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POLY(o-ETHOXYANILINE): CONTROL OF STRUCTURE AND CHARGE TRANSPORT THROUGH DERIVATIZATION

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ABSTRACT

It is shown that a large ring substituent such as -OC_2H_5 causes the polyaniline HCl salt to form a different crystal structure. Though there is substantial crystallinity, the bulky side groups make it more difficult to achieve three-dimensional metallic delocalization and, for the samples studied, the conduction electrons behave as if localized to single chains.

INTRODUCTION

The polyaniline (PAN) family of polymers has been under increasing study for the past half dozen years since it has been demonstrated that this family of materials is readily derivatized and processed into strong films and fibers.[1] Most of the earlier studies focused on the insulating parent polyaniline in its emeraldine base oxidation state and its conducting HCl salt. Structural studies[2] showed that substantial crystallinity was possible while transport experiments demonstrated three-dimensional metallic charge delocalization was possible in the crystalline regions.[3] Later studies explored the effects of small ring substituent groups such as methyl (-CH_3) groups (poly(o-toluidine) or POT)[4] and sulfonic acid[5] (-SO_3H) groups (SPAN). The small expansion of the unit cell and decrease in interchain order for POT-HCl[6] leads to an increase in electronic localization and a three order of magnitude decrease in conductivity.[7] In contrast to the crystallinity of POT-HCl, the self-doped SPAN is essentially disordered[8] with charge localization in the conducting state.[9]

We examine here the effects of a larger ring substituent group, ethoxy (-OC_2H_5), on the structure and electronic state of polyaniline.[10] We find that though the base is amorphous, the larger substituent causes the poly(o-ethoxyaniline hydrochloride), (PEA-HCl), to form a different structure than that of the earlier studied emeraldine hydrochloride[2] and its methyl derivative.[6] The results of temperature dependent dc conductivity and thermoelectric power studies of pressed pellets and stretched (up to eight times elongation) fibers of the PEA-HCl shows that there is increasing delocalization of charge along the individual chains with increasing orientation, though evidence for regions forming a three-dimensional metallic state is not observed.

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STRUCTURAL STUDIES

The structure of poly(o-ethoxyaniline) (PEA) was investigated with the CuKα (1.542Å) radiation and with the experimental set up already used for a previous structural study of PAN[2]. Both unstretched and 6 or 8 times stretched fibers of PEA base and HCl salts were investigated.

PEA base is quasi-amorphous both in its unstretched (Fig. 1) and 8x stretched forms . In contrast to PAN, no significant conversion from amorphous to crystalline occurs upon stretching. Only a slight increase of the intensity of the two amorphous halos in the equatorial (⊥) directions and the onset of a well defined polymer chain (//) reflection are observed upon stretching. The d-spacings and intensity of the main features of the diffraction pattern of PEA base are summarized in Table I.

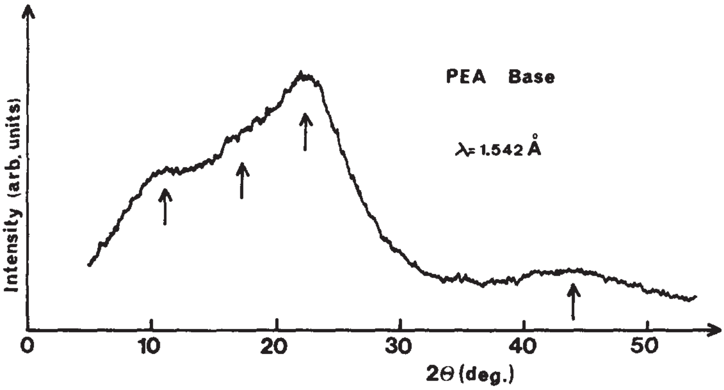

Figure 1 : Microdensitometer reading of an X ray pattern from unstretched PEA base (λ = 1.542Å).

Table I : Structural characteristics of the main broad amorphous halo observed in 7.7x stretched (unstretched) PEA bases

d-spacing (Å)	Intensity	Orientation
~8.1 (~8.8)	W	⊥
(~5.5)	V W	?
4.75	W	//
4.04 (4.04)	S	⊥
2.06 (2.06)	W	?

In amorphous PAN-EB the position of the most intense amorphous halo gives a d-spacing close to the average interchain packing distance.[11] This is apparently not the case for PEA base because the associated d-spacing (4Å) is much smaller than the one of PAN-EB (4.45Å) [2,11] and of POT-EB (4.75Å) [6].

This and the observation of another broad halo at a larger d-spacing of about 8.1-8.8Å means that, probably, because of the necessity to accommodate a bulky ring substituant, the interchain packing distances of PEA base are anisotropic. Consistant with this anisotropy, the geometrical average of 4Å and 8.5Å (5.8Å) is larger than the above quoted packing distances of PAN-EB and POT-ES. A somewhat similar anisotropic packing certainly occurs in SPAN and K-SPAN where, in spite of the presence of bulky SO_3^- groups, the maximum of the amorphous halo gives short d-spacings of 3.7Å and 3.8Å respectively.[12] Finally it is found that the (half) intrachain periodicity (4.75Å) of PEA base is significantly smaller than the one (5Å) of PAN-EB[2].

X-ray patterns similar to the one of Fig. 2 show that PEA HCl salt is partly crystalline (fraction of crystallinity X_c~50%). The d-spacing, intensity, and domain length (L) of the Debye Scherrer rings of these patterns are given in Table II. X_c and L are comparable to those found in PAN-ES[2]. These quantities do not evolve significantly upon 6x stretching. It is suggested that the two strongest rings correspond to:

i) an interchain peridocity of 3.6Å already observed in PAN-ES[2] and amounting to about the close contact distance between two adjacent chains with the phenyl rings nearly located in the plane of nitrogens.

ii) an intrachain periodicity of 10.9Å, which is larger than the zig-zag repeat periodicity (10-10.4Å)[2] of PAN chains.

It is likely the placement of bulky $-OC_2H_5$ group (and Cl^- ions) in a structure with phenyl rings nearly in the plane of the nitrogens requires a new chain conformation opening larger cavities. Fig. 3 presents a hypothetical chain conformation of 2_1 symmetry and (half) chain periodicity of 10.9Å accounting for the placement of these entities. From $L_{//}$~65Å such a conformation will be established over about 3 chain periodicities.

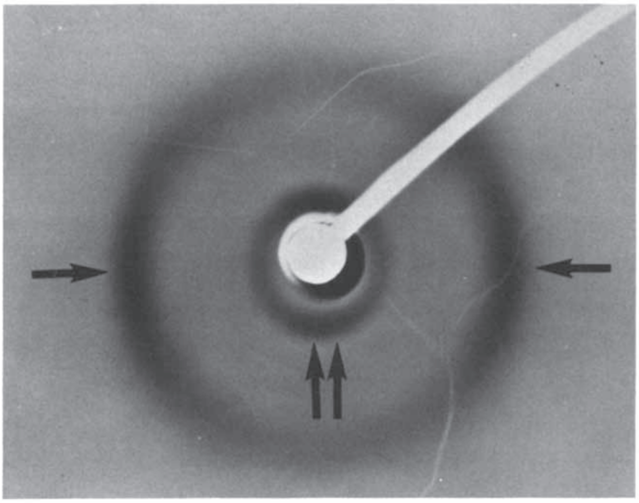

Figure 2 : X-ray pattern from a 6x stretched PEA HCl salt showing the strongest intrachain (single arrow) and interchain (double arrow) reflections (λ = 1.542Å).

Table II : Structural characteristics of the Debye Scherrer "rings" observed in 6x stretched and unstretched PEA HCl salts.

d-spacing (Å)	Domain length L (Å)	Intensity	Orientation
10.9	65	S	//
~7.2	-	V W	?
~5.4	-	V W	?
3.6	35	S	⊥
2.06	-	W	?

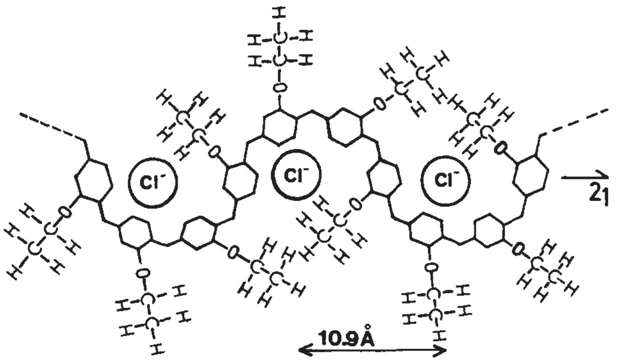

Figure 3 : Possible conformation of 2_1 symmetry of the PEA polymeric chain allowing the placement of bulky $-OC_2H_5$ groups and Cl^- ions in the polymer plane.

CHARGE TRANSPORT STUDIES

Temperature (T) dependent four-probe DC conductivity (σ) and thermoelectric power (S) studies were carried out on the same samples of fully protonated (emeraldine salt state) of PEA using the techniques previously described.[3,7] Samples were pumped on for more than 17 hours before commencing the transport measurements. The conductivity results for pressed powder pellets and 4x and 6x stretched fibers (Fig. 4) were similar, with $\sigma(T)=\sigma_0\exp(-(T_0/T)^{1/2})$ as expected[7] for quasi-one-dimensional variable range hopping. Though σ(295K) increases from 2.5×10^{-3} to 0.2 to 4.5 S/cm upon progressing from powder to 4x and 6x stretched fibers respectively, the value of T_0 is not reduced dramatically (T_0 = 20,000K, 32,000K and 23,000K respectively).

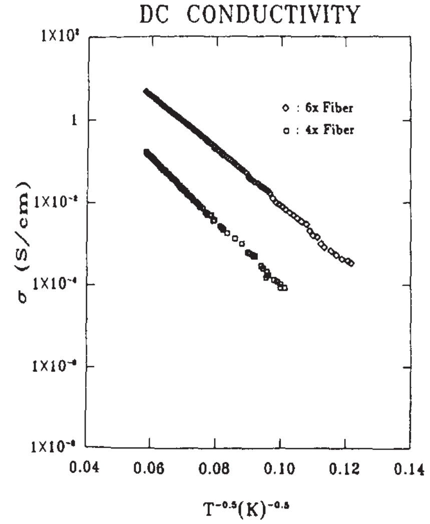

Fig. 4. DC conductivity vs T-0.5 for 4x and 6x stretched fibers of PEA-HCL.

Thermoelectric power for powder and 6x fiber varies at low T as S(T)=(A+B/T) and at high T (>250K for powder, >180K for 6x fiber) as S(T)=(A'+CT), with A, B, A', and C constants. The variation of C (0.016 and 0.039 $\mu V/K^2$ for powder and 6x stretched fiber respectively) is contrary to the constant value that is expected[3] for a 'metallic' thermopower. Therefore it is suggested that the linear term may be due to delocalization along the chain (varying with fiber stretching). The constant "B" is also larger for the 6x stretched fiber than for the unoriented pressed powder sample. The proportionality of S to T^{-1} at low T is suggestive of intrachain one-dimensional variable range hopping,[3,7] with the degree of in-chain localization changing with fiber stretching. Figure 5 illustrates the S(T) for the 6x stretched fiber.

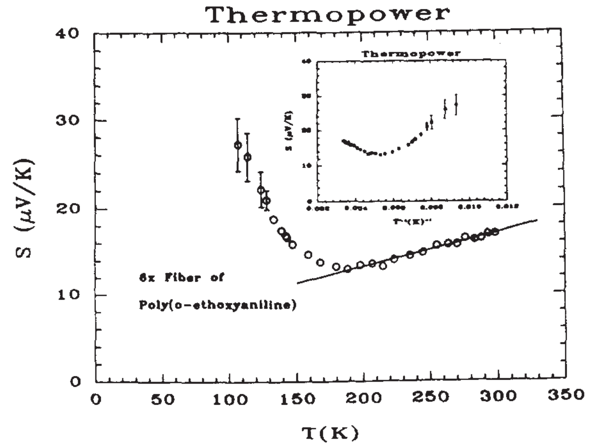

Figure. 5. S(T) vs T for 6x stretched PEA-HCl fiber. The inset shows the data for low T plotted vs T^{-1}.

SUMMARY

It is found that use of a large ring substituent such as -OC_2H_5 causes the PAN HCl salt to form a different crystal structure to accommodate the side groups. Though there is substantial crystallinity, the bulky side groups make it more difficult to achieve three-dimensional metallic delocalization and, for the samples studied, the conduction electrons behave as if localized to single chains.

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