Absolute molecular weight of poly-*o*-toluidine base using laser light scattering.

Solvent (oxidation state)	dn/dc	M_w	M_n^a	N^b
NMP/LiBF ₄ (emeraldine) ^c	0.43	4690	2039	~19
CHCl ₃ (emeraldine) ^c	0.48	4732	2232	~21
NMP/LiBF ₄ (pernigraniline) ^d	0.53	4040	1393	~13
CHCl ₃ (pernigraniline) ^d	0.28	3985	1364 ^e	~13

^a M_n calculated using PDI (M_w/M_n) from Table 1.

^b Number of repeat units = $M_n/105$ (toluidine repeat unit).

^c Isolated at point “b” in Fig. 1.

^d Isolated at point “a” in Fig. 1.

^e Calc using PDI = 2.93 from NMP/LiBF₄.

mentioned above, since refractive index increment, dn/dc , values are also required for the calculation of the absolute MW, it is important for the differential refractometer to also be equipped with a 785 nm light source. The absolute molecular weight M_w value of 4690 g mol⁻¹ obtained above translates to a very low value of 19 toluidine repeat units using M_n values derived from PDI values obtained from SEC. In previous MW studies using poly-*o*-toluidine base, the low MW values observed were believed to be representative of a low MW fraction of the polymer. The (presumed) higher MW fraction was believed to have molecular mass beyond the range of the instrument (e.g., mass spectrometry), or have a tendency to form aggregates in solution (SEC using pure NMP). In one study using field-desorption mass spectrometry [8], the “low MW” fraction of poly-*o*-toluidine base was reported to be oligomeric having 12–17 toluidine repeat units. This study shows that what was assumed to be the low MW fraction is fully representative of the sample. Similar results were obtained of *o*-ethyl, *o*-methoxy and *o*-ethoxy substituted polyanilines. The low number of repeat units for poly-*o*-toluidine is to be contrasted with the much higher value of ~203 units for the parent polyaniline synthesized under very similar experimental conditions (23 °C) [11] suggesting that ring substituents significantly inhibit chain growth.

Low transition energy solvents like NMP/LiBF₄ significantly overestimate the MW_{SEC} whereas high transition energy solvents like CHCl₃ underestimate it. The higher transition energy in CHCl₃ is consistent with a coil-like conformation that is much more compact than the relaxed coil conformation of the polystyrene standards. Conversely, a polar aprotic solvent like NMP promotes a more extended and delocalized rod-like conformation yielding relative MW values that are further away from the absolute value. An extended rod-like conformation in solution could also promote aggregation of polymer chains, further exacerbating the error in relative MW. This is consistent with bimodal peak distributions often observed in SEC when NMP is used as the mobile phase [9]. One of the main reasons to use Li⁺ salts in our mobile phase (NMP/LiBF₄) is to diminish this intrinsic tendency of polyanilines in the emeraldine oxidation state to aggregate in polar solvents. Presumably, the dissolved Li⁺ ions interrupt the H-bonds associated with chain aggregation resulting in a single, unimodal peak in SEC [9]. Expectedly, the dissolved Li⁺ ions would contribute to conformational changes in solution by promoting (and stabilizing) a more rod-like chain conformation which is consistent with solutions of poly-*o*-toluidine base NMP/LiBF₄ having the lowest transition energy among the solvents used in this study (Fig. 2, SI section).

The solvent-driven conformational coil-like to rod-like transition in polyaniline derivatives in the emeraldine oxidation state could be driven by changes in the local isomeric composition (*cis*, *trans*, *E/Z*) relative to the quinoneimine groups in solution. Coupling of independent local *cis* (*E*) isomers could result in a global coil-like conformation. For example, solvatochromism in aniline tetramer (emeraldine) is reported to be due to a change in isomeric composition that is solvent dependent [13]. In addition, parent polyaniline

(emeraldine) is believed to be a random block co-polymer consisting of extended runs of reduced and oxidized segments that is solvent dependent [14].

To determine specific solvent properties underlying this phenomenon, the magnitude of the solvatochromic shift was evaluated against several single parameter solvent polarity scales, such as, dielectric constant (ϵ), Dimroth–Reichard's $E_T(30)$, dipole moment (μ), Taft's (β), Hilebrand's solubility parameter (δ), Gutman's acceptor number (AN), donor number (DN) [15] and the multiparameter amphoteric scale AN + DN (SI section) [16]. No meaningful correlations are observed against widely used polarity scales like dielectric constant, or $E_T(30)$ suggesting that the observed solvatochromic changes cannot be rationalized solely on the basis of local electronic effects. Interestingly, a fairly linear correlation is observed against the DN polarity scale [17] (Fig. 3) and a weaker correlation against the Taft's hydrogen bonding acceptor (β) scale (SI section), suggesting that increased solvent donicity and H-bonding play an important role in stabilizing the excitonic transition (emeraldine) by favoring a more rod-like conformation in solution. Since the DN-scale specifically reflects solvent ability to stabilize positively charged centers, this would involve interaction with the electron deficient quinoneimine groups, and the correlation with the β scale suggests that H-bonding with the reduced aminobenzene units is also playing a role.

The pernigraniline oxidation state isolated at point “a” in Fig. 1 also exhibits a large solvent-dependent variation in MW_{SEC} (Table 1). The violet-blue color in organic solvents is caused by a Pierels transition the 450–550 nm range that also displays solvatochromism (Table 1). The shift in λ_{max} is smaller, ~21 nm, compared to the emeraldine oxidation state which is consistent with the fundamentally different molecular origins of the Pierels and excitonic transitions. It is instructive to compare the observed solvatochromic trends with analogous thermochromic trends in parent polyaniline [4]. In parent emeraldine base, the excitonic transition of a solution in NMP shifts to higher energy when the temperature is increased, which is similar to the solvatochromic shift in poly-*o*-toluidine when the solvent is changed from NMP/LiBF₄ to CHCl₃. In both instances, the phenomenon could be attributed to a rod-like to coil-like change in conformation in solution. In contrast, the pernigraniline oxidation state behaves differently, e.g., whereas the Pierels transition in parent polyaniline anomalously shifts to lower energy when the temperature is increased, the corresponding peak in poly-*o*-toluidine shifts to

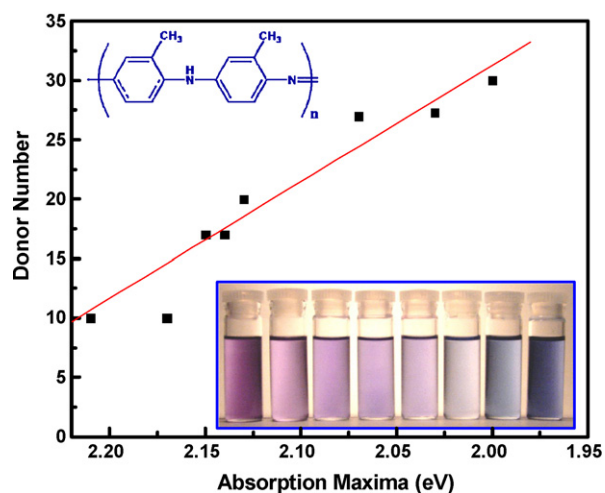


Fig. 3. Plot of λ_{max} of the excitonic transition of poly-*o*-toluidine base (emeraldine) against solvent donor number (DN-scale). Inset: pictures of solutions in CH₂Cl₂, CHCl₃, ethyl acetate, acetone, THF, DMF, NMP, and DMSO (left to right).

higher energy when the solvent is changed from NMP/LiBF₄ to CHCl₃ consistent with a less delocalized, coil-like conformation. Although the thermochromic shift to lower transition energy has been attributed to sterically induced valence band narrowing [4], which may be a localized electronic phenomenon, the present study is consistent with an expected increase in the Pierels gap energy as the conformation becomes more coil-like.

There are also differences in solvatochromism between the polyaniline and polythiophene systems where the high transition energy observed in “good solvents” like CHCl₃ shifts to lower energy (closer to solid-state values) upon addition of poor solvents or a non-solvent like methanol [18]. In contrast, low transition energy solvents like NMP and DMPU are reported to be good solvents for parent polyaniline where “solvent quality” is linked to how expanded the polymer chains are in solution (more rod-like) [19]. In this study we observe that both CHCl₃ and NMP are excellent solvents for poly-*o*-toluidine where the addition of a non-solvent like methanol to both shifts the transition energy closer to the solid-state value of ~590 nm. Given the tendency of NMP solutions poly-*o*-toluidine to aggregate and form gels it may not come as a surprise should future solution viscometry studies show that a high transition energy solvent like CHCl₃ is a thermodynamically better solvent for the polyaniline system [20].

4. Conclusions

In conclusion, the absolute molecular weight of ring-substituted polyaniline has been determined for the first time using laser light scattering. The pronounced shift in λ_{\max} in the electronic spectra of polyaniline derivatives in different solvents (solvatochromism) can be traced to changes in polymer conformation which is consistent with dramatic differences in relative molecular weights obtained by size exclusion chromatography. One has to be careful while interpreting MW data obtained solely from SEC, e.g., unlike parent polyaniline which is soluble only in a few selected solvents, ring-substituted polyanilines are soluble in a wide range of organic solvents commonly used as the mobile phase in SEC. This could lead to dramatically different apparent molecular weight values due to different chain conformations in different solvents. Correction factors for MW_{SEC} vs. MW_{LS} for poly-*o*-toluidine are dramatically different compared to parent polyaniline, i.e., size exclusion chromatography in NMP/LiBF₄ overestimates the MW

of parent polyaniline by +27% [11] whereas in the case of poly-*o*-toluidine there is an overestimation of +330% in NMP/LiBF₄ and an underestimation of –700% in CHCl₃.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.synthmet.2009.07.018.

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