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POLY(2-ETHYLANILINE) IN ZEOLITE HOSTS: CONJUGATED NANOMETER SIZE FILAMENTS

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ABSTRACT

Poly(2-ethylaniline) chains were synthesized within the three-dimensional channels of dehydrated zeolites X and Y. The Na- and acidic forms of the zeolite hosts were loaded with the monomer from hexane solution, which was subsequently oxidized with aqueous $(NH_4)_2S_2O_8$. The steric demands for the polymerization are illustrated by the inability of the polymer to form in the one-dimensional channel system of mordenite. Since protons are not necessary for the polymerization to occur, the polymer is formed in the acid form of the zeolites as well as in the Na-forms. Polymerization occurs also at the outer surfaces of the zeolite crystals. The external polymer can be removed with chloroform after it was converted to the soluble base form. The intrazeolite polymer chain length peaks at about 0.1 μm (determined from gel permeation chromatography), and is substantially greater than that obtained in bulk polymerizations.

INTRODUCTION

If taken to the extreme, the design of 'molecular electronics' components such as interconnects, rectifiers, and storage functions seeks to utilize true molecular species.[1,2] Organic conducting polymers are promising candidates for this goal because they are low-dimensional with directional bonding, can principally be synthesized to desired lengths, and because they have adjustable conductivity.[3,4,5] It is of great interest to explore the physical properties, particularly the conductivity, of separated, ordered filaments of conducting polymers at nanometer dimensions.

Our research efforts have recently demonstrated the encapsulation of conjugated polymers such as polypyrrole, polyaniline and polythiophene in the crystalline channel systems[6] of zeolites.[7] Precursor monomers are introduced into the zeolite host and are subsequently polymerized by appropriate oxidants in the pore system. The synthesis of these and related systems represents an important step towards stabilized and oriented *"molecular wires"*, that could in principle allow to process signals or to store information inside channel systems with nanometer dimensions.

With the goal of achieving molecular alignment of conjugated polymer chains, several groups have designed routes to either synthesize the polymers in ordered systems, such as liquid crystals[8], or to encapsulate conjugated polymeric chains inside crystalline inorganic host materials by in-situ polymerization.

Polypyrrole and polythiophene fibers of only 30 nm in width have been grown electrochemically within microporous membranes, such as

Anopore alumina filtration membranes[9]. The higher conductivity of these fibers was associated with the high degree of orientation of the polymers along the fiber axis.

Pyrrole, thiophene, and aniline were intercalated and in-situ polymerized in the interlayer space of iron-oxychloride (FeOCl)[10] and vanadium oxide ($V_2O_5.nH_2O$)[11]. Polyaniline intercalates were also formed by polymerization of aniline in the galleries of Cu-exchanged fluorohectorite[12].

Pyrrole has been spontaneously oxidized and in-situ polymerized in 6.8 Å channels of the three-dimensional coordination polymer $[(Me_3Sn)_3Fe^{III}(CN)_6]_\infty$[13]. Methylacetylene gas reacts with the acid sites in zeolites L, Y, beta, ZSM-5, omega, mordenite, and SAPO-5 to form reactive, conjugated oligomers[14]. Short-chain oligomers of polythiophene were prepared, oxidatively doped to the conducting state and stabilized in Na-pentasil zeolites[15].

The electronic properties of the encapsulated single chains of conjugated polymers as a function of structure and interactions with the host are of particular interest. In the first physical study of spin and charge carriers in zeolite-encapsulated polypyrrole[16], we find that although the chains are fully oxidized and contain bipolaronic charge carriers, they do not exhibit significant a.c. conductivity at 1 GHz. This observation as well as the relatively large linewidth of the ESR signal can be explained with trapping of polarons and bipolarons by the periodic zeolite framework.

Polymer chain length is an important issue in the correlation of electronic properties of the encapsulated polymers with structure. It was therefore of interest to form conjugated polymers that are known to be soluble in the bulk, so that techniques such as gel permeation chromatography could be employed for the chain length determination. This article describes recent results on the intrazeolite synthesis of poly(2-ethylaniline), and initial chain length determinations of the resulting molecular filaments.

Polyaniline (PANI) is unique among the conducting polymers. Its conductivity depends mainly on two variables: a) the oxidation state of the polymer and b) the degree of protonation of the nitrogen atoms in the backbone[17]. The chemical oxidation of aniline in acidic aqueous solution yields the "emeraldine salt" form of bulk PANI as a dark blue-green precipitate[18]. It is believed to consist at a protonation level of 0.5 H^+/N of equal numbers of reduced, and oxidized, protonated quinone diimine repeat units.

PANI can also be formed upon 'doping' the corresponding 'emeraldine base' form of polyaniline with aqueous HCl. This results in a large increase in the number of unpaired spins[19], probably as diaminobenzene radical cations[20]. Protonation of PANI in the emeraldine oxidation state leads to a dramatic change in conductivity from 10^{-10} Scm^{-1} for the unprotonated polymer to ~5 Scm^{-1} when protonated.

Polyaniline is not completely soluble in common organic solvents because of the stiffness of its backbone. The incorporation of polar functional groups or long flexible alkyl chains in the polymer backbone is a common technique to prepare, respectively, water or organic solvent soluble polymers. This concept was successfully applied to polyaniline. Alkyl ring-substituted anilines, where the alkyl group is either methyl, ethyl or propyl, have been polymerized by chemical and electrochemical methods[21]. The chemical synthesis involves the oxidation of the substituted monomer with ammonium peroxodisulfate in acidic aqueous media, analogous to polyaniline.

As-synthesized polyaniline derivatives are insoluble in common organic solvents but become completely soluble in chloroform or tetrahydrofuran after deprotonation in 0.5M NH_4OH. Since one ortho position is blocked in 2-substituted anilines, a lower content of ortho couplings can be expected to lead to a more regular head-to-tail polymer structure and thereby, to higher polymerization yields. The conductivities of the alkyl ring-substituted polyanilines are lower than those of the parent polyaniline, by two orders of magnitude. This is consistent with a reduction of the π-conjugation of the alkyl derivatives caused primarily by steric effects[22]. The steric demands of the side chains will distort the planar arrangement that is most favorable for the conjugated system.

Chemically synthesized poly(2-ethylaniline) hydrochloride salt is a green powder. Its base form is blue. The salt form is believed to exist primarily as a polysemiquinone radical cation, similar to the parent polyaniline[24].

EXPERIMENTAL

The dehydrated Na- and acidic forms of the zeolite host were loaded with 2-ethylaniline from a hexane solution of the monomer. The intrazeolite 2-ethylaniline was oxidized with aqueous ammonium peroxodisulfate with stoichiometry oxidant : monomer = 1.5. This ratio was adopted from literature procedures[28].

The polymer was extracted from the host framework by dissolution of the zeolites with citric acid. Deprotonation of intrazeolite poly(2-ethylaniline) was performed by treating the sample with an aqueous solution of NH_4OH.

RESULTS AND DISCUSSION

The polymerization reaction as a function of host and oxidant. Table 1 summarizes the results of monomer loading and polymerization with different oxidants and hosts. It can be noticed that oxidation with peroxodisulfate yields polymer regardless of the proton concentration present in the zeolite. 2-ethylaniline is more easily oxidized than the unsubstituted aniline. The anodic peak potential for the oxidation of aniline appears at 0.8 V vs. standard calomel electrode (SCE), and for the oxidation of 2-ethylaniline the peak potential appears at 0.41 V vs. SCE[29]. The monomer can be polymerized in the bulk in the absence of protons. However, oxidation with other oxidants such as hydrogen peroxide solution, oxygen treatment at 100°C for 12 hours, or an acidic solution of iodate did not result in polymer formation. In the case of sample H_6Y-ETAN oxidized with H_2O_2, an orange product is obtained, apparently due to the formation of an azo compound analogous to azobenzene.

The zeolite/polymer adducts were treated with base solution, and rinsed thoroughly with chloroform, to remove any possible external polymer. All the zeolite powders remained blue after this treatment confirming that the base form of the polymer remained encapsulated within the zeolite channels. Although the chloroform solutions were blue, confirming the presence of some removable polymer, or oligomer chains, no attempts to quantify the amount of polymer present were made due to the extremely small amounts of material that was extracted.

2-Ethylaniline did not polymerize in mordenite even though a considerable amount of monomer was loaded into it (Table 1). Taking into account the ease with which the monomer polymerizes in the other hosts, it can be concluded that the one-dimensional framework of mordenite introduces steric restrictions and precludes polymerization due to geometric constraints.

Citric acid was used to dissolve the framework, since it is a much milder acid than HF, and is known to complex aluminate species in solution. Although it dissolves the framework, this process is very slow and involves successive extractions, which makes establishing a quantitative mass balance difficult.

Table 1: Intrazeolite Poly(2-ethylaniline) as a function of zeolite host and oxidant.

Sample	Monomers[a]	Oxidant	Product[b]
NaY-ETAN[c]	33 (46)	persulfate	+ blue
		iodate, H^+	- white[d]
H_6Y-ETAN[c]	27, 32[e] (46)	persulfate	+ blue
		iodate, H^+	- white[d]
		H_2O_2	- orange[f]
		O_2, 100°C	- white[d]
NaX-ETAN[c]	22 (35)	persulfate	+ blue
		iodate, H^+	- white[d]
$H_{35}Na_{53}X$-ETAN[c]	26 (35)	persulfate	+ blue
		iodate, H^+	- white[d]
H_8M-ETAN[c]	6.5 (8)	persulfate	- bluish
		H_2O_2	- white[d]
		O_2, 100°C	- white[d]

[a] Molecules of 2-ethylaniline adsorbed per unit cell of zeolite. Numbers in parentheses correspond to the amount of monomers offered in the loading solutions.

[b] Polymerization is observed (+) or not (-). [c] ETAN = 2-ethylaniline.

[d] White is the original color of the parent zeolite.

[e] Amount of loading can vary from batch to batch.

[f] Orange byproduct.

Spectroscopic characterization. The FTIR spectra of the zeolite/poly(2-ethylaniline) samples are shown in Figure 1. Band positions and their assignments are summarized in Table 2. The infrared spectra of sample H_6Y-ETAN and of the extracted polymer show bands similar to those of the bulk polymer. The band around 1598 cm^{-1} indicates probably the existence of quinone diimine species as in polyaniline[23]. The absorption at 1642 cm^{-1} is characteristic of zeolitic water. The spectra of other zeolite samples (Table 2) are very similar to that of H_6Y-ETAN.

The strong absorption starting at 1600 cm^{-1} and extending to the near-IR, attributed to the presence of free carriers in the bulk polymer, is not observable in the zeolite sample, and only slightly in the extracted intrazeolite polymer. These observations indicate a different doping level of the encapsulated chain.

The intensity of all the polymer bands in the zeolites spectra is diminished (by 30 %), by the treatment with an aqueous base solution and subsequent washing with chloroform. This indicates that poly(2-ethylaniline) was washed from the external crystal surfaces.

Table 2. FTIR spectra of the poly(2-ethylaniline) samples

H_6Y-ETAN[a] (cm^{-1})	Recovered PETAN[a] (cm^{-1})	PETAN bulk[a] (cm^{-1})	Assignment
2971	2966	2972	ν_{as} CH_3
2934	2933	2936	ν_{as} CH_2
2876	2873	2876	ν_s CH_3
1642			zeolitic H_2O
1593	1598	1594	quinoid
1500	1498	1504	benzenoid
1455	1457	1457	$-CH_2-C=C-$ δ_{as} CH_3
1404			byproduct[b]
1335	1345	1331	Phenyl-N (quinoid)

[a] ETAN = 2-ethylaniline, PETAN = poly(2-ethylaniline).

[b] Due probably to overoxidation of the aniline ring with peroxodisulfate.

The electronic absorption spectra of the zeolite/poly(2-ethylaniline) inclusion compounds (Figure 2) display features similar to those observed in polyaniline adducts. The band around 800 nm (1.55 eV) is attributed to the presence of radical cations, while that around

600 nm (2.1 eV) is assigned to quinone diimine moieties in the base polymer. Deprotonation with an aqueous solution of NH_4OH causes the disappearance of the radical cation bands and an increase of the base band, as expected. Subsequent washing with chloroform retrieves the peak around 800 nm of the polymer salt. Probably, the intrazeolite poly(2-ethylaniline) in the emeraldine salt form is inaccessible to the base since the zeolite crystals are covered with an external layer of polymer. The coating of base polymer is dissolved with chloroform, leaving behind only zeolite with encapsulated polymer.

Chain length determination. Figure 3 shows the molecular size distribution curves for poly(2-ethylaniline) bulk and the polymer extracted from H_6Y-ETAN, obtained from gel permeation chromatography (GPC) measurements with polystyrene standards. The distributions are bimodal. For poly(2-ethylaniline) bulk, the main fraction displays a molecular weight (relative to polystyrene) of 5000 as reported[29], and a minor fraction with a molecular weight of 63000. For the polymer extracted from the zeolite, this trend is inverted, with the main fraction corresponding to a molecular weight of 56000, and a smaller one with molecular weight of 320.

In order to determine accurate molecular weights with GPC, the calibration standard used should be of the same structure as the polymer of unknown molecular weight. Since poly(2-ethylaniline) does not have the same structure as polystyrene, a correction factor has to be taken into account. For polyaniline, a correction with a tetramer of aniline was suggested[24]. The ratio of the real molecular weight and the polystyrene-based GPC molecular weight of the tetramer is considered as a correction factor. As the conformations of polyaniline and poly(2-ethylaniline) are probably similar in a solution of THF, a correction with the same factor should provide a reasonable estimate for the chain lengths. The molecular weight of poly(2-ethylaniline) recovered from sample H_6Y-ETAN, obtained from the polystyrene calibration with the correction factor of 0.38[32], is 21280. This value corresponds to an extended polymer about 0.1 µm long. This is just about 10 times shorter than the average size of zeolite crystals utilized in this study. It can be concluded that the polymer extends throughout a substantial fraction of the crystals.

Correcting the GPC results with the same factor, a length of only 9 nm is obtained for the main fraction of the bulk polymer. The striking differences in molecular weight between the bulk polymer and the one extracted from the zeolite could be attributed to different mechanisms of polymerization in both media. One might envision that in the bulk there are many possibilities for radical encounters resulting in quenching of the polymerization. In the confined spaces of the zeolite channels, these encounters should be greatly reduced, and the polymer obtained in the zeolite can grow much longer.

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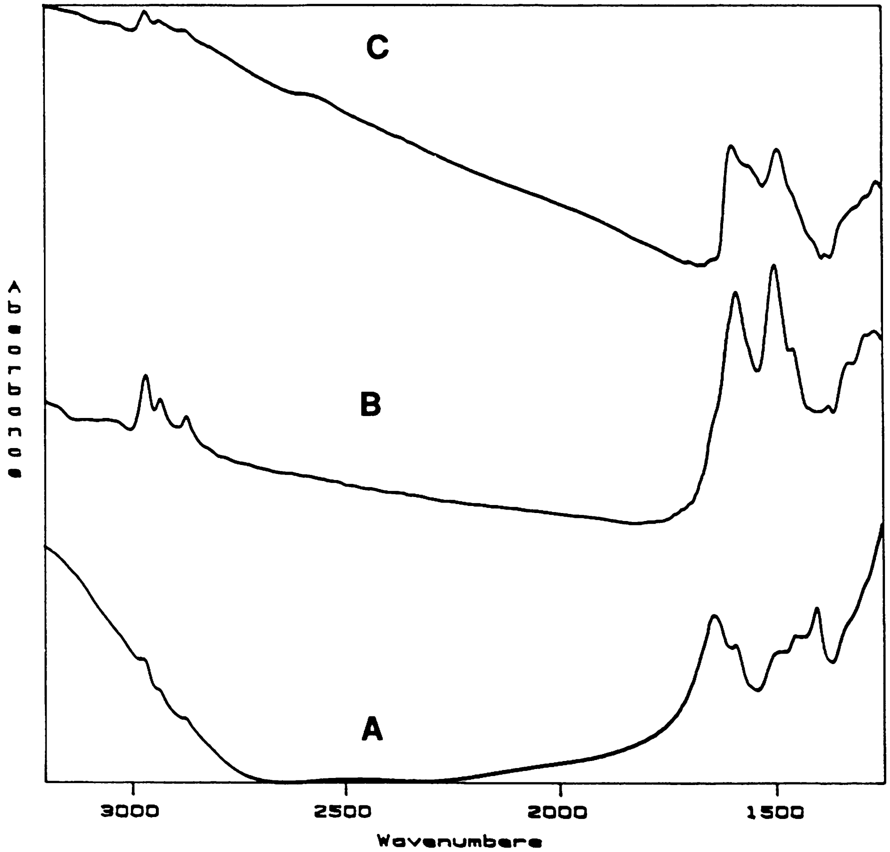

Figure 1. FTIR spectra of poly(2-ethylaniline) samples. A) H_6Y-ETAN, B) poly(2-ethylaniline) recovered from A, and C) poly(2-ethylaniline) bulk.

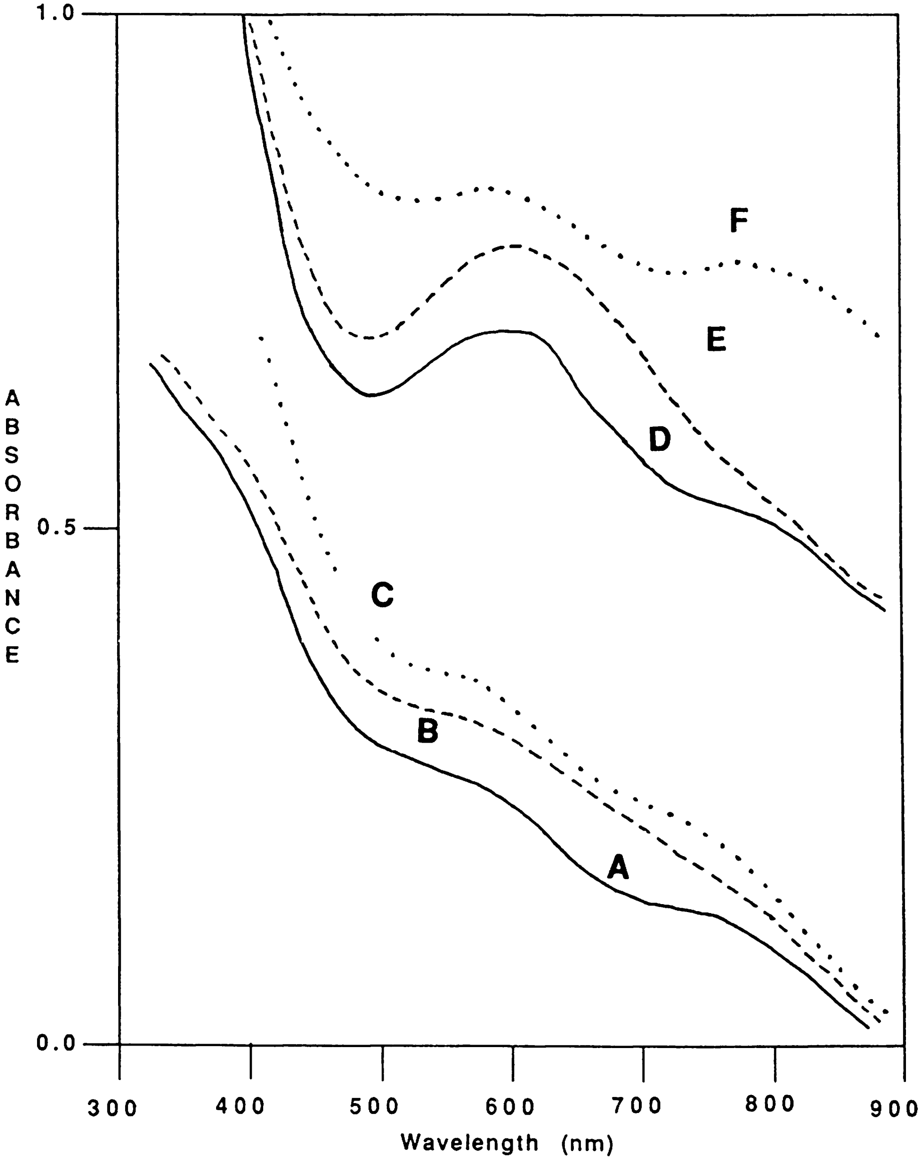

Figure 2. Electronic absorption spectra of zeolite/poly(2-ethylaniline) samples. A) NaY-ETAN, B) sample A + base, C) sample B washed with chloroform, D) H_6Y-ETAN, E) sample D + base, and F) sample E washed with chloroform.

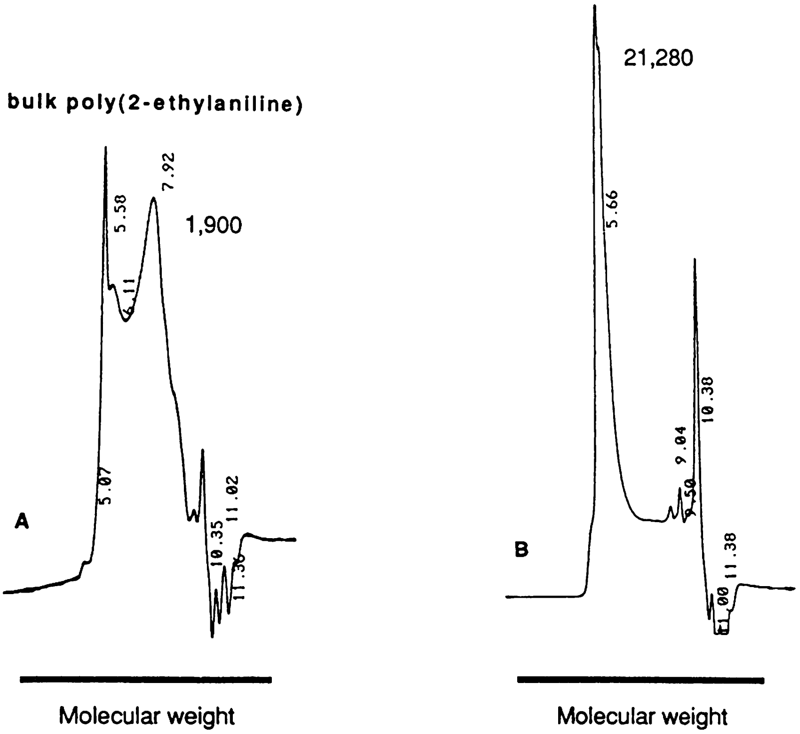

Figure 3. Molecular size distribution curves for poly(2-ethylaniline) samples. A) bulk poly(2-ethylaniline), and B) poly(2-ethylaniline) extracted from H_6Y-ETAN.