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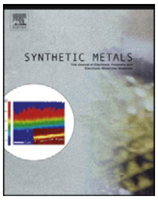

Short communication

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 ($M_w \sim 15{,}000\,g\,mol^{-1}$) whereas a high transition energy solvent like $CHCl_3$ (excitonic transition, λ_{max} 570 nm) yields an absurdly low value ($M_w \sim 650\,g\,mol^{-1}$). An absolute molecular weight value, $M_w \sim 4700\,g\,mol^{-1}$, 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.

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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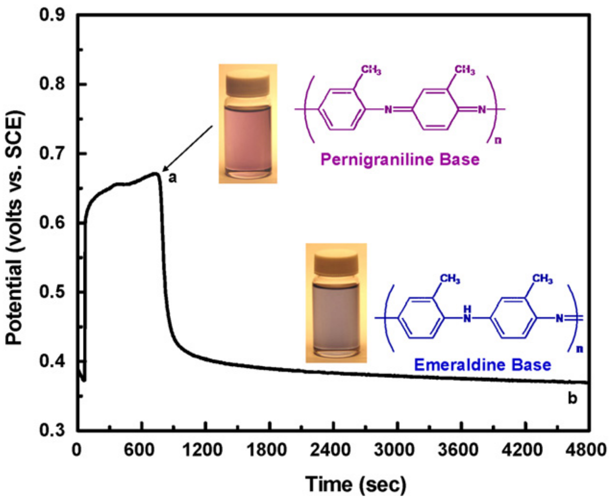

Fig. 1. Potential-time profile of chemical oxidative polymerization of *o*-toluidine in aqueous 1.0 M HCl using peroxydisulfate oxidant at 21 °C. Reaction quenched in aqueous 0.1 M NH_4OH at point “a” to isolate pernigraniline base and at point “b” to isolate emeraldine base.

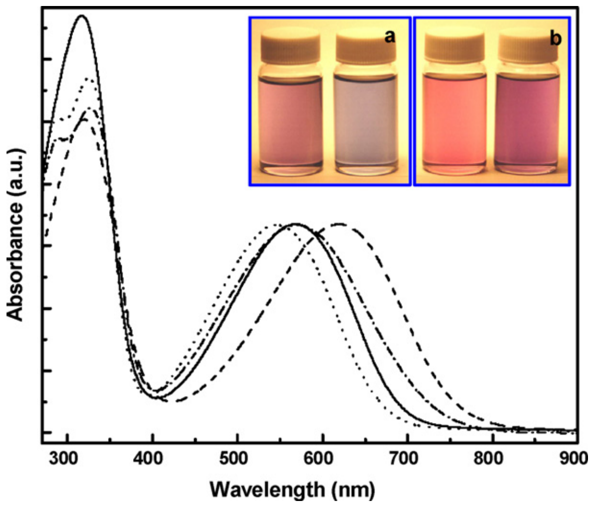

Fig. 2. Electronic absorption spectra of poly-*o*-toluidine base. Pernigraniline oxidation state in $CHCl_3$ (dotted line) and NMP/$LiBF_4$ (dot-dash line). Emeraldine oxidation state in $CHCl_3$ (solid line) and NMP/$LiBF_4$ (dashed line). Inset: images of emeraldine (a), and pernigraniline (b) in $CHCl_3$ (left vial) and NMP/$LiBF_4$ (right vial).

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 colored 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)/$LiBF_4$ (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 g mol^{-1} for NMP/$LiBF_4$ vs. ∼655 g mol^{-1} for $CHCl_3$ (Table 1)! The values in $CHCl_3$ are at the lower detection limit of the column, ∼500 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/$LiBF_4$ 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/$LiBF_4$ (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 g mol^{-1}).