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Communication

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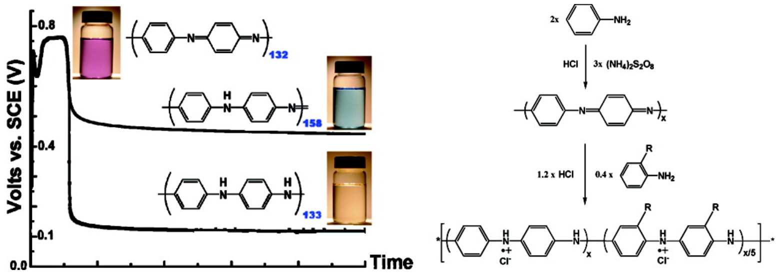

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Absolute Molecular Weight of Polyaniline

Harsha S. Kolla, Sumedh P. Surwade, Xinyu Zhang, Alan G. MacDiarmid,[†] and Sanjeev K. Manohar*

Alan G. MacDiarmid Laboratory for Technical Innovation, Department of Chemistry,
The University of Texas at Dallas, Richardson, Texas 75080

Received August 4, 2005; E-mail: sanjeev.manohar@utdallas.edu

The absolute molecular weights of parent polyaniline bases in the pernigraniline, emeraldine, and leucoemeraldine oxidation states have been measured by light scattering and the exact number of aniline repeat units determined. A three-angle LS instrument equipped with a 785 nm laser has been used to measure the absolute molecular weight, a wavelength at which there is no absorbance by parent polyaniline bases. The molecular weight of the pernigraniline intermediate formed during the chemical oxidative polymerization of aniline increases by 17−20% when it is converted to emeraldine, which is consistent with a two-step polymerization mechanism. These findings establish a solid experimental framework to chemically synthesize block copolymers of polyaniline by using different monomers to intercept the reaction at the pernigraniline oxidation state.

Polyaniline is an environmentally stable and technologically important conducting polymer, whose electronic conductivity can be altered reversibly by both oxidation/reduction and acid/base chemistries.[1] Polyaniline can exist as “salts” or “bases” in three isolable oxidation states, leucoemeraldine (LES or LEB), emeraldine (ES or EB), and pernigraniline (PS or PB), among which only emeraldine salt (ES) is electrically conductive. The conventional chemical synthesis of polyaniline in aqueous acids is an unconventional precipitation polymerization system in which chain growth beyond the dimer stage occurs in the solid state and not in solution.[2] This has been leveraged to advantage by using nanofiber seeding[3] and other methods[4] to affect a granular to fibrillar change in the bulk morphology. Understanding these dramatic effects requires insight into chain growth kinetics and evolution of polymer molecular weight (MW) as a function of reaction time. While there are several reports on the molecular weight of EB using gel permeation chromatography (GPC)[5,6] and one report on light scattering studies on ring-sulfonated polyaniline,[7] there are no reports on the absolute MW of as-synthesized parent polyaniline (EB) using light scattering. Solutions of parent polyaniline (EB) absorb strongly in the 500−700 nm range, which interferes with the laser light source used in conventional laser light scattering (LS) instruments, and our earlier attempt to circumvent this issue by reducing EB to the colorless LEB using hydrazine was complicated by significant chain scission.[8] In addition, a majority of the chain growth during aniline polymerization occurs in the intermediate pernigraniline state (PS), which is also highly colored.[8] The 785 nm laser light source enabled us to accurately determine the absolute molecular weight since LEB, EB, and PB do not absorb in this region. The absolute MW values of all three oxidation states have been compared with GPC values and correction factors established.

All three polyaniline bases were synthesized by potential-time profiling the chemical oxidative polymerization of aniline[9,10] using $(NH_4)_2S_2O_8$ oxidant and quenching the reaction in aqueous 0.1 M NH_4OH at appropriate times (Figure 1). For example, PB and EB were obtained upon quenching the reaction at points a and b, respectively, and LEB was obtained by adding L-ascorbic acid at point “a” and quenching at point “c”. Three different MW polyanilines were synthesized by carrying out the reaction at 23, 0−5, and 0−5 °C/salt. Additional details on the synthesis and characterization are provided in the Supporting Information.

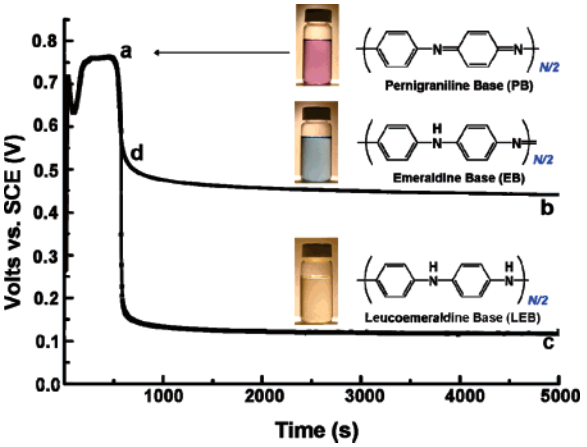

Figure 1. Potential-time profiling of aniline polymerization using (NH_4)-S_2O_8 oxidant at 0 °C. The reaction was quenched in aqueous 0.1 M NH_4-OH at (a) for PB and (b) for EB. For LEB, ascorbic acid was added at point (a) and product isolated at (c).

Refractive index increment (*dn*/*dc*) values were determined using a differential refractometer, equipped with a 785 nm laser light source. While 1-methyl-2-pyrrolidinone (NMP) containing 0.8% dissolved $LiBF_4$ ($NMP/LiBF_4$) was suitable for LEB and EB samples,[6] solutions of PB were unstable in the presence of added Li^+ salts, and pure NMP was used instead. The same solvent systems were used as the mobile phase in GPC equipped with a refractive index (RI) detector. The LS detector can also be used in the GPC mode, allowing measurements on the polydispersity index (PI), M_w/M_n, by both LS and RI detectors. Absolute M_n values (M_w/PI) and the number of aniline repeat units (N) were then obtained ($M_n = 90−91$, Table 1 caption).

Light scattering data show that $N = 316$ in EB synthesized by the conventional chemical method at 0−5 °C (Table 1). A value of $N = 378$ was obtained by GPC, indicating an overestimation by 17%, which is typically rationalized on the basis of different hydrodynamic radii of EB and polystyrene standards used in GPC. However, the overestimation by GPC is itself molecular weight dependent (Table 1); for example, it can be as high as 29% for low molecular weight EB with $N = 117$, and as low as 2% for commercial high molecular weight EB with $N = 800$.[6] This suggests that narrow distribution polystyrene can indeed be used as reliable standards in GPC provided that the molecular weight of EB is above a threshold value. This narrowing of the difference between LS and GPC values at high molecular weights is unexpected since the

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[†] Also at: Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

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Table 1. Number of Aniline Repeat Units (*N*) and Weight Average Molecular Weight (M_w) for Polyaniline Measured by Light Scattering (LS) and Gel Permeation Chromatography (GPC)

		0–5 °C/salt		0–5 °C		23 °C	
	dn/*dc*[a]	M_w LS *GPC (PI)*[c]	*N*[b] LS/*GPC* (diff)[d]	M_w LS *GPC (PI)*[c]	*N*[b] LS/*GPC* (diff)[d]	M_w LS *GPC (PI)*[c]	*N*[b] LS/*GPC* (diff)[d]
pernigraniline (PB)[e]	0.50[e]	74900	362/*406*	52470	265/*323*	24160	117/*166*
		84135 (2.3)	(10.9%)	*64092 (2.2)*	(17.9%)	*34365 (2.3)*	(29.6%)
emeraldine (EB)[f]	0.41[f]	95800	441/*482*	68580	316/*378*	30102	145/*203*
		104707 (2.4)	(8.6%)	*82296 (2.4)*	(16.6%)	*42206 (2.3)*	(28.6%)
leucoemeraldine (LEB)[f]	0.29[f]	84550	404/*445*	55950	267/*321*	26100	130/*181*
		93085 (2.3)	(9.3%)	*67257 (2.3)*	(16.9%)	*36279 (2.2)*	(28.2%)

[a] Refractive index increment. [b] Number of aniline repeat units [(M_w/PI)/wt of repeat unit] (PB = 90; EB = 90.5; LEB = 91). [c] Polydispersity index (M_w/M_n). [d] Percent difference between $N_{GPC} - N_{LS}$. [e] NMP solvent. [f] NMP/LiBF$_4$ solvent. MW values in Daltons.

conformation in solution of a polar, H-bonding polymer such as EB in NMP is expected to be significantly different from nonpolar polystyrene standards. A similar conformational leveling at high molecular weights is observed in the narrowing of LS and GPC values in LEB, and also in PB, which cannot form H-bonds with NMP (Table 1).

Interestingly, the percent difference between LS and GPC falls in clusters, 9−11, 17−18, and 28−30%, which are differentiated by molecular weight and not oxidation state; for example, for a given molecular weight range, LEB, EB, and PB all fall within a given cluster. This suggests that the conformation in solution of LEB, EB, and PB, while expectedly different from PS standards, differs from it by similar amounts. The reasons for this are unclear, for one might have expected PB to be more rod-like versus PS standards compared to LEB or EB.

Light scattering data show $N = 265$ for PB isolated at the edge plateau of the potential-time profile (Figure 1, point a) for the synthesis carried out at 0 °C. An additional 51 aniline units are added during the conversion of pernigraniline to emeraldine (EB, $N = 316$), an increase of ~19% that is consistent with our proposed two-step mechanism of aniline polymerization.[9] In this mechanism, 84% of ES originates from the pernigraniline intermediate when it is reduced to emeraldine (ES_p) by excess aniline. The remaining 16% comes from the freshly oxidized aniline that can either polymerize independently to emeraldine (ES_a) to yield a physical mixture of $[ES_p]_{84\%}$ and $[ES_a]_{16\%}$ or couple with existing ES_p chains to yield a "block copolymer" of $\{[ES_p]_{84\%}-[ES_a]_{16\%}\}$. The increase in MW observed in this study also validates this mechanism and our earlier study on electrochemically synthesized block copolymers of polyaniline and poly(2-methylaniline), where confirmatory evidence was lacking since there was no access to absolute molecular weight values.[11] Polymer molecular weight was also continuously monitored with reaction time by quenching aliquots at appropriate points along the potential-time profile, and again, a ~19% increase in molecular weight was observed during the conversion of PB to EB. Importantly, we found that it takes time for the freshly oxidized aniline units to couple with existing polyaniline chains; that is, the polyaniline isolated immediately upon fall of potential at 0.52 V (Figure 1, point d) still had the same number of aniline repeat units as that isolated at 0.75 V (Figure 1, point a). It should therefore be possible to synthesize a variety of block copolymers by adding a different monomer at the edge of the plateau region. Indeed, when excess 2-methylaniline is added at the edge of the potential-time plateau (0.75 V), after first converting all the aniline to pernigraniline (using an aniline/$S_2O_8^{2-}$ ratio of 1:1.5), a 11−13% increase in MW is observed. Since the product was washed with dichloromethane to remove any residual poly(2-methylaniline) homopolymer, the observed MW increase is consistent with the coupling of 2-methylaniline units to existing parent polyaniline chains. This coupling must have occurred at the chain ends, similar to the parent polyaniline system. The cyclic voltammogram in aqueous 1.0 M HCl shows redox peaks that have features common to both polyaniline and poly-2-methylaniline. Elemental analysis (carbon/nitrogen ratio) is also consistent with the formation of a $(\text{polyaniline})_{89}-(\text{poly-2-methylaniline})_{11}$ block copolymer (see Supporting Information for details).

In summary, this study describes, for the first time, (i) the absolute molecular weight of parent polyaniline in all three isolable oxidation states, synthesized at three different temperatures, (ii) the molecular weight dependent correction factors for GPC measurements, (iii) evidence consistent with a two-step aniline polymerization mechanism that opens a simple and rapid chemical route to synthesize block copolymers of polyaniline.

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Supporting Information Available: Synthesis, UV/vis, FT/IR, *dn*/*dc*, light scattering, and GPC. This material is available free of charge via the Internet at http://pubs.acs.org.

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