INCLUSION POLYMERIZATION AND DOPING IN ZEOLITE CHANNELS: POLYANILINE

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Abstract   Aniline has been polymerized in the three-dimensional channel
system of zeolite Y. The monomer was diffused into zeolites with different levels
of acidity from hexane solution. Subsequent admission of peroxydisulfate or
iodate from aqueous solution yielded the intrazeolite polymers, as demonstrated
by FT-IR, electronic absorption data and recovery of the included polymer.
With $S_2O_8^{2-}$, the intrazeolite products are a function of the proton content of the
zeolite. Polymer is only formed when a sufficient supply of protons is present
in the zeolite host. When neutral iodate solution is used, no polymer is formed
in NaY and acid zeolites, but at low pH aniline polymerizes in all zeolites.   The
open pore system of the zeolite host can be accessed by base such that the
intrazeolite protonated polymer is transformed into the corresponding neutral
polymer.
The polymer chains encapsulated in zeolite hosts represent a new class of low-
dimensional electronic materials.

INTRODUCTION

Conducting polymers are of considerable interest based on potential applications in
energy storage, antistatic equipment, microelectronics, and molecular electronic
concepts[1,2,3,4]. We explore strategies to stabilize *single strands of conducting
polymers in well-defined crystalline hosts*, particularly in zeolites[5]. These
systems allow us to study the transport properties of decoupled, ordered chains
under controlled conditions, and they promise to be an entry into the design of
molecular electronic functions. Zeolites[6,7] are crystalline open framework oxide
structures (classically aluminosilicates) with pore sizes between 0.3 and 1.2 nm
and exchangeable cations compensating for the negative charge of the framework.
Zeolite Y is characterized by a three-dimensional open framework structure,
composed of interconnected 'sodalite' and supercages, with pore openings of ca. 8 Å
and cage diameter of ca. 13 Å.

    Polypyrrole, polythiophene and polyaniline have recently been included in
layered FeOCl and V_2O_5.[8] Polypyrrole and poly(3-methylthiophene) fibrils with
diameters between 0.03 and 1 μm at 10 μm length have been synthesized in

Nuclepore membranes.[9] Stretch alignment has often been employed to create directional anisotropy in pre-formed polymers, e. g., in polyacetylene,[10] while liquid crystal polymerization under a magnetic field is an alternative technique to achieve alignment.[11]

This report describes recent studies of polyaniline synthesis in large-pore zeolite Y. The effect of different intrazeolite proton levels as well as different oxidants on the resulting polymer yield is discussed. We have also for the first time demonstrated the intrazeolite reaction of protonated polyaniline with proton acceptors. Based on host dissolution experiments, size exclusion experiments, kinetic data, XPS data, conductivity, and electron micrographs, our previous studies have established that the polyaniline chains are accomodated inside the zeolite host system[5b].

EXPERIMENTAL

Zeolite NaY and NH_4Y (LZ-Y52, LZ-Y62; Alfa) were used as precursors for the host materials. Stoichiometric ion exchange with NH_4^+ and degassing at 670 K [5b] resulted in a series of Y zeolites listed in Table 1. The dry zeolites (2 g) were suspended in 100 ml of dry hexane that contained the desired amounts of aniline (Table 1). The intrazeolite aniline was oxidized with aqueous $(NH_4)_2S_2O_8$ at 273 K under nitrogen with constant stoichiometry aniline : oxidant = 4:1 (suffix S). Alternatively, the intrazeolite aniline was oxidized with potassium iodate in water at 295 K, at a ratio aniline : oxidant = 1 (suffix I). Reaction was only observed after lowering the pH to 4 and stirring for 12 h.

Deprotonation of the intrazeolite polyaniline was performed in two different sets of experiments. In aqueous phase, 500 mg of sample was treated with NH_4OH at 295 K for 24 h at stoichiometries 1:1 and 1:10 excess, based on the aniline content of the zeolites. These samples were also treated with dilute HCl, but there is evidence that the zeolite lattice was attacked. Deprotonation was also explored in gas adsorption experiments. A sample equivalent to H6Y-AN-S (but with 27 aniline/u. c.), was pressed into a self-supporting wafer, introduced into a stainless steel vacuum IR cell with CaF_2 windows, degassed under vacuum up to 670 K, and cooled to 295 K. At this temperature, 1 Torr of NH_3 was admitted for a few minutes. The sample was subsequently evacuated and heated at 2 K/min to 470 K (1 h) under vacuum. The IR cell allowed us to record spectra (Mattson Polaris, resolution 4 cm^{-1}) at all intermediate treatment steps in situ.

TABLE 1. Description of polyaniline/zeolite samples.

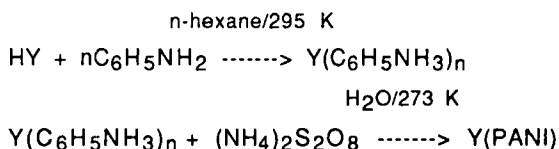| Sample[a]	Zeolite	Aniline per unit cell
NaY-AN	$Na_{56}(AlO_2)_{56}(SiO_2)_{136}$	35
H2Y-AN	$H_{16}Na_{40}(AlO_2)_{56}(SiO_2)_{136}$	16
H4Y-AN	$H_{32}Na_{24}(AlO_2)_{56}(SiO_2)_{136}$	32
H6Y-AN	$H_{46}Na_{10}(AlO_2)_{56}(SiO_2)_{136}$	32

[a] The numbers indicate average proton contents per zeolite supercage.

Bulk polyaniline[12] (PANI) was prepared by chemical oxydation of aniline with $(NH_4)_2S_2O_8$ (4:1) and with KIO_3[13] (15:1) in acidified water.

RESULTS AND DISCUSSION

Effect of oxidation conditions on aniline polymerization.

The intrazeolite polymerization of aniline is believed to proceed in analogy to bulk chemical synthesis, e. g.:[5b]

$$HY + nC_6H_5NH_2 \xrightarrow{\text{n-hexane/295 K}} Y(C_6H_5NH_3)_n$$

$$Y(C_6H_5NH_3)_n + (NH_4)_2S_2O_8 \xrightarrow{\text{H}_2\text{O/273 K}} Y(PANI)$$

PANI differs from most conducting polymers because its conductivity depends on both oxidative and proton doping levels. The initial 'emeraldine salt' product of PANI (at the protonation level of 0.5 H^+/N) is believed to have the following composition, containing quinoid and aromatic components:[14]

$\{[-(C_6H_4)-N(H)-(C_6H_4)-N(H)-][-(C_6H_4)-N^+(H)=(C_6H_4)=N^+(H)-]\}_x^+$ 2 A^-,
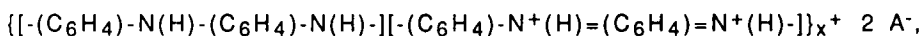
where A^- is an anion. This material can also be formed upon "doping" the corresponding 'emeraldine base' form of polyaniline with aqueous HCl, resulting in a large increase of the number of unpaired spins,[15] probably as diaminobenzene radical cations.[16]

If the aniline-containing, acid zeolites are treated with an appropriate oxidant, the color of the samples changes slowly from white to deep blue within one to several hours. It should be emphasized that *no added acid* is necessary for the

polymerization to occur with peroxydisulfate. The infrared spectra of the samples oxidized with this reagent are shown in Figure 1.
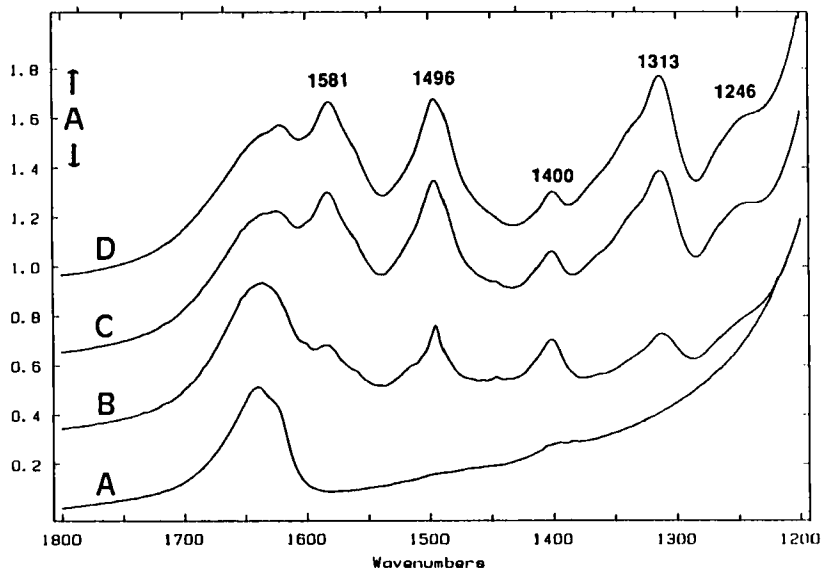

FIGURE 1   FTIR spectra of (A) NaY, (B) sample H2Y-AN-S, (C) H4Y-AN-S, and (D) H6Y-AN-S.

The following trends are observed. In samples with high acid content (H4Y-AN-S, H6Y-AN-S), IR bands at 1581s, 1496s, 1313s, and 1246sh cm^{-1} are indicative of the formation of protonated polyaniline[17,18] (Figure 1.C,D). The vibration at 1581 cm^{-1} is characteristic for the dominant presence of quinone diimine radical cations. A small band at 1400 cm^{-1} is not found in the spectrum of bulk polymer (not shown), but it can be correlated with reactions proceeding at lower intrazeolite acidity: If sample H2Y-AN-S is compared with the highly acid samples (Figure 1.B), the reduction of intensity of the 1581 band as well as others related to the conducting polymer is apparent. The 1400 cm^{-1} vibration is more dominant in this sample, and even more so in the non-acidic, orange-colored sample NaY-AN-S (not shown), with vibrations at 1509, 1444, and 1401 cm^{-1} related to an unknown oxidation product. We can conclude from the presence of the small band at 1400 cm^{-1} in even the samples with highest acidity that a small proton deficit causes formation of the byproduct.

The corresponding electronic absorption spectra show bands typical for emeraldine salt[19,20,21] at 370 and 850 nm (3.4 and 1.5 eV) at higher intrazeolite

acidity (Figure 2.B,C), while features of the orange product at 420 and ca. 600 nm (Figure 2.A) are observed for NaY-AN-S.

When aniline-loaded acidic zeolite samples are treated with iodate in deaerated water (at 295 K), no polymerization is observed within several days. However, this changes dramatically if the pH is lowered to 4, at an aniline-to-oxidant stoichiometry of unity. After 12 h, the samples change color to dark blue *irrespective of the initial intrazeolite acid content.* Two examples are shown in Figure 3.A,B (samples NaY-AN-I, H6Y-AN-I); the observed IR pattern is almost identical with that of sample H6Y-AN-S, with the notable exception of the band at 1401 cm^{-1}. This indicates that the intrazeolite iodate oxidation of aniline proceeds without formation of the orange byproduct. It should be added that the bulk synthesis of polyaniline with iodate, compared to other oxidants, gave also the highest quality samples[13].
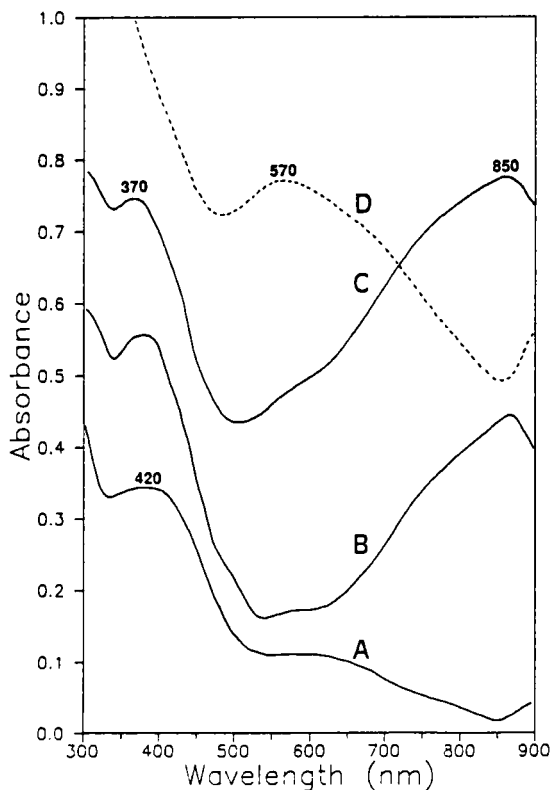

FIGURE 2   Electronic absorption spectra of zeolite/PANI samples dispersed in glycerol.   (A) NaY-AN-S, (B) H4Y-AN-S, (C) H6Y-AN-S, and (D) sample H6Y-AN-S reacted with 10-fold excess of NH$_4$OH.

The electronic spectra of these samples (not shown) all match very closely that of sample H6Y-AN-S. A comparison with bulk PANI made via iodate oxidation (aniline : oxidant 15:1, Figure 3.C) shows that all important vibrations are shifted to lower energies by about 10 cm^{-1}: they occur at 1564, 1482, 1293, and 1238 cm^{-1}. This effect can be related to the different anions compensating for the positive charge of the protonated polymer; if oxidized with peroxydisulfate, the bulk emeraldine salt has bands at 1578, 1496, 1302, and 1220 cm^{-1}.

The perfect match between intrazeolite PANI samples made with *either oxidant* strongly suggests that the counterion in both cases is the *charged zeolite framework* as opposed to individual oxidant ions, e. g.,

$$H6Y/AN \ + \ IO_3^- \ \xrightarrow{H^+} \ H6Y^-PANIH^+/HI,$$
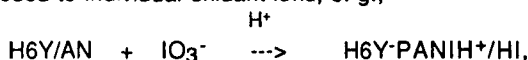
H6Y = charge balanced zeolite framework, AN = aniline, $PANIH^+$ = emeraldine salt.

Treatments with other oxidants result either in unknown oxidation products (H_2O_2) or do not afford oxidative coupling at appreciable rates (O_2), while an alternative precursor route[5e] (ion exchange with $[C_6H_5NH_3]^+Cl^-$, oxidation with $(NH_4)_2S_2O_8$) produces also intrazeolite PANI.

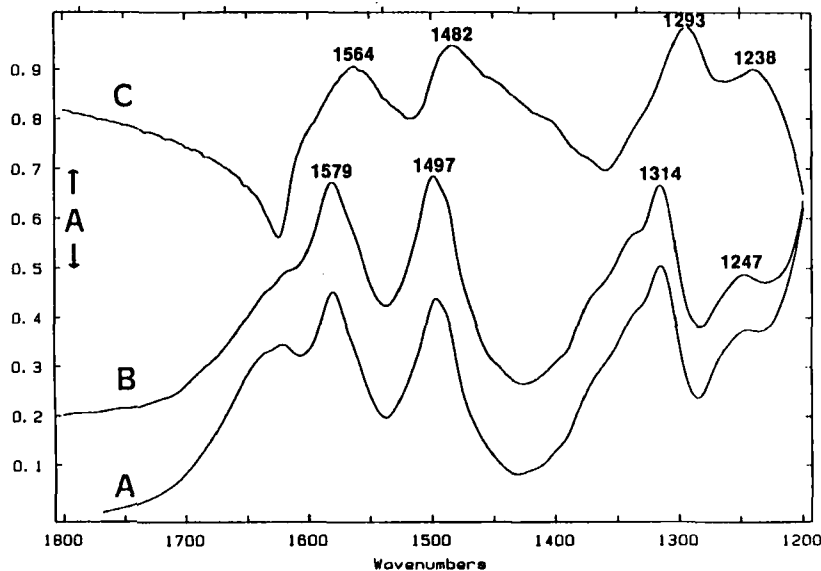

FIGURE 3   FTIR spectra of (A) sample NaY-AN-I, (B) H6Y-AN-I, and (C) bulk PANI oxidized with iodate

Reaction of intrazeolite PANI with Base Molecules

As discussed above, inclusion polymerization of aniline results in zeolite-encapsulated PANI. However, the unique porous nature of the zeolite host allows

chemical access to the polymer even after it has been synthesized. In particular, in the case of three-dimensional pore systems with appropriate channel cross-sections, polymer chains can be envisioned extending along one dimension, while other *molecules can diffuse accross the channel system and interact with the encapsulated polymer.* We have explored this possiblity in a number of doping/undoping experiments involving diffusion from the liquid and vapor phase.

Sample H6Y-AN-S was immersed in aqueous NH_4OH, at a ratio of total intrazeolite aniline to base of 1:1, and at a ten-fold excess of base. After 24 h at 295 K, the corresponding IR spectra (Figure 4.B) reveal significant changes of the polymer: The strong bands at 1581 cm^{-1} (assigned to the quinoid part of the polymer) and at 1313 cm^{-1} are strongly reduced, the peak at 1496 has moved to 1506 cm^{-1}, and new features at 1403s and ca. 1450sh cm^{-1} appear. The latter features are probably due to different ammonium species in the zeolite. The spectral changes of the intrazeolite polymer are all consistent with a deprotonation of the emeraldine salt. As in corresponding bulk experiments, the band at 1581 cm^{-1}, associated with quinone diimine radical cations, is reduced upon deprotonation and shifts to about 1590 cm^{-1} [17,18,22], while the band at about 1500 cm^{-1} moves to higher energy by about 10 cm^{-1}. The corresponding electronic absorption data show drastic spectral changes; the band at 850 nm is replaced by a new absorption at 570 nm (2.18 eV). Again these spectral changes correspond closely to those observed in bulk experiments[17,22]: Treatment of bulk PANI with aqueous NH_4OH results in the growth of an absorption near 2 eV, while that near 1.5 eV is reduced in intensity. The extent of the intrazeolite deprotonation reaction is a clear indication that the base has access to a large fraction of the protonated polymer. Attempts to simulate the bulk polymer *protonation with aqueous HCl* ($< 5 \times 10^{-3}$ M) were not successful; changes in zeolite framework vibrations indicate partial attack at the lattice.

Deprotonation of PANI in H6Y zeolite host is also possible with gaseous base molecules. A thin self-supporting, degassed wafer of sample H6Y-AN-S was equilibrated with 1 Torr of ammonia. As in the aqueous experiments, we observe a reduction of the band at 1583 cm^{-1} (and a shift to 1592 cm^{-1}; Figure 5), and a new broad absorption at 1457 cm^{-1} which is assigned to intrazeolite NH_4^+. It is remarkable that desorption of ammonia from the pore system is possible upon evacuation at about 350 K, and that the original spectrum of the protonated polymer is restored. This experiment demonstrates *reversible doping and undoping of PANI in the pore system of zeolite Y.* We note that the different basicity of the two bases should have a pronounced effect on the position of the intrazeolite equilibrium
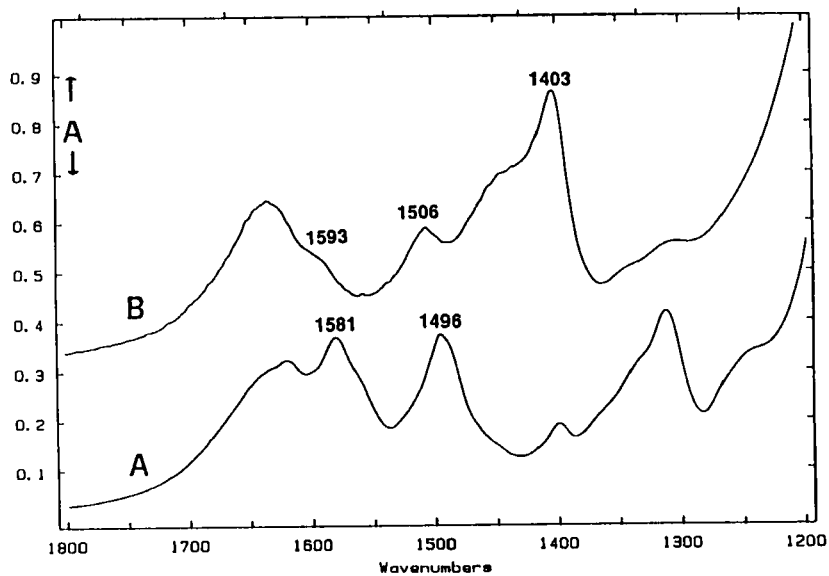
FIGURE 4   FTIR spectra of (A) sample H6Y-AN-S, and (B) the same sample deprotonated with NH_4OH at 1:1 stoichiometry.
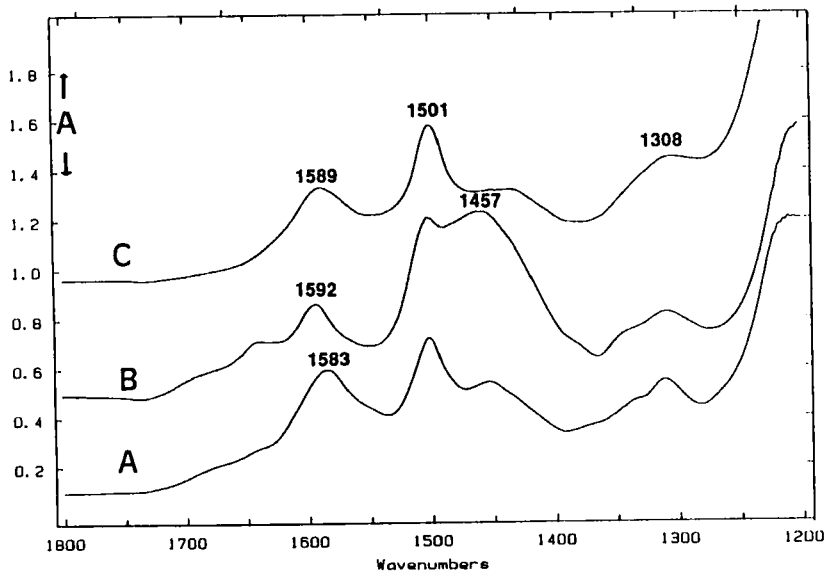

FIGURE 5   FTIR spectra of (A) sample H6Y-AN-S after degassing at 295 K in a vacuum IR cell, (B) the same sample exposed to 1 Torr of ammonia at 295 K, (C) sample B evacuated at 295 K.

PANI-H$^+$/H6Y + B   <--->   PANI/HB$^+$/H6Y   (B, base molecule).

In conclusion, this study shows that different oxidation conditions for the intrazeolite polymerization of aniline allow one to control the level of polymer purity, and the level of intrazeolite acidity required for reaction. Thus, utilizing iodate, polyaniline can even be polymerized in non-acidic zeolite hosts. The porosity of the zeolite enables deprotonation of the emeraldine salt with different bases, both in aqueous suspension and from the gas phase. The gas phase reaction with NH$_3$ is reversible.

The intrazeolite polymers presented in this report are members of a new family of "molecular wires" stabilized in dielectric hosts.

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