

Lower-Dimensional Systems and Molecular Electronics

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ENCAPSULATION OF CONDUCTING POLYMERS WITHIN ZEOLITES

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INTRODUCTION

A great deal of current research efforts are aimed at the design and understanding of conducting and semiconducting structures at sub-micrometer dimensions. The term 'molecular electronics' describes the ultimate reduction of electronic circuitry to the molecular level.¹ Beyond the development of concepts,² a major challenge in this area is to create isolated, addressable molecular units that function as useful electronic components. We study the *encapsulation of conducting polymers within the crystalline channel systems of zeolite hosts* as a promising approach to isolated, well-defined chains of molecular conductors. The molecular-size channels of these hosts limit the dimensions of the polymer chains to molecular dimensions. The conducting polymers polypyrrole and polythiophene have previously been studied in larger scale host structures such as layered FeOCl and V₂O₅.³ Polypyrrole fibrils with diameters between 0.03 and 1 μm at 10 μm length have been synthesized in Nucleopore membranes.⁴

Zeolites are open-framework aluminosilicates with pore sizes between 0.3 and 1.2 nm, and exchangeable cations compensating for the negative charge of the framework.^{5,6} Zeolite Y, mordenite (MOR) and zeolite A were used in this study (Figure 1). Zeolite Y is composed of interconnected "sodalite" cages, and mordenite features a twelve-ring channel system. Both structures have an open pore size of about 0.7 nm. The structure of zeolite A is based upon sodalite cages interconnected via double four-rings, with pore-openings of about 0.4 nm.

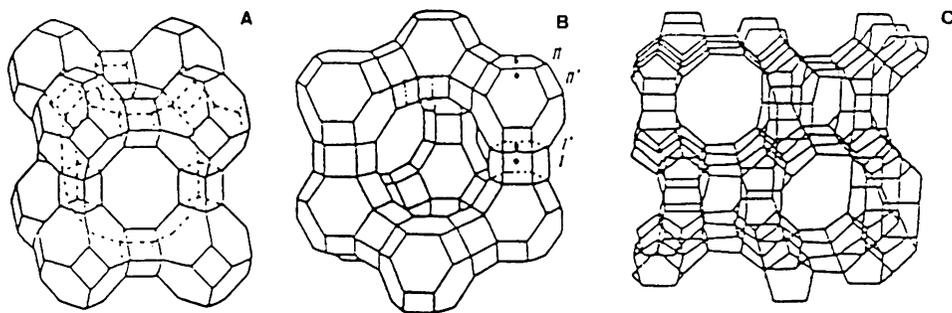


Figure 1. Zeolite structures. Three-dimensional channel systems of zeolite A (A), zeolite Y (B), and the pseudo one-dimensional channel system of mordenite (C).

Table 1. Composition of zeolite/polymer samples.

Samples	Aniline ^a PANI	Pyrrrole ^a PPy	Thiophene, 3MTh ^a PTh, P3MTh
Na ₅₆ Y	43/uc, orange ^b		
H ₄₆ Na ₁₀ Y	31/uc, deep blue		
Na ₈ MOR	5/uc, light orange ^b		
H ₈ MOR	3/uc, blue		
Na ₅₆ Y-V ^c		41/uc, white	37 and 31/uc, white
Na ₅₆ Y-H ^d		7/uc, white	white
Fe ₁₂ Na ₃₂ Y-V ^c		39/uc, dark turquoise	29 and 25/uc, dark turquoise
Cu ₁₅ Na ₂₆ Y-V ^c		50/uc, dark blue	35 and 32/uc, dark blue
Cu ₁₅ Na ₂₆ Y-H ^d		6.5/uc, dark blue	5.4 and 5.7, dark blue
Na ₈ MOR-V ^c		2/uc, white	2 and 2/uc, white
Na ₈ MOR-H ^d		1/uc, white	white
Fe ₃ Na ₂ MOR-V ^c		1/uc, turquoise	1 and 1/uc, grey-green
Cu _{2.5} Na ₃ MOR-V ^c		0.8/uc, blue-grey	1.5 and 1/uc, blue-grey
Cu _{2.5} Na ₃ MOR-H ^d		0.5/uc, blue	blue
Cu ₈ Na ₈₀ A-V ^c		0.3/uc, light blue	0.2/uc, light blue

a- Monomer loadings and color of the resultant products; uc = zeolite unit cell. The loading levels were determined gravimetrically (vapor loadings) or spectroscopically (solution experiments).

b- Unknown oxidation products, no polymer was detected.

c- Vapor phase loadings; samples were saturated with monomer vapor at 295 K.

d- Hexane solution loadings, adjusted to achieve approximately optimum reaction stoichiometries.

We recently succeeded in forming intrazeolite polyaniline (PANI)^{7,8}, polypyrrole (PPy)⁹, polythiophene (PTh) and poly(3-methylthiophene) (P3MTh)¹⁰ by oxidative polymerization inside the cavities of different zeolites, as demonstrated by vibrational, ESR, and electronic absorption data. It was observed that the dimensionality and pore size of the host determine the polymerization rates and intrazeolite products. This communication compares the above zeolite/polymer systems and discusses evidence for polymerization inside the host channel structures.

EXPERIMENTAL

Zeolite host materials were derived from the sodium and ammonium forms of zeolite Y (LZ-Y52, LZ-Y62; Alfa), Na-mordenite (MOR; LZ-M5; Union Carbide), and zeolite A (Alfa 5A). The ammonium form of MOR was obtained by refluxing Na-MOR two times in excess of 0.1 M NH₄Cl for 12 h. Cu(II) and Fe(II) ions were introduced into the zeolites via ion exchange with 0.1 M Cu(NO₃)₂ and 0.1 M FeSO₄, respectively. All zeolites were degassed in an oxygen stream followed by evacuation (620 K, 10⁻⁵ Torr). This treatment generates the acidic forms in the case of ammonium zeolites, and oxidizes the Fe(II) zeolites to Fe(III) zeolites, respectively. The resulting zeolite cation contents per unit cell are Na₅₆Y, H₄₆Na₁₀Y, Cu₁₅Na₂₆Y, Fe₁₂Na₃₂Y, Na₈MOR, H₈MOR, Cu_{2.5}Na₃MOR, Fe₃Na₂MOR, and Cu₈Na₈₀A. Intrazeolite PANI was synthesized in the acidic zeolite forms by analogy with the chemical polymerization of aniline in acidic solution.¹¹ Aniline was loaded into the degassed zeolites from hexane solution (Table 1) and subsequently reacted with an aqueous solution of (NH₄)₂S₂O₈ at a ratio of 4:1 intrazeolite aniline:oxidant. Intrazeolite Cu(II) and Fe(III) ions served as oxidants for the oxidative polymerization reaction of pyrrole¹² and thiophenes.¹³ Pyrrole, thiophene and 3-methylthiophene monomers were loaded into the degassed zeolites from either the vapor phase in small quartz reactors, or from zeolite suspensions in water and hexane (Table 1). Bulk polymers were synthesized according to published procedures.^{11,12,13}

RESULTS AND DISCUSSION

The monomer-loaded zeolite samples display dramatic color changes from white to different hues of blue and green when (a) aniline in different acidic zeolite forms is treated with the oxidant, or when (b) pyrrole or thiophene monomers are admitted into Cu(II)/Fe(III)-containing zeolites Y or MOR from the vapor phase or from hexane (or other hydrocarbon) solutions (Table 1). These color changes correspond to those observed in bulk synthesis reactions.¹¹⁻¹³ No reaction is observed with the zeolite sodium forms, indicating that the polymerizations proceed only in the presence of intrazeolite protons and/or appropriate oxidants. No polymer formation is detected in zeolite Cu(II)A (pore size 0.4 nm, smaller than pyrrole or thiophene). This is

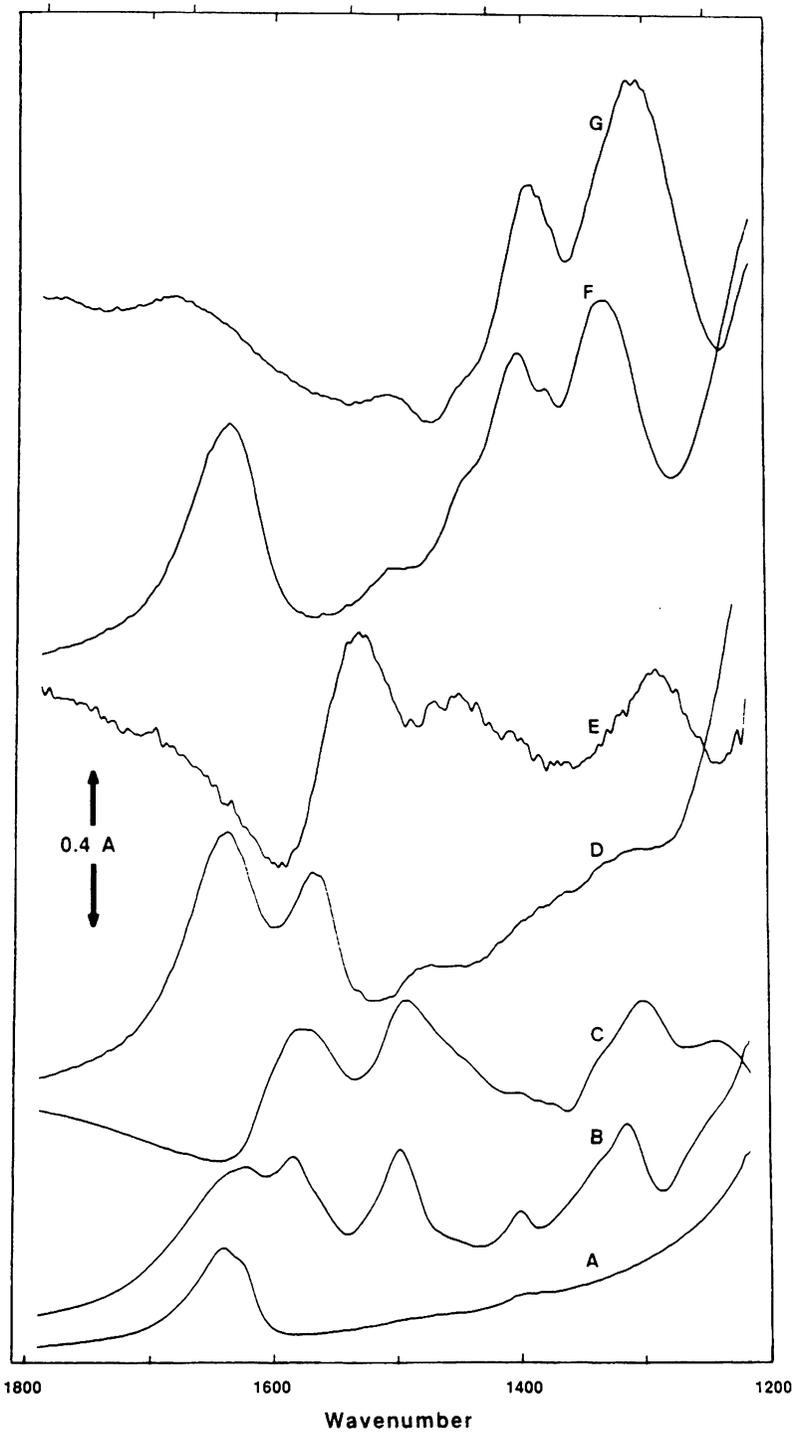


Figure 2. FTIR spectra of zeolites, conducting polymers, and zeolite/polymer adducts (KBr pellets, 4 cm^{-1} resolution). Na_{56}Y (A), $\text{H}_{46}\text{Na}_{10}\text{Y/PANI}$ (B), PANI (C), $\text{Fe}_{12}\text{Na}_{32}\text{Y-V/PPy}$ (D), PPy (E), $\text{Cu}_{15}\text{Na}_{26}\text{Y-V/P3MTh}$ (F), P3MTh (G). For sample names, see Table 1.

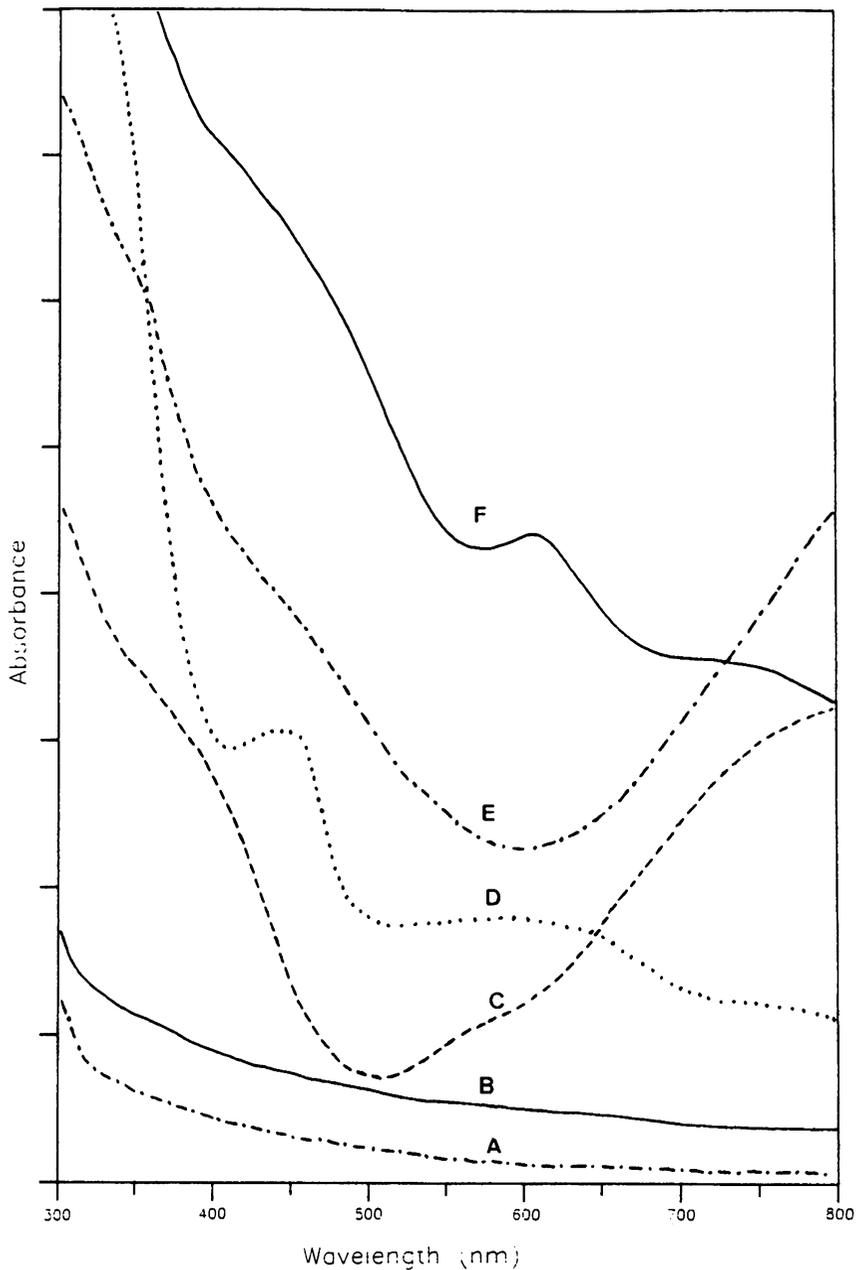


Figure 3. Electronic absorption spectra (samples dispersed in glycerol) of zeolites and zeolite/polymer adducts. Na_8MOR (A), Na_5Y (B), $\text{H}_4\text{Na}_{10}\text{Y/PANI}$ (C), $\text{Fe}_3\text{Na}_2\text{MOR-V/PPy}$ (D), $\text{Fe}_{12}\text{Na}_{32}\text{Y-V/PPy}$ (E), $\text{Cu}_{15}\text{Na}_{26}\text{Y-V/P3MTh}$ (F). For sample names, see Table 1.

consistent with the inability of the monomers to diffuse into the zeolite cavities where the majority of the oxidant ions are located. In contrast to trends observed in bulk synthesis reactions, polar solvents such as water do not favor the intrazeolite polymerization of pyrrole and thiophenes, probably because the intrazeolite metal ions are screened by the polar solvent molecules. Based upon the small surface capacity of the zeolite crystals relative to the total pore volume (ca. 0.2 monomer molecules per unit cell of zeolite Y, for 1 μm crystals), and the high monomer uptake (Table 1), it is evident that most of the monomer molecules will reside in the pore system of the zeolite host. Hence, it can be concluded that most of the polymer is also formed inside the zeolites. It should be noted that in the zeolite/PPy and PTh systems derived from vapor phase-saturated zeolites, the excess of monomer vs. oxidant ions will prevent 100% conversion to the polymer. However, since the monomers have no visible absorption and much smaller absorption coefficients in the IR than the polymers, no spectroscopic interference is expected. No deposition of polymer on the surface of the zeolite crystals was detected in scanning electron micrographs, while zeolite samples deliberately coated with polymer showed distinct bulk polymer features.

Intrazeolite polymers show mid-IR bands similar to those typical for the bulk polymers PANI¹⁴, PPy¹⁵, and P3MTh¹⁶, and a characteristic tail of the electronic excitation corresponding to free carrier absorption (Figure 2). Certain shifts are observed between IR frequencies of the bulk polymers and the zeolite/polymer adducts, suggesting some interaction of the polymer chains with the host. The intrazeolite polymers could be recovered by dissolution of the zeolite host with HF. IR spectra of the recovered products are comparable to those of chemically synthesized bulk materials.

The electronic absorption spectra of the zeolite/polymer samples (Figure 3) show absorption bands that are related to different electronic transitions in the bulk polymers. The zeolite/PANI samples display a weak band at 560 nm (2.2 eV) associated with quinone diimine structures of polymer at high oxidation levels. Shoulders at 400 nm (3.1 eV) and the broad features in the red (<1.8 eV) are associated with radical cations supporting *polarons* as charge carriers.¹⁷ The electronic spectra of intrazeolite polypyrrole are influenced by the nature of the zeolite host. The spectrum of sample Fe₁₂Na₃₂Y-V/PPy (Figure 3E) shows a shoulder at ca. 450 nm (2.7 eV) and at energies lower than 650 nm (1.9 eV). The red absorption of zeolite Y samples is generally stronger than that in mordenite. In addition, sample Fe₃Na₂MOR-V/PPy shows a feature between 520 and 700 nm (ca. 2 eV, Figure 3D). Absorption maxima at 2.3 and 0.7 eV have been observed with electrochemically formed, highly doped polypyrrole; the higher energy band shifted to lower values at lower oxidation levels.¹⁸ Thus, we assign the bands at 2.7, 2.0 eV and that in the near infrared to *bipolaron* absorptions typical for PPy at different oxidation levels, and conclude that the oxidation level of PPy in zeolite Y is high, while in MOR probably a bimodal distribution of PPy at high and intermediate oxidation levels is present. Intrazeolite PTh and P3MTh show bands at 450 nm (2.8 eV), 600 nm (2 eV) and absorption extending into the near infrared (< 1.7 eV, Figure 3F). Transitions at about 2.5 eV have been associated with interband excitations of neutral P3MTh¹⁹ which decrease in intensity with progressive oxidation. The additional bands at 2 eV and in the red/near IR are assigned to *bipolaron* transitions typical of intermediate oxidation levels (in bulk P3MTh: 1.6 and 0.6 eV). It would not be unexpected if the decoupled intrazeolite polymer chains had a different electronic structure (and band positions) than the corresponding bulk material. Additional bands, observed for some of the zeolite/polymer samples, can be attributed to different chain-lengths and/or oxidation levels of the constrained polymers in the zeolites channels.

ESR data of the intrazeolite PANI show the presence of ca. 0.0025 Curie-type spins per aniline loaded (comparable to bulk spin densities if the lower polymer content in the zeolites is considered), with g-values (g=2.0034) similar to bulk polymers.²⁰ ESR spectra of intrazeolite PPy confirm the low spin count expected for bipolaron formation and g-values (2.0027) characteristic of polypyrrole.²¹ Large linewidths in both cases (8-10 G) could indicate strong dipolar interactions with the zeolite host.

No bulk conductivity is observed in pressed wafers of the zeolite/polymer samples (detection limit: 10^{-8} S/cm). However, pressed pellets of zeolite samples deliberately coated with a thin film of polymer show conductivities of about 10^{-6} S/cm, compared to 1-10 S/cm for bulk polymers. The products recovered after dissolution of the zeolite/polymer adducts in HF have conductivities at the order of 0.001 S/cm. These observations indicate that the polymers do not coat the zeolite crystals and that the intrazeolite polymer chains are probably decoupled from each other.

The location of the polymer phase is further illustrated by the polymerization rates in the zeolite hosts which are orders of magnitude slower than in bulk chemical solution syntheses (no reaction in A, MOR < Y << solution). The oxidant and/or the monomers have to diffuse into the channels of the zeolites in order to reach the intrazeolite reaction partners. These diffusion and pore volume limitations would not have been observed if the polymers had only formed on the crystal surfaces.

CONCLUSION

We have demonstrated that oxidative polymerization reactions leading to conducting polymers can be carried out within the channel systems of zeolites. Acidic zeolite forms are required to synthesize intrazeolite polyaniline by analogy to the oxidative coupling of aniline in acidic solutions. The presence of intrazeolite oxidants such as Cu(II) and Fe(III) ions is fundamental for the polymerization of pyrrole, thiophene and 3-methylthiophene. The degree of polymer chain oxidation and probably the chain lengths are influenced by the dimensionality of the zeolite channels.

This is the first approach towards the encapsulation and stabilization of *molecular wires* in well-defined hosts of molecular dimensions.

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