Macromolecules **1997,** *30,* 2953−2955

Experimental Evidence for Hydrogen Bonding in Polyaniline: Mechanism of Aggregate Formation and Dependency on Oxidation State

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Received January 7, 1997; Revised Manuscript Received March 18, 1997[⊗]

ABSTRACT: Aggregation in the nondoped polyaniline, emeraldine base (EB), as observed by GPC in a *N*-methyl-2-pyrrolidinone (NMP) solution, was found to be closely related to the fraction of the imine nitrogen atoms in the nondoped polymer, i.e., to the oxidation state of the polymer. As EB was reduced to leucoemeraldine base (LEB), the degree of aggregation was significantly reduced. The results of gel permeation chromatography (GPC) and infrared studies suggest that the aggregation of the polymer is due to *inter*chain hydrogen bonding between the imine and amine nitrogen sites on adjacent polymer molecules. The degree of hydrogen bonding and, thus, aggregation found in the polymer is greatly affected by solvents, LiCl, and the oxidation state of the polymer.

1. Introduction

The solution characteristics of polyaniline have been of particular recent interest since they determine the polymer morphology in the solid state and, in turn, the overall properties of the material.[1−4] Polyaniline in the emeraldine base (EB) form has most commonly been processed in *N*-methyl-2-pyrrolidinone (NMP). Free-standing films as well as fibers have been processed from relatively concentrated NMP solutions.[5] It has been noted that EB solutions gel with time. It was proposed that gelation was due to some kind of physical cross-linking of the polymer.[6] More recently, it has been shown that the as-made EB is aggregated as a result of interchain interactions. The aggregation was found to persist in solution, in particular in NMP solution, giving rise to “pseudo” high molecular weight fractions in gel permeation chromatography (GPC).[2,3] The addition of LiCl was found to disrupt the internal interactions and thus deaggregate the polymer chains.[2,3] The mechanism for aggregate formation has been speculated to be interchain hydrogen bonding between amine and imine sites. The present communication provides direct experimental evidence for interchain hydrogen bonding in EB and establishes a correlation between interchain hydrogen bonding and aggregate formation. This is done by combining GPC with infrared spectroscopy and comparing measurements obtained on EB, the mixed oxidation state of polyaniline consisting of amine and imine sites, with measurements done on the reduced form of the polymer, leucoemeraldine base (LEB), consisting solely of amine sites.

2. Experimental Section

Polyaniline (emeraldine base, EB) was synthesized according to the standard procedure.[7] Leucoemeraldine base (LEB) powder was prepared by reducing EB powder with phenylhydrazine.[8] The solid-state FTIR spectra of EB and LEB powder were taken by diffuse reflectance spectroscopy with a Perkin-Elmer 1760 spectrometer under a nitrogen atmosphere.

Thin films of polyaniline were spin-coated onto a KBr crystal substrate from a 5 wt % solution of EB in *N*-methyl-2-pyrrolidinone (NMP) (99.5%, Aldrich) or from a solution of this type containing, in addition, 5 wt % of LiCl. The residual NMP in the films was removed by methanol extraction followed by pumping in a dynamic vacuum for ∼30 min. Films containing LiCl (which is insoluble in $CHCl_3$) were treated with $CHCl_3$ to remove the residual NMP. The transmission FTIR spectra of all the polyaniline thin films were recorded by the same spectrometer used for the diffuse reflectance studies.

An EB thin film on a KBr substrate was reduced by exposure to hydrazine (98%, Aldrich) vapor for selected time periods. The film was then treated with methanol to remove the residual hydrazine and further pumped in a dynamic vacuum for ∼30 min. The FTIR spectra were then immediately recorded under a nitrogen atmosphere.

The samples for gel permeation chromatography (GPC) studies were made by dissolving EB powder in NMP at a concentration of 0.1 wt %. The reduced samples were prepared by adding 10 and 20 drops of a 1 wt % hydrazine (N_2H_4) solution in NMP to 10 mL of the 0.1 wt % EB solution in NMP. The solutions were allowed to stand for 2 h at room temperature and were then filtered through a 0.20 μm filter. Careful attention was given to maintain the reduced solutions under a N_2 atmosphere. The solutions were then injected into the GPC column. The GPC studies were performed using a JordiGel linear column operating at 85 °C. Polystyrene was employed as the standard, and the UV/vis absorption at 330 nm was used as the detector response.

3. Results and Discussion

(I) Solid Emeraldine Base and Leucoemeraldine Base Powder. The diffuse reflectance FTIR spectrum of EB powder (Figure 1a) shows the following five major vibrational bands: 1598, 1492, 1310, 1160, and 830 cm^{-1}. These are in excellent agreement with previously published values.[9,10] In addition, it is important to note that there are two bands associated with the N−H stretching vibrations—a major broad band located at ∼3290 cm^{-1} and a minor sharp band located at ∼3383 cm^{-1}. In contrast, the FTIR spectrum of LEB powder (Figure 1b) shows only one sharp N−H band located at ∼3384 cm^{-1} associated with a free (non-hydrogen-bonded) N−H stretching vibration.[11] It is apparent that there is a significant difference in the N−H stretching characteristics of EB and LEB powder.

EB is a “mixed oxidation state” polymer containing amine (reduced) and imine (oxidized) sites, whereas

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[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1997.

S0024-9297(97)00013-2 CCC: $14.00

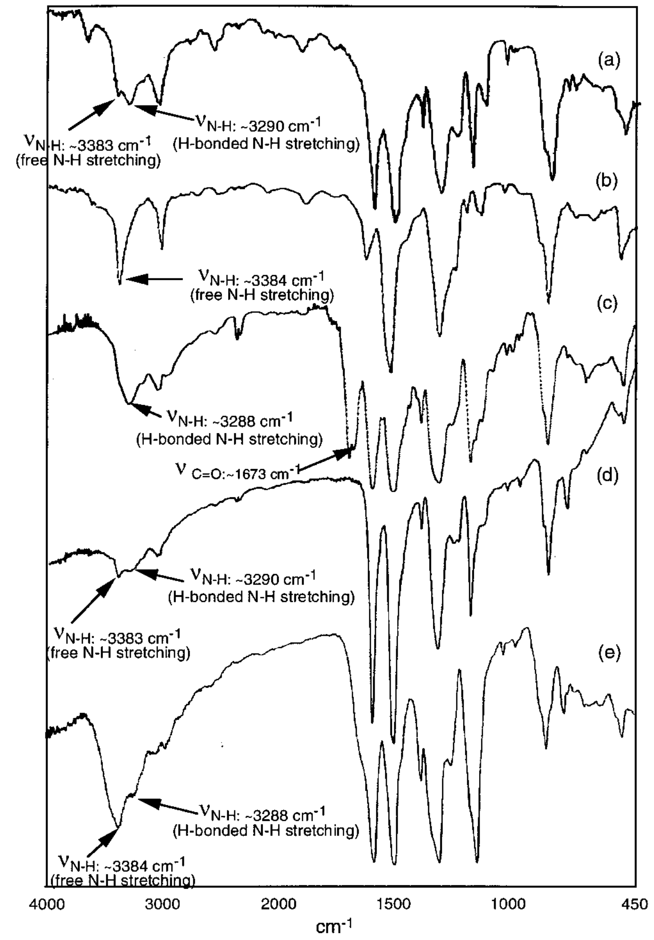

Figure 1. Diffuse reflectance FTIR spectra of (a) emeraldine base (EB) powder, (b) leucoemeraldine base (LEB) powder, (c) emeraldine base (EB) thin film (with NMP), (d) emeraldine base (EB) film (no NMP), and (e) emeraldine base (EB) film containing LiCl (no NMP).

LEB contains only amine sites. The present study shows that hydrogen bonding between amine and imine sites is much stronger than amine−amine hydrogen bonding, and thus, significant hydrogen bonding is observed in EB, whereas no hydrogen bonding is observed in LEB. This is consistent with the fact that amine−amine H-bonding is generally weak[11] and with theoretical calculations on the phenyl-capped tetramer of polyaniline which indicated that amine−imine hydrogen bonding was energetically favorable in contrast to amine−amine hydrogen bonding.[12] The strong, broad band in EB at ~3290 cm^{-1} is the hydrogen-bonded N−H band between amine and imine sites. The weak 3383 cm^{-1} band in EB is a non-hydrogen-bonded N−H vibration similar to that seen in LEB. It is important to note that the intensity of the hydrogen-bonded N−H stretching band is significantly higher than that of the free N−H band in EB powder. This indicates that the as-synthesized EB is significantly self-associated via hydrogen bonding. These specific results do not distinguish between *inter*chain hydrogen bonding between different polyaniline molecules and *intra*chain hydrogen bonding between different "folded back" segments of the same polyaniline molecule. It should also be noted that a quantitative determination of the degree of hydrogen bonding cannot be made from the present infrared data alone.

(II) Thin Films of Emeraldine Base Containing NMP and LiCl. Figure 1c gives the FTIR spectrum of a freshly made thin EB film cast from a NMP solution. As can be seen, there is a sharp intense carbonyl stretch at ~1673 cm^{-1}, which we assign to a hydrogen-bonded C=O stretch, i.e., −C=O···H···N−. This is consistent with the observed reduction in stretching frequency of the C=O group as compared to that in pure NMP (~1695 cm^{-1}). This is also consistent with the observation that no significant free N−H stretch is present in EB. However, when NMP is removed by methanol extraction, the C=O peak disappears completely and is accompanied by the appearance of a free N−H stretch at ~3383 cm^{-1} (see Figure 1c,d). This strongly suggests that the hydrogen bonding in the polymer chains (N···H···N) in EB powder is partially broken by the hydrogen bonding nature of the NMP solvent due to the formation of −C=O···H···N− bonds.

It is interesting to note on comparing parts a and d of Figure 1 that the relative amount of hydrogen bonding (as compared to non-hydrogen-bonding) in the film cast from a NMP solution is less than that in the as-synthesized EB powder. This suggests that, upon dissolving EB powder in NMP, the solvent partially disrupts the hydrogen bonding in the polymer. Once the hydrogen bonding is disrupted, it does not re-form, at least in the solid film, to the extent present in the as-synthesized material in the time scale of the experiment.

When LiCl is present in the EB film, as shown in Figure 1e, the intensity of the free N−H stretch increases markedly while at the same time the intensity of the hydrogen-bonded N−H stretch is greatly reduced, as compared to as-synthesized EB powder (Figure 1a) and to EB cast from NMP alone (Figure 1c). The addition of LiCl results in significant breaking of the interchain hydrogen bonds in emeraldine base. We have shown previously that Li$^+$ ions act as a "pseudo protonic acid" dopant and can coordinate to the imine nitrogen atoms of EB.[13] Such coordination would tend to displace the interchain hydrogen bonding. This is also consistent with previous (GPC) studies which have shown that addition of LiCl to an emeraldine base solution in NMP results in deaggregation of the polymer as evidenced by the elimination of the high-MW fractions.[2,3] This indicates that the hydrogen bonding in polyaniline, more specifically interchain hydrogen bonding, is mainly responsible for aggregate formation in EB.

(III) Reduction of Emeraldine Base Films by N_2H_4 Vapor. As shown in Figure 2, exposure of a thin EB film to N_2H_4 vapor produces a progressive marked decrease in the hydrogen-bonded N−H stretching vibration with a concomitant increase in the free N−H stretch as the hydrazine exposure time is increased.

It is well-known that the oxidation state of polyaniline base refers to the relative molar ratio of imine and amine nitrogen atoms in the polymer.[5] As the polymer becomes reduced to a lower oxidation state by increasing the N_2H_4 vapor exposure time, the fraction of imine groups in the polymer decreases as the imine groups are converted to amine groups. The results given in Figure 2 show that the degree of hydrogen bonding decreases with decreasing proportion of the imine groups in the polymer. Figure 2 also indicates that the hydrogen bonding in polyaniline base is mainly between the imine and amine nitrogen sites rather than between the amine and amine sites.

(IV) GPC Studies of Polyaniline Base Solutions. Figure 3 gives the GPC chromatograms of an EB solution in NMP together with the same solution treated with different quantities of N_2H_4. As can be seen, the

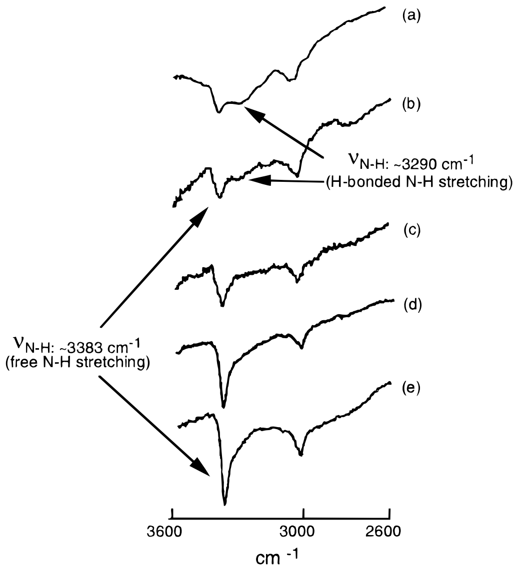

Figure 2. Infrared spectra of (a) emeraldine base (EB) thin film, (b) film after treatment with hydrazine vapor for ~15 min, (c) film after treatment with hydrazine vapor for ~30 min, (d) film after treatment with hydrazine vapor for 1 h, and (e) film after treatment with hydrazine vapor for ~12 h.

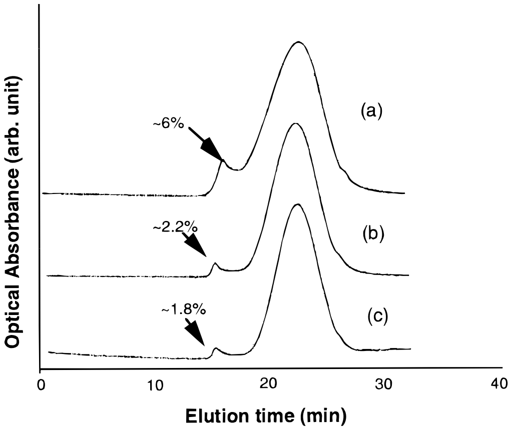

Figure 3. GPC chromatograms of (a) 0.1 wt % emeraldine base (EB) in NMP solution, (b) the same solution after treatment with hydrazine, and (c) the same solution after additional treatment with hydrazine.

high molecular weight peak decreases significantly with increasing amounts of added N_2H_4. This strongly suggests that the degree of aggregation of EB in a NMP solution is controlled by the degree of *inter*chain hydrogen bonding. When different molecules "combine" by *inter*chain hydrogen bonds, "pseudo" high molecular weight (smaller GPC peak) species are formed. In addition, a narrowing of the larger GPC peak is also observed upon reduction. This may indicate that hydrogen bonding may also be present in the larger GPC fraction of EB and that the hydrodynamic volumes of EB and partially reduced EB are therefore different. A decrease of the oxidation state of polyaniline base significantly reduces the amount of imine nitrogen sites and hence the extent of *inter*chain hydrogen bonding and results in deaggregation of the polymer chains in a NMP solution.

4. Conclusions

It is concluded that "as-synthesized" emeraldine base (EB) powder is significantly self-associated via *inter*chain hydrogen bonds between the imine and amine nitrogen sites on the polymer backbone, and as shown experimentally, this interchain hydrogen bonding in EB is predominately responsible for aggregate formation. The actual number of interchain hydrogen bonds that are necessary to form an aggregate is not obvious. As chains are brought in close proximity by hydrogen bonding, a subsequent "zipper effect" may occur whereby additional hydrogen-bonded interactions and possibly other types of interactions might proceed readily between chains already joined by at least one hydrogen bond.

Lithium chloride and also a decrease in the oxidation state of the polymer, both of which partially or completely break the hydrogen bonding, cause a marked reduction in the degree of aggregation of the polymer. Thus, hydrogen bonding and resultant aggregate formation require a mixed oxidation form of polyaniline and do not occur to any substantial level in the fully reduced LEB nor is it expected to occur in the fully oxidized pernigraniline.

Acknowledgment. The authors thank Dr. Y.-H. Liao and Dr. Stephen Buchwalter at the IBM T.J. Watson Research Center and Mr. J. Feng at the University of Pennsylvania for useful discussions. This work is in part supported by NIST ATP 1993-01-0149.

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MA9700136