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SYNTHESIS OF OLIGO- AND POLYTHIOPHENES IN ZEOLITE HOSTS

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ABSTRACT

Oligomers and polymers of thiophene derivatives were synthesized in the channels of zeolite Y and mordenite. Intrazeolite oxidation of monomers such as thiophene, 3-methylthiophene, and bithiophene by Fe(III) or Cu(II) ions results in formation of insoluble polymers that have spectroscopic properties similar to the corresponding bulk polymers. The zeolites containing the polymers are nonconducting, but when extracted from the host, the polymers show d.c. conductivities typical for the bulk materials. Oligothiophene species with well-defined electronic transitions could be produced in acidic zeolite Y.

INTRODUCTION

The synthesis of molecule-based conducting materials has attracted growing interest due to their potential for applications in microelectronics and electrical components such as batteries.[1] Work in this laboratory has recently demonstrated the encapsulation of conjugated polymers 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.

Other inclusion techniques, e.g., growth of polymer fibers in membranes,[3] and intercalation of pyrrole in layered vanadium oxide[4] 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 oligomers[5]. Short-chain oligomers of polythiophene were prepared in Na-pentasil zeolites[6]. In the latter study it was found that the presence of aluminum in the zeolite framework is essential for oxidation, but the cause for the formation of the cationic species remained unresolved.

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 sites 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 $Fe(ClO_4)_3$ or $Cu(ClO_4)_2$, 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.

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EXPERIMENTAL

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 techniques[9]. The resulting zeolite unit cell compositions are: $Cu^{II}Y$: $Cu_{15}Na_{26}(AlO_2)_{56}(SiO_2)_{136}$, $Fe^{III}Y$: $Fe_{12}Na_{32}(AlO_2)_{56}(SiO_2)_{136}$, $Cu^{II}M$: $Cu_{2.5}Na_3(AlO_2)_8(SiO_2)_{40}$, $Cu^{II}A$: $Cu_8Na_{80}(AlO_2)_{96}(SiO_2)_{192}$.

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/ß-cage), and $Fe^{III}Y$. 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 media[14]. 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 $Fe(ClO_4)_3$ in MeCN.

RESULTS AND DISCUSSION

Intrazeolite polymerization. If thiophene monomers are admitted 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, due to the absence of oxidation centers.

No polymer formation is observed with $Cu^{II}A$, 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. Pyrolysis mass spectrometry detects considerably less monomer evolution from the zeolite/polymer samples than from those containing unreacted monomers in the Na-forms, as expected if polymerization has taken place. The above observations demonstrate that the polythiophene chains form within the zeolite pore systems.

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.

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.

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 polythiophenes[12]. The IR spectra of the black 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 $(9^{2+})^6$, it can be concluded that the intrazeolite polymer chains should be much longer than 10 units.

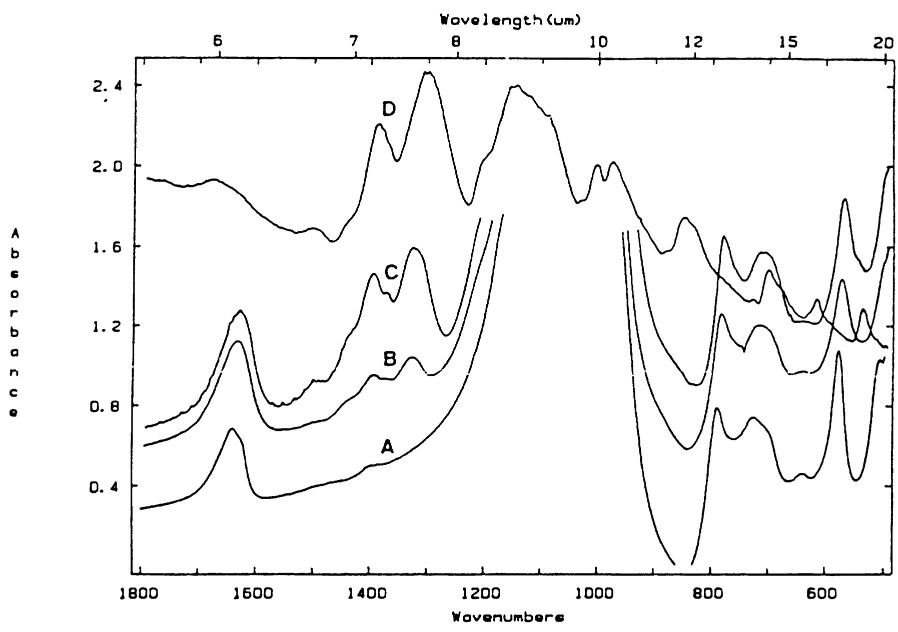

Figure 1. FTIR spectra of poly(3-methylthiophene) samples. (A) NaY, (B) Fe^{III}Y-3MTh-V, (C) Cu^{II}Y-3MTh-V, and (D) bulk poly(3-methylthiophene).

The ESR spectra of the Cu^{II}-PTh samples present signals at g=2.0027. This value is typical of a delocalized carbon-based radical[15]. 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 $\sigma < 10^{-8}$ 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. In a recent study, thiophene oligomers were formed within the channels of zeolite beta and Na-ZSM-5[6]. 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 acids[16]. Accordingly, one might assume that the formation of polythiophene could proceed through the same mechanism as in polypyrrole. We propose that the presence of acid groups in the zeolite is responsible for the formation of the thiophene oligomers. To test this assumption, short oligomers of thiophene (Th), bithiophene (BTh) and terthiophene (TTh), were loaded from hexane into the acid and Fe^{III} forms of zeolite Y. Different concentrations of protons per unit cell of zeolite Y, $H_{16}Na_{40}Y$ (H_2Y) and $H_{48}Na_8Y$ (H_6Y) 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.

H_2Y and H_6Y 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. It is not quite clear if the species observed here are radical cations, dications, or rather protonated heterocycles. Related studies[17] on these and other monomers suggest the formation of protonated species.

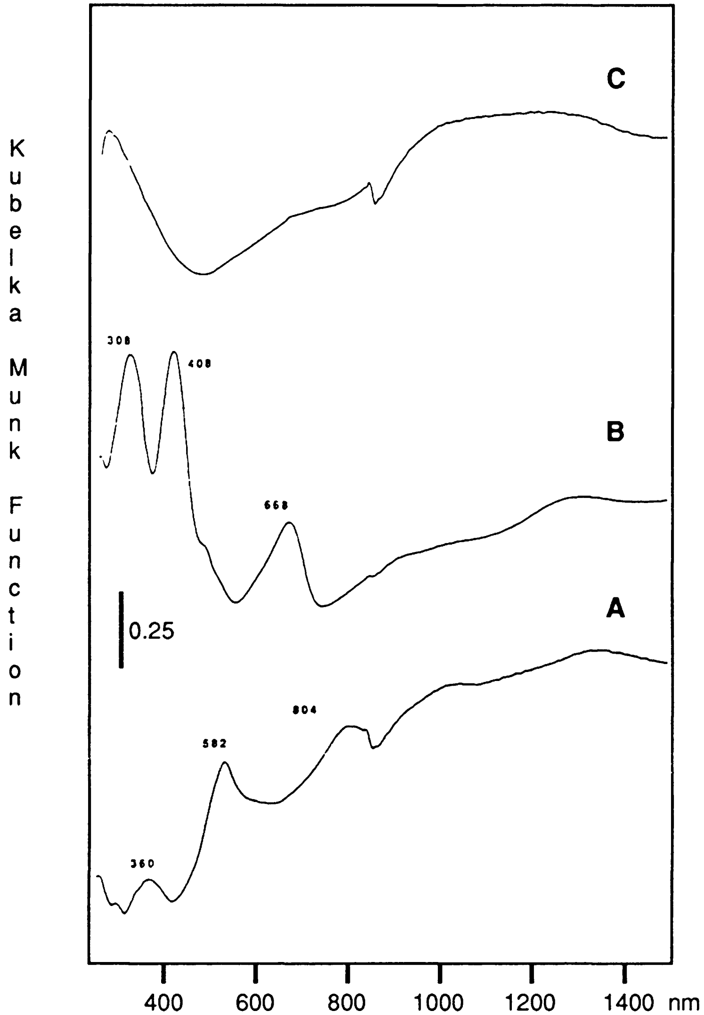

Figure 2. UV/VIS/NIR reflectance spectra of thiophene oligomers in acid zeolites. (A) H6Y-TTh-H, (B) H6Y-BTh-H, and (C) Fe(III)Y-BTh-H.
The feature at 850 nm is an artifact due to change of detectors.

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)	$2^{\bullet+}$(407)	8^{2+}(661)	
H_2Y-BTh-H	308s	408s	668s	1274 broad
	2	$2^{\bullet+}$	8^{2+}	8^{2+}... (1383)
H_6Y-BTh-H	308s	408s	668s	1300 broad
	2	$2^{\bullet+}$	8^{2+}	8^{2+}...
Fe^{III}Y-BTh-H				broad NIR band
				oxidized PTh
NaY-TTh-H	370s	528sh		
	3(354)	$3^{\bullet+}$(522)		
H_2Y-TTh-H	360s	532s	788s	broad NIR band
	3	$3^{\bullet+}$	$6^{\bullet+}$(775)	**oxidized PTh**
H_6Y-TTh-H	360s	528s	804s	1024 + broad NIR
	3	$3^{\bullet+}$	$6^{\bullet+}$ **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; 6^{2+}, hexathiophene dication; 8^{2+}, octathiophene dication. H, hexane; sh, shoulder; s, strong; and w, weak.

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 oligomer[6]. 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, $2^{\bullet+}$, in acid zeolites as shown by the band at 408 nm. Additionally, two bands at 668 nm and at about 1300 nm, assigned to the octamer dication 8^{2+}, are present in the spectra (Figure 2, B). For terthiophene, a band at 528 nm assigned to the radical cation $3^{\bullet+}$, and a band around 800 nm related to the hexamer $6^{\bullet+}$ 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 presence of protons. 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 as well. However, the reactivity of the thiophene species in proton vs. Fe^{III} zeolite forms is still not completely understood. If a strong oxidant ion is present in the zeolite, such as Fe^{III}, the oxidation is driven to completion forming oxidized polymers. The reaction pathway is apparently a function of the oxidation potential of the oxidant.

CONCLUSIONS

In summary, 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.

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