

**POLYTHIOPHENES AND OLIGOTHIOPHENES IN ZEOLITE HOSTS:
CONJUGATED NANOMETER SIZE FILAMENTS**

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ABSTRACT

The polymerization of different thiophenes in the channels of molecular sieve zeolite hosts is described. Thiophene, 3-methylthiophene, 2,2'-bithiophene, and terthiophene were introduced into dehydrated proton-, Cu(II)- or Fe(III)-containing zeolites (NaY and Na-mordenite) from organic solvents or vapor-phase. In the large-pore hosts, green-black products are formed from the monomers within several minutes. Spectroscopic characterization (IR, UV-NIR) confirms the formation of oxidized polymer chains in the zeolite channels. UV-Near IR reflectance spectra of the zeolite/polythiophene samples exhibit a broad absorption from 500 to about 2500 nm as the bulk and not the resolved spectra of short oligomers, thus fairly long polymer chains are formed in the zeolites. Conducting polymers can be recovered after dissolution of the zeolite host in HF. 2, 2'-bithiophene and a-terthiophene in acidic H₂Y and H₆Y zeolites (2 and 6 protons per super cage/ β -cage) yield yellow-green and purple products, respectively. UV-NIR reflectance data indicate that the acidic zeolite hosts oxidize the thiophene oligomers to yield stable radical cations and dications in their channel systems.

INTRODUCTION

Work in this laboratory has recently demonstrated the encapsulation of conjugated polymers¹ such as polypyrrole, polyaniline and polythiophene in the crystalline channel systems of large-pore zeolites.² Precursor monomers are introduced into the zeolite host and are subsequently polymerized by appropriate oxidants in the pore system. The related growth of polymer fibers in membranes,³ and intercalation of pyrrole in layered vanadium oxide⁴ have recently been explored. Methylacetylene gas was found to react with the acid sites in zeolites L, Y, beta, ZSM-5, omega, mordenite, and SAPO-5 to form reactive, conjugated oligomers⁵. Short-chain oligomers of polythiophene were prepared in Na-pentasil zeolites⁶.

The present article addresses the polymerization of different thiophenes and the question of the active site in the formation of oligothiophene species in large-pore zeolites. Spectroscopic

measurements show that the presence of Bronsted and probably related Lewis acidity is essential for the formation of the same oligothiophene species as observed by Caspar et al. in ZSM-5.⁶

In the chemical synthesis of polythiophene (PTh)^{7,8}, the direct oxidation of the monomers with $\text{Fe}(\text{ClO}_4)_3$ or $\text{Cu}(\text{ClO}_4)_2$, produces the corresponding doped polymers. The polymerization reaction involves removal of 2.25 to 2.50 electrons per molecule of thiophene. The resulting polymer is produced in the oxidized state with 0.25 to 0.50 positive charges per thiophene unit, depending on the synthesis conditions.

EXPERIMENTAL

The zeolites NaY (LZY-52), NH_4Y (LZY-62), and Na-mordenite (LZ-M5) were generously donated by the Union Carbide Corporation. Zeolite A (5A) was obtained from Alfa. The zeolites were dehydrated in a flow of oxygen (1 °C/min to 100 °C, 10 h at 100 °C, and 8 h at 400 °C (4 h under vacuum)). Fe^{III} and Cu^{II} zeolites were prepared according to conventional ion-exchange and oxidation techniques⁹. The resulting zeolite unit cell compositions are: $\text{Cu}^{\text{II}}\text{Y}$: $\text{Cu}_{15}\text{Na}_{26}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$, $\text{Fe}^{\text{III}}\text{Y}$: $\text{Fe}_{12}\text{Na}_{32}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$, $\text{Cu}^{\text{II}}\text{M}$: $\text{Cu}_{2.5}\text{Na}_3(\text{AlO}_2)_8(\text{SiO}_2)_{40}$, $\text{Cu}^{\text{II}}\text{A}$: $\text{Cu}_8\text{Na}_{80}(\text{AlO}_2)_{96}(\text{SiO}_2)_{192}$.

2,2'-Bithiophene (BTh) and terthiophene (TTh) were introduced into the zeolites from a hexane solution. The zeolites used were NaY, H_2Y , H_6Y (2 and 6 protons per supercage/ β -cage), and $\text{Fe}^{\text{III}}\text{Y}$. Typically, 0.5 g of zeolite was mixed with 20 ml of hexane containing 0.01 g of the oligomer (0.06 mmol 2,2'-bithiophene, or 0.04 mmol terthiophene), stirred for 12 hours, washed with an excess of hexane, and dried under nitrogen. The other monomers were introduced into the zeolites from solutions in water, chloroform, acetonitrile, hexane, toluene, or from the vapor-phase. Bulk-like polymers could be recovered from the zeolites after dissolution of the framework with a 25% aqueous solution of HF. Polythiophene and poly(3-methylthiophene) are not attacked in acidic media¹⁴. Additionally, a blank experiment shows that the monomers do not polymerize after exposure to acids for 24 hours. Bulk polymers were prepared chemically by oxidative polymerization with $\text{Fe}(\text{ClO}_4)_3$ in MeCN.

RESULTS AND DISCUSSION

Intrazeolite polymerization.

On admitting thiophene monomers into the Fe^{III} or Cu^{II} forms of zeolites Y or mordenite from the vapor phase or from hexane and toluene solutions (Table 1), the colors of the resultant adducts change slowly (within 30-120 min) from white to different shades of blue or dark green. These color changes correspond to those observed in bulk polymerization. Thiophene monomers in zeolite containing only sodium ions do not react to form polymers. No polymer formation is observed with $\text{Cu}^{\text{II}}\text{A}$, with a pore size of 4.1 Å, which is too small for the thiophene monomers. The monomers have a kinetic diameter of approximately 6 Å and can not diffuse into the zeolite cavities, where the majority of the oxidant ions are located. In contrast to trends observed in the bulk polymerization reactions, polar solvents such as water, acetonitrile, and chloroform do not favor the intrazeolite polymerization of thiophene and 3-methylthiophene. The intrazeolite metal

ions are probably screened by the polar solvent molecules. From the estimated surface capacity of the zeolite crystals, 0.2 molecules per unit cell of zeolite Y (based on 1 μm crystals), and the observed monomer loadings (Table 1), it can be concluded that most of the monomer molecules are introduced into the pore system of the zeolite host. Scanning electron micrographs indicate no evidence of polymer covering the surfaces of zeolite/polymer crystals. The above observations demonstrate that the polythiophene chains form within the zeolite pore systems.

Table 1: Zeolite/thiophene and 3-methylthiophene samples

Sample	Monomer loaded per unit cell		Product color
	Th ^a	3MTh ^a	
NaY--V	37	30.5	white
NaY--H	5.6 (6.5)*	5.6 (6.5)*	white
Cu ^{II} Y--V	35	32	dark blue
Cu ^{II} Y--W	5.6 (6.5)*	5.6 (6.5)*	white
Cu ^{II} Y--H	5.4 (6.5)*	5.7 (6.5)*	dark blue
Fe ^{III} Y--V	29	25	dark green
NaM--V	2	2	white
NaM--H	1 (1)*	1 (1)*	white
Cu ^{II} M--V	1.5	1	blue-grey
Cu ^{II} M--W	1 (1)*	1 (1)*	white
Cu ^{II} M--H	1 (1)*	1 (1)*	blue
Fe ^{II} M--V	1	1	grey-green
Cu ^{II} A--V		0.2	light blue

^a Abbreviations: Y, zeolite Y; M, mordenite; Th, thiophene; 3MTh, 3-methylthiophene; V, vapor; H, hexane (similar with toluene); and W, water (similar with acetonitrile, chloroform).
* The numbers in parentheses correspond to the amount of monomers dosed from solution to achieve 2.3:1 oxidant to monomer stoichiometry.

After dissolution of the framework (Cu^{II}Y-3MTh-V) with an aqueous solution of HF, a black powder is obtained with a 16 % yield, based on the amount of monomer loaded into the zeolite. In the case of Cu^{II}Y-3MTh-V, this value corresponds to 5 molecules of 3-methylthiophene reacted per unit cell of zeolite, which corresponds well to the 2.3 to 1 ratio of oxidant to monomer necessary for oxidative polymerization.

Spectroscopic characterization

The IR spectra of Fe^{III}Y-3MTh-V and of Cu^{II}Y-3MTh-V^{2b} show typical vibrations of poly(3-methylthiophene)^{10,11}. The weak band at 1506 cm^{-1} is assigned to aromatic C=C stretching vibrations, and two strong bands around 1400, and 1331 cm^{-1} are related to the heterocycle C-N stretching vibrations (Figure 1). The presence of the intense, fairly broad bands at 1400 and 1331 cm^{-1} indicates that the polymer chains are in the oxidized form. At higher energy (not shown), the spectra also exhibit a characteristic tail of the electronic transition correlated with the presence of free carriers in highly conducting polythiophenes¹². The IR spectra of the black

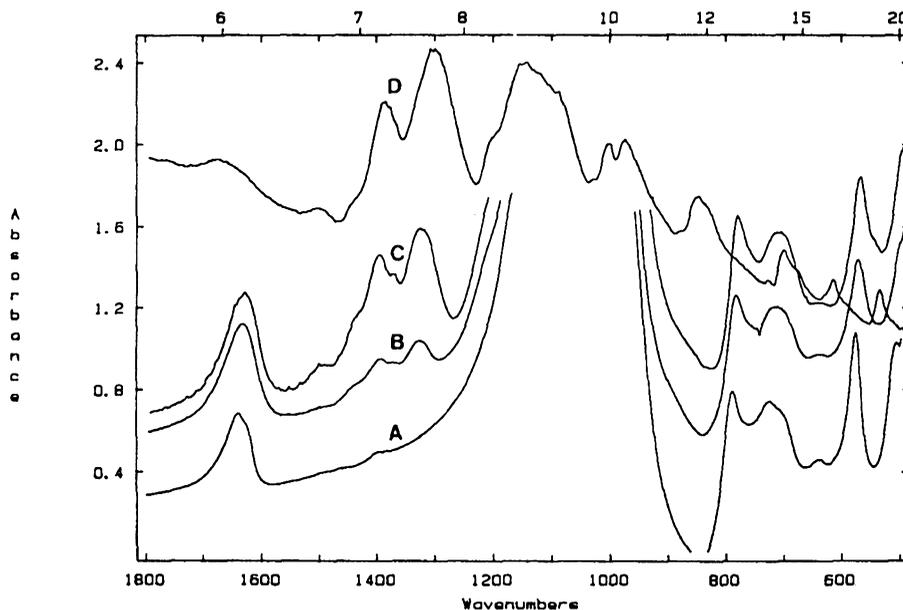


Figure 1. FTIR spectra of poly(3-methylthiophene) samples. (A) NaY, (B) Fe^{III}Y-3MTh-V, (C) Cu^{II}Y-3MTh-V, and (D) bulk poly(3-methylthiophene).

agglomerated products extracted from the zeolites and those of the zeolite/polythiophene samples are comparable to the IR spectra of chemically synthesized bulk materials.

Neutral poly(3-methylthiophene) (and polythiophene) films formed electrochemically show absorption in the visible region at about 2.5 eV, associated with the $\pi \rightarrow \pi^*$ transition of long conjugated polymer chains^{13,14}. When the bulk polymer is oxidized, two intra-gap absorptions associated with bipolarons develop at about 0.65 and 1.6 eV. With progressive oxidation, the 2.5 eV absorption decreases in intensity. A representative zeolite sample, Cu^{II}Y-Th-V, shows corresponding features at about 440 nm (ca. 2.8 eV), 670 nm (1.9 eV), and a broad absorption between ca. 1.4 and 0.25 eV (see also Figure 2C). Similar features are observed with the Fe^{III}-containing hosts and with 3MPTh-loaded zeolites. If the NIR absorption of these samples is compared with data for thiophene nonamers (9²⁺)⁶, it can be concluded that the intrazeolite polymer chains should be much longer than 10 units.

The ESR spectra of the Cu^{II}-PTh samples show signals at $g=2.0027$. This value is typical of a delocalized carbon-based radical¹⁵. The signals are rather broad, with bandwidths greater than 6 Gauss, characteristic of localized radical spins and an indication of interaction of the encapsulated polymer with the zeolite hosts. The presence of only about 2.0×10^{-3} spins per monomer is consistent with the existence of bipolarons as charge carriers. Pressed zeolite/polymer pellets show no significant 'bulk' conductivity, with $s < 10^{-8} \text{ Scm}^{-1}$. Therefore, there is no significant deposition of polymer on the external crystal surfaces. Agglomerated P3MTh recovered from Cu^{II}Y-3MTh-V after dissolution of the host shows a conductivity of about

0.01 Scm^{-1} . This value is close to that obtained for poly(3-methylthiophene) synthesized by chemical methods.

Stabilization of thiophene oligomers within zeolites

An important issue in intercalative polymerization relates to reactant delivery and to the polymerization mechanism. In a recent study, thiophene oligomers were formed within the channels of zeolite beta and Na-ZSM-5⁶. Charged short-chain oligomers are inherently reactive species, and in the particular case of polythiophene, oxidized oligomers are unstable with respect to further oligomerization in solution. Thus, the zeolite is an excellent matrix to stabilize them. One of the questions that the above study did not address relates to the nature of the reactive sites and the reaction mechanism in the zeolite, since the oligomers were formed without any traditional oxidant, such as ferric or cupric ions.

A related polyheterocycle, polypyrrole, is known to form in the presence of protonic acids¹⁶. Accordingly, one might assume that the formation of polythiophene could proceed through the same mechanism as in polypyrrole. We propose that the presence of (probably Lewis) acid centers in the zeolite is responsible for the formation of the thiophene oligomers. Short oligomers of thiophene (Th), bithiophene (BTh) and terthiophene (TTh) were loaded from hexane into the proton-containing and Fe^{III} forms of zeolite Y. Different concentrations of protons per unit cell of zeolite Y, H₁₆Na₄₀Y (H₂Y) and H₄₈Na₈Y (H₆Y) were used to study the effect of proton stoichiometry on the products formed. After a few minutes a change in color was noticeable in the zeolites, but to drive the reaction to completion, it was continued for 12 hours. NaY-monomer adducts produced only minor but detectable spectral changes.

H₂Y and H₆Y zeolites loaded with bithiophene yield a yellow-green complex. The same zeolites loaded with terthiophene produce an intense purple complex. These colors are very different from the green-black color obtained when thiophene, bithiophene, or terthiophene were loaded in Fe^{III}Y, where polymerization to polythiophene takes place. The main features of the UV/VIS/NIR reflectance spectra (Figure 2) and their assignments to different oligomer cations according to ref. [6] are summarized in Table 3. Because formation of the dry zeolite proton forms by heating under vacuum is usually accompanied by some dealumination, it is reasonable to assume a correlation between proton content and reactivity of the zeolite for oligomerization. However, treatment of similar colored samples with ammonia in a related study¹⁷ resulted in bleaching, which could indicate deprotonation of the intrazeolite species. Further work is required to clarify the nature of the reactive sites for thiophene oligomerization.

The strong bands at about 308 nm for the bithiophene loaded zeolites and at 360 nm for the terthiophene loaded zeolites correspond to the band gap transition in the neutral oligomer⁶. In the spectra of NaY zeolites loaded with these monomers, the above bands are dominant. Distinctive bands at lower energies, only present in the acid zeolites, are tentatively assigned to radical cations and dications typical of the thiophene oligomers. Bithiophene can form a stable radical cation, 2^{+•}, in acid zeolites as shown by the band at 408 nm.

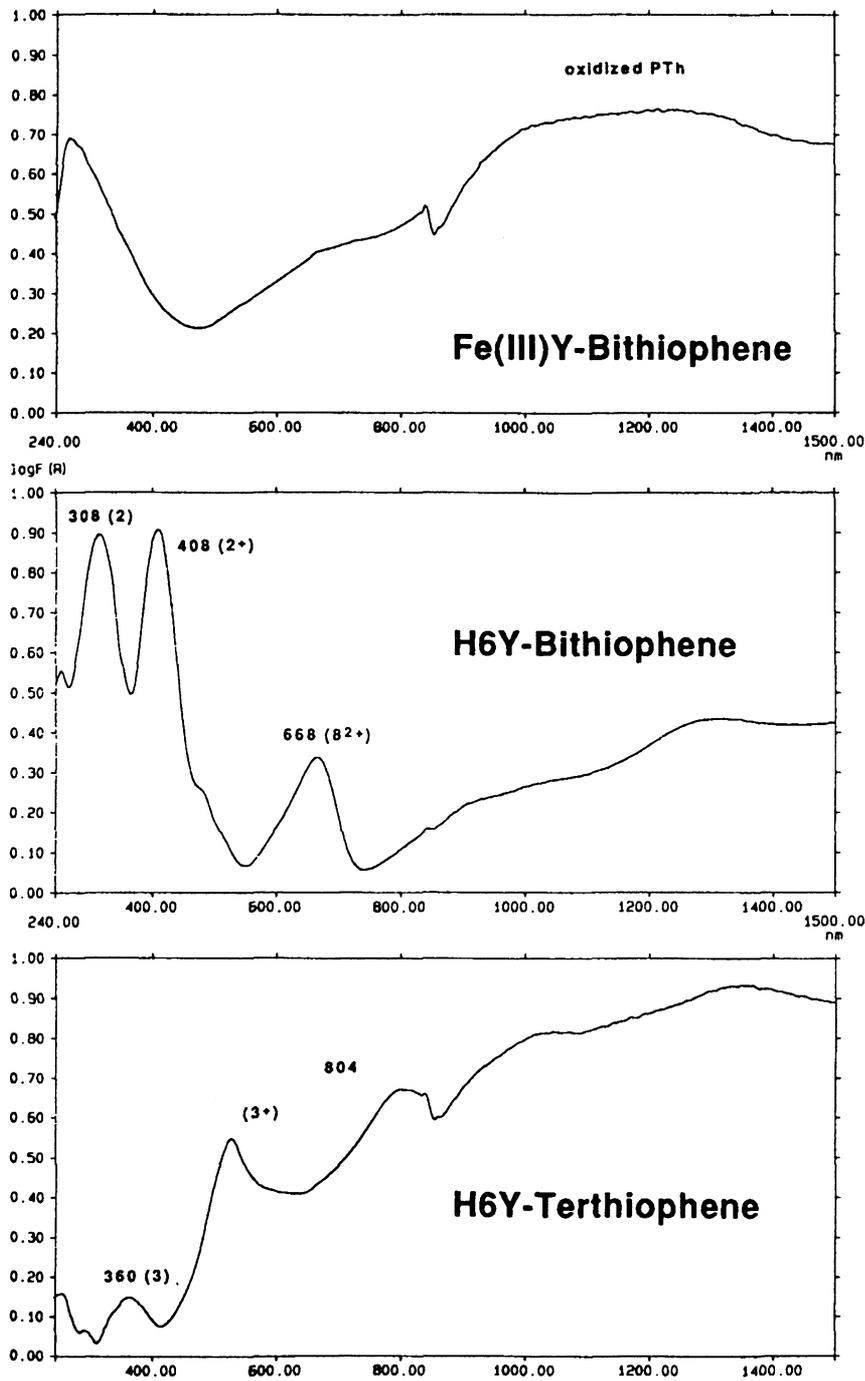


Figure 2. Electronic reflectance spectra of thiophene oligomers in acid zeolites. The feature at 850 nm is an artifact due to change of detectors.

Table 3: UV/VIS/NIR bands for thiophene oligomers in zeolite Y^a

Sample	Band Positions (nm) and Assignments (after reference 6, in parentheses)			
Fe ^{III} Y-Th-H		470sh		broad NIR band
		π - π^* in neutral PTH		oxidized PTH
NaY-BTh-H	308s	402sh	678w	
	2(300)	2 ^{o+} (407)	8 ²⁺ (661)	
H ₂ Y-BTh-H	308s	408s	668s	1274 broad
	2	2 ^{o+}	8 ²⁺	8 ²⁺ ... (1383)
H ₆ Y-BTh-H	308s	408s	668s	1300 broad
	2	2 ^{o+}	8 ²⁺	8 ²⁺ ...
Fe ^{III} Y-BTh-H				broad NIR band
				oxidized PTH
NaY-TTh-H	370s	528sh		
	3(354)	3 ^{o+} (522)		
H ₂ Y-TTh-H	360s	532s	788s	broad NIR band
	3	3 ^{o+}	6 ^{o+} (775)	oxidized PTH
H ₆ Y-TTh-H	360s	528s	804s	1024 + broad NIR
	3	3 ^{o+}	6 ^{o+} or 3 ²⁺ (833)	6 ²⁺ +ox. PTH
Fe ^{III} Y-TTh-H				broad NIR band
				oxidized PTH

^a 2, neutral bithiophene; 2⁺, bithiophene radical cation; 3, neutral terthiophene; 3⁺, terthiophene radical cation; 6⁺, hexathiophene radical cation; 6²⁺, hexathiophene dication; 8²⁺, octathiophene dication. H, hexane; sh, shoulder; s, strong; and w, weak.

Additionally, two bands at 668 nm and at about 1300 nm, assigned to the octamer dication 8²⁺, are present in the spectra (Figure 2, B). For terthiophene, a band at 528 nm assigned to the radical cation 3⁺, and a band around 800 nm related to the hexamer 6⁺ are observed (Figure 2, A). The spectra of Fe^{III}Y-BTh and Fe^{III}Y-TTh are very similar to the spectrum of Fe^{III}Y-Th, in which the main spectral characteristic is a broad absorption band extending into the near-IR, assigned to the oxidized form of polythiophene (Figure 2, C). It is important to note that the spectra of the adducts in acid zeolite show also the broad near IR absorption typical for the polymer, which indicates the concomitant formation of oligomers and polymers in the zeolites.

The distinctive bands related to radical cations and dications of short oligomers of thiophene in zeolites are only observed in the acidic zeolites. These results can also explain the formation of the same species in Na-ZSM-5 since this zeolite can contain a small amount of protons and/or Lewis acidity as well. The different reactivity of the thiophene species in acidic vs. Fe^{III} zeolite forms may be related to the different channel densities and/or oxidation potential of the reactive sites in these systems. If a strong oxidant ion is present in the zeolite at high concentration, such as Fe^{III}, the oxidation is driven to completion forming oxidized polymers.

CONCLUSIONS

This study demonstrates that it is possible to polymerize thiophene, 3-methylthiophene, and small oligomers within the channel systems of zeolites, analogous to the oxidative coupling of thiophene and 3-methylthiophene in solution in the presence of Cu^{II} and Fe^{III} oxidants.

Oligomerization and polymerization reactions proceed to different degrees in acidic and oxidant-containing zeolites.

ACKNOWLEDGEMENTS

The authors thank Dr. Francois Beuneu (Ecole Polytechnique, Paris) for taking the ESR spectra. Partial funding for this work from Sprague Electric Company is appreciated.

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