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The molecular weight of polyaniline by light scattering and gel permeation chromatography

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Abstract

Polyaniline base in the emeraldine oxidation state displays strong absorption between 450 and 800 nm which precludes its use at these wavelengths for light scattering (LS) measurements. Therefore, as-synthesized polyaniline in the emeraldine base form was first reduced with hydrazine to polyaniline in the almost colorless leucoemeraldine oxidation state. Absolute weight average and number average molecular weights and polydispersity of the leucoemeraldine base by LS measurements were found to be 25 200, 11 560 and 2.18, respectively. However, the relative weight average molecular weight obtained by gel permeation chromatography of the emeraldine base, used to synthesize the leucoemeraldine base, was found to be ~52 000 and that of emeraldine base obtained by the air oxidation of the above leucoemeraldine base was ~36 800. Thus, subjecting emeraldine base to a cycle consisting of reduction with hydrazine followed by air oxidation results in significant chain scission and, hence, in a reduction of molecular weight. It is concluded that a lower limit of the number of ring-nitrogen units per polymer chain in the as-synthesized emeraldine base is 128.

1. Introduction

Polyanilines constitute a large family of polymers which are formed by the chemical or electrochemical oxidative polymerization of aniline or its derivatives [1]. Certain electrically insulating compositions of these polymers can be doped either chemically or electrochemically with a concomitant increase in electronic conductivity of about 10 orders of magnitude to produce powders, films or fibers having conductivities in the metallic conductive regime [2].

Synthesized for the first time over a century ago [3], polyaniline was subjected to extensive investigation in the early part of this century [4] when it was proposed that it was composed of octameric units that could, in principle, exist in different, isolable oxidation states. Although it was shown in later studies that the molecular weight of chemically synthesized polyaniline was significantly higher than that of an octamer [5], it is interesting to note that the electrical and electronic properties of a chemically synthesized octamer of polyaniline [6] are just as fully developed as those of the polymer. The molecular weight of polyaniline as determined by gel permeation chromatography (polystyrene standards, NMP/LiCl eluent), synthesized in the approximately emeraldine oxidation state, by the chemical oxidative polymerization of aniline using acidic ammonium peroxydisulfate was found to be in the range ~66 000–78 000 [7]. The molecular weight of polyaniline can also be increased by lowering the temperature of polymerization ($\bar{M}_w \sim 160\,000$) [8], and, in a recent study, we have found that by lowering the concentration of aniline species in solution and, hence, the number of nucleation sites, and by carrying out the polymerization at low temperatures in the presence of added inorganic salts, molecular weights ($\bar{M}_w$) in excess of 400 000 can be obtained [9].

However, all molecular weight values obtained by gel permeation chromatography (GPC) must be viewed with caution since they are values relative to an external standard such as monodisperse polystyrene. This study is therefore directed towards the determination and comparison of the absolute weight average molecular weight values ($\bar{M}_w$) of polyaniline obtained by light scattering with the $\bar{M}_w$ and $\bar{M}_n$ values obtained by gel permeation chromatography.

Polyaniline base in the emeraldine base oxidation state displays strong absorption between 450 and 800 nm which precludes the use of these wavelengths in

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obtaining meaningful data in light scattering measurements. Even at very low dilutions, the bulk absorption is too intense for light scattering measurements. However, the fully reduced polyaniline, leucoemeraldine base, was found to be essentially colorless in this region in 1-methyl-2-pyrrolidinone (NMP) solution and was therefore adopted for the light scattering measurements.

2. Experimental

2.1. Synthesis of leucoemeraldine base

Approximately 20 ml of hydrazine hydrate was placed in a 150 ml two-necked (24/40) round-bottomed flask equipped with a magnetic stir bar. One neck of the flask was connected to an argon inlet system and the other neck to a system equipped for filtration under inert atmosphere. The system was purged under argon for ~15 min and emeraldine base, prepared according to the procedure described in ref. 2, was added to the hydrazine hydrate in ~0.05 g portions via the argon inlet port making sure that leakage of atmospheric air into the flask was kept to a minimum by increasing the argon flow. Immediately upon contact of the emeraldine base powder with the hydrazine hydrate, bubbles of a colorless gas were observed on the surface of the powder (probably nitrogen from the reduction of the emeraldine base to leucoemeraldine base) with the simultaneous color change of the polymer from dark blue–bronze to light blue. Upon completion of the addition of the emeraldine base, the resulting heterogeneous system was stirred under an atmosphere of argon at room temperature (~25 °C) for ~48 h. The polymer was then found to be greyish white in color. The argon outlet system was then connected to a water aspirator, and the whole apparatus was inverted and the greyish-white solid filtered under a stream of argon. The light yellow filtrate was then discarded by detaching the bottom flask while the argon was still flowing. The bottom flask was then refitted and the argon flow stopped. The top flask was quickly removed and 50 ml of anhydrous ether (not degassed) was poured from the top directly on to the precipitate and the argon inlet filter system was again connected. The side arm of the filtration flask was then opened in order to evacuate the system (~0.5 min) and then closed again, forcing thereby the solvent ether through the fritted filter, effectively washing the leucoemeraldine base in the process. The above washing procedure was repeated five times and the solid was allowed to dry under a stream of argon for ~2 h. The resulting grey powder was dried under dynamic vacuum (<1 micron pressure) for ~24 h at 25 °C and was used for the light scattering measurements.

2.2. Gel permeation chromatography (GPC)

2.2.1. Emeraldine base (used for synthesis of leucoemeraldine base)

Emeraldine base (~4 mg, sample used to synthesize leucoemeraldine base above) was added to ~10 ml 1-methyl-2-pyrrolidinone (NMP) containing ~0.5% by weight LiCl (NMP/LiCl) in a ~20 ml glass vial equipped with a small magnetic stir bar and the resulting bright blue solution was stirred at ~25 °C for ~1 h and then filtered through a ~0.45 micron filter. Approximately 20 μl of the above solution was injected into a GPC column (Waters Chromatographic System, linear column, polystyrene reference, 0.44 ml/min flow rate, refractometer detector, 35 °C column temperature). From the retention time of the resulting chromatogram, the $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values obtained were 52 653, 21 061 and 2.5, respectively.

2.2.2. Air-oxidized leucoemeraldine base

Leucoemeraldine base (~4 mg) synthesized in Section 2.1 was dissolved in ~10 ml NMP/LiCl solution in a manner similar to that described in Section 2.2.1. The resulting faintly blue solution was allowed to stand in air at ~25 °C for ~52 h in an open vial. The color of the solution changed to bright blue indicating a change in oxidation state of the polyaniline from leucoemeraldine to emeraldine. The UV–Vis spectrum of this solution was essentially identical to the solution of emeraldine base in NMP/LiCl prepared as described in Section 2.2.1. The GPC of the above air-oxidized leucoemeraldine base gave $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of 36 844, 16 019 and 2.3, respectively.

2.3. Light scattering of leucoemeraldine base

2.3.1. Sample preparation

A stock solution of 0.01 gm/ml of leucoemeraldine base (synthesized in Section 2.1) in NMP was prepared in a dry box under nitrogen (all subsequent solutions were exposed only to dry nitrogen), then diluted to 2.0×10^{-3} gm/ml. Approximately 0.07 ml of hydrazine was added to 1 ml of this solution to ensure that the leucoemeraldine base was fully reduced. The solution, a pale yellow in color, was then used to make a series of solutions having a minimum concentration of 5.0×10^{-4} gm/ml which were found to be suitable for light scattering measurements. Dilutions were made with NMP containing 0.07 ml of hydrazine per ml of NMP to keep the concentration of hydrazine relatively constant in each solution. Solutions were filtered into a sample tube through a 0.5 micron filter.

These solutions were still slightly absorptive in the 450 to 800 nm range. Since light absorption in this range caused the measured molecular weight to be lower than its actual value, the absorbance had to be measured quantitatively so that a correction of the measured $\bar{M}_w$ could be made. The absorbance was measured using a Cary 2300 spectrophotometer and the value equivalent to 5% light loss was used to correct the measured $\bar{M}_w$. In addition, the solutions fluoresced slightly. However, since a narrow wavelength filter was used to eliminate the fluorescent light, corrections for this effect were not required.

The specific refractive index increment (d*n*/d*C*), where *n* is the refractive index and *C* is the concentration in gm/ml of the solutions, is necessary for the determination of molecular weight. This value defines the change of refractive index of a solution as a function of solution concentration. The measurement could not be carried out in a dry box, but was done with a C.N. Wood differential refractometer with sample cells that were constantly purged with nitrogen. The d*n*/d*C* value was determined to be 0.27 for the solutions.

2.3.2. *Light scattering measurements and data reduction*

Static light scattering measurements as a function of solution concentration and scattering angle were made at room temperature with a Brookhaven BI200SM spectrometer and BI2030AT correlator. The light source used was an argon ion laser operating at a wavelength of 514.5 nm. The $\bar{M}_w$ value of light scattering particles in solution is related to their light scattering properties [10] by the expression:

$$KC/R(\theta)=1/\bar{M}_w(P(\theta)+2A_2C+3A_3C^2+\ldots) \qquad (1)$$

where K is the wave vector, C the solution concentration, $R(\theta)$ the reduced Rayleigh ratio, $P(\theta)$ the particle scattering function, θ the scattering angle, and A_2 and A_3 are the second and third osmotic virial coefficients. K is given by the expression:

$$K=2\pi^2 n_o^2(\mathrm{d}n/\mathrm{d}C)^2/N_a\lambda^4 \qquad (2)$$

where n_o is the refractive index of the solvent, λ the light wavelength and N_a Avagadro's number. The particle scattering function is expressed as

$$1/P(\theta)=1+16\pi^2 n_o^2\{R_g^2\}\sin^2(\theta/2)/3\lambda^2 \qquad (3)$$

where R_g is the radius of gyration. In the limit of zero angle and zero concentration, eqn. (1) becomes

$$KC/R(\theta)=1/\bar{M}_w \qquad (4)$$

These limits are typically obtained by measuring scattering intensities over a range of angles for several different concentrations, then performing a Zimm plot analysis [11] in which $KC/R(\theta)$ is plotted versus $\sin^2(\theta/2)+AC$, where A is a constant. Extrapolations at zero angle and at zero concentration result in an intersect having a value of $1/\bar{M}_w$.

3. Results and discussion

The light scattering data were treated in three ways to obtain the most reliable value for the molecular weight. A Zimm plot of the data is shown in Fig. 1. The straight line extrapolations to the slightly curved data yields a $\bar{M}_w$ value of 25 000. A Berry plot [12], in which the square root of $KC/R(\theta)$ is plotted versus $\sin^2(\theta/2)+AC$, sometimes leads to a more accurate result in the case of curvature in the data. This plot is shown in Fig. 2 and yields a value of 23 700. For molecular weights in this range, a plot of $KC/R(\theta)$ versus C at 90° should be linear and an extrapolation to zero concentration should yield the reciprocal of $\bar{M}_w$. This plot is shown in Fig. 3, which leads to a value for $\bar{M}_w$ of 23 200. Since all three ways of determining $\bar{M}_w$ are equally valid, an average value of 24 000 is taken for $\bar{M}_w$. Correcting for the light absorbance of the solutions then yields a $\bar{M}_w$ of 25 200 for the leucoemeraldine base material. The estimated accuracy of the result is ±5%.

Figure 4, a plot of $\sin^2(\theta/2)$ versus $KC/R(\theta)$, shows the initial and asymptotic regions of the angular de-

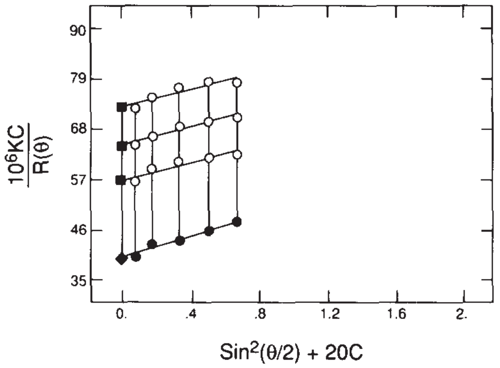

Fig. 1. Zimm plot of light scattering data: ○, experimental points obtained from three different concentrations at five different angles; ■, extrapolated values to zero angle; ◆, extrapolated value to zero concentration and zero angle.

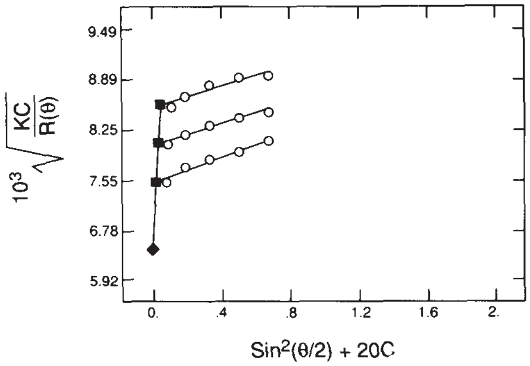

Fig. 2. Berry plot of light scattering data: ○, experimental points obtained from three different concentrations at five different angles; ■, extrapolated values to zero angle; ◆, extrapolated value to zero concentration and zero angle.

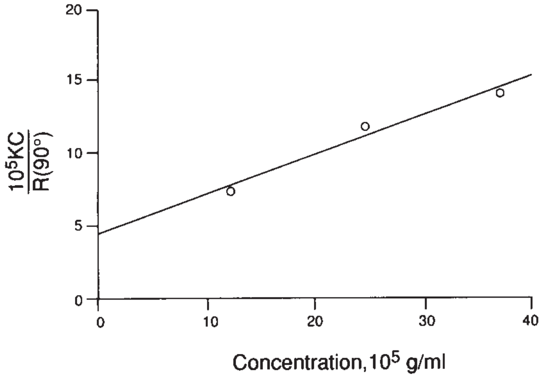

Fig. 3. Plot of 90° measurements from light scattering data.

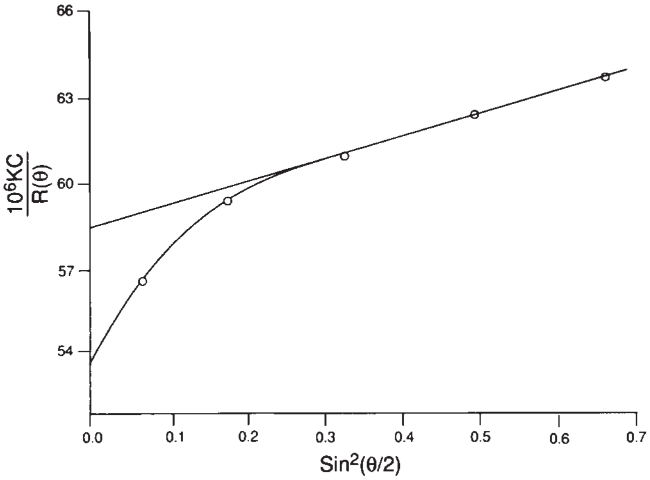

Fig. 4. Plot of initial and asymptotic regions of the angular dependence of scattered light intensity.

pendence of scattered light intensity for 0.001 gm/ml concentration. Using the intercept of the asymptotic portion of the curve (I_a) and the intercept of the initial curve (I_i) the $\bar{M}_w/\bar{M}_n$ value can be obtained using the relation $\bar{M}_w/\bar{M}_n=2I_a/I_i$. A detailed explanation of this method can be found in ref. 13. Inserting the values for I_a and I_i, which are 5.84×10^{-5} and 5.37×10^{-5}, respectively, yields a $\bar{M}_w/\bar{M}_n$ of 2.18 and a $\bar{M}_n$ of 11 560.

The results of light scattering and GPC measurements can be summarized as follows: (i) as-synthesized emeraldine base afforded $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of 52 653, 21 061 and 2.5, respectively, by GPC; (ii) leucoemeraldine base synthesized by the reduction of emeraldine base with hydrazine afforded $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of 25 200, 11 560 and 2.18 by light scattering; (iii) emeraldine base synthesized by the reoxidation of leucoemeraldine base afforded $\bar{M}_w$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of 36 844, 16 019 and 2.3, respectively, by GPC.

The GPC data show that there is significant chain scission upon subjecting as-synthesized emeraldine base to reduction followed by oxidation, as evidenced by the lowering of $\bar{M}_w$ values (GPC) from 52 653 to 36 844 and the $\bar{M}_n$ values from 21 061 to 16 019. It is not possible to determine unambiguously which of the two steps, namely, reduction or oxidation (or both), is responsible for chain scission. However, it is possible to estimate the lower limit of the number of aniline ring units per polymer chain in the as-synthesized emeraldine base. The estimate is derived from the absolute $\bar{M}_n$ (11 560) value which represents 128 ring-nitrogen units per polymer chain. Therefore, it is concluded that the lower limit of the number of ring-nitrogen units per polymer chain is 128.

4. Conclusions

The lower limit of the absolute weight average molecular weight and of the absolute number average molecular weight of chemically synthesized polyaniline in the emeraldine oxidation state upon conversion to the leucoemeraldine oxidation state have been determined for the first time to be 25 200 and 11 560, respectively, by light scattering measurements. The absolute molecular weight of emeraldine base could not be determined by light scattering measurements because of its intense absorption in the visible region of the electronic spectrum. From the above $\bar{M}_n$ value it is concluded that the lower limit of the number of aniline ring units per polymer chain in the as-synthesized emeraldine base is 128.

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