Intrinsically Conducting Polymers: An Emerging Technology

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TABLE OF CONTENTS

vi

INCLUSION OF CONDUCTING POLYMERS IN INORGANIC HOSTS: TOWARDS CONDUCTING NANOSTRUCTURES

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ABSTRACT. A discussion of various strategies for the intrazeolite encapsulation of polymer filaments is given. Two examples are discussed in more detail: Poly(2-ethylaniline) and pyrolyzed polyacrylonitrile in zeolite hosts. Poly(2-ethylaniline) chains were synthesized within the three-dimensional channels of dehydrated zeolites X and Y via oxidation of the intrazeolite monomers 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. The intrazeolite polymer chain length peaks at about 0.1 μm (determined from gel permeation chromatography), and is greater than that obtained in bulk polymerizations. Intrazeolite polyacrylonitrile (PAN) was formed from preadsorbed acrylonitrile in zeolite Y and mordenite on reaction with radical initiators. Chain length analysis with gel permeation chromatography revealed a peak molecular weight of 19,000 for PAN in NaY, and about 1,000 for the polymer in mordenite. When intrazeolite PAN was pyrolyzed under nitrogen, black encapsulated material resulted that had lost the nitrile groups and hydrogen. After removal from the zeolite hosts, the pyrolyzed polyacrylonitrile showed electronic DC conductivity at the order of 10^{-5} Scm^{-1}.

1. Introduction

The design of 'molecular electronics' components such as interconnects, rectifiers, and storage devices seeks to utilize true molecular species to perform electronic functions.[2,3] 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.[4,5,6] It is of great interest to explore the physical properties, particularly the conductivity, of separated, ordered filaments of conducting polymers at nanometer dimensions.

Research efforts in this group have recently demonstrated the encapsulation of conjugated polymers such as polypyrrole, polyaniline and polythiophene in the crystalline channel systems[7] of zeolites.[8] 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[9], or to encapsulate conjugated polymeric chains inside crystalline inorganic host materials by in-situ polymerization. Polypyrrole and polythiophene fibers of only 30

51

nm in width have been grown electrochemically within microporous membranes, such as Anopore alumina filtration membranes[10]. 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 $(FeOCl)$[11] and vanadium oxide $(V_2O_5.nH_2O)$[12]. Polyaniline intercalates were also formed by polymerization of aniline in the galleries of Cu-exchanged fluorohectorite[13].

Pyrrole has been spontaneously oxidized and in-situ polymerized in 6.8 Å channels of the three-dimensional coordination polymer $[(Me_3Sn)_3Fe^{III}(CN)_6]_\infty$[14]. Methylacetylene gas reacts with the acid sites in zeolites L, Y, beta, ZSM-5, omega, mordenite, and SAPO-5 to form reactive, conjugated oligomers[15]. Short-chain oligomers of polythiophene were prepared, oxidatively doped to the conducting state and stabilized in Na-pentasil zeolites[16].

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[17], 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.

## 2. Structure and Properties of Zeolite Host Materials

The microporous aluminosilicates called zeolites have gained great importance for host/guest chemistry.[18,19,20] While many layered materials are known, including aluminosilicate clays, group 4 phosphates, graphite, and metal chalcogenides, zeolites are the archetypical three-dimensional "molecular sieves". One major difference between these materials is that structural integrity of the zeolites upon encapsulation or intercalation of guest molecules is maintained, while the layered structures change the interlayer spacing and interlayer orientation when intercalation takes place. There are several other groups of crystalline microporous structures of growing importance, for example molybdenum phosphates,[21] or metal sulfides,[22] which are not subject of this discussion.

Zeolites are open framework oxide structures (classically aluminosilicates with hydrophilic surfaces) with pore sizes between 0.3 and 1.2 nm and exchangeable cations. The fundamental building blocks of the classical zeolite structure are the SiO_4 and AlO_4 tetrahedra that are conceptually viewed as joining up in "secondary building units" such as single six-rings (S6R, which are in fact twelve-rings consisting of six metals and six alternating oxygens arranged much like a crown ether), double-six-rings (D6R) and complex 5-1 structures. Other important structural units are the "sodalite cage" (a truncated octahedron) and the "supercage" (a unit with 12.5 Å internal diameter). These units are then joined to form open pore structures with channels based on rings containing 6 to 20 (in a gallophosphate) metal and oxygen atoms. Not only channels but also cage structures can be formed. There are now more than seventy different structure types known and new ones continue to emerge. Zeolites have remarkable temperature stability; survival of structures at 1000 K is not uncommon. The presence of Al atoms in the silica framework results in one negative charge per Al atom such that cations are required to balance the charge. The zeolitic pores constitute a significant fraction of the crystal volume (up to about 50%) and are usually filled with water. In hydrated zeolites, the cations have a high mobility giving rise to ion exchange capability, and the water molecules can be removed at elevated temperature. A general formula for zeolite-type materials based on 4-connected networks is the following[23]:

$$M_xM'_yN_z[T_mT'_n..O_{2(m+n+..)-e}(OH)_{2e}](aq)_p \cdot qQ$$
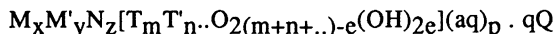
with tetrahedral T-atoms Be, B, Al, Ga, Si, Ge, P, transition metals, and M, M' exchangeable and nonexchangeable cations, N nonmetallic cations (normally removable on heating), (aq)

chemically bonded water and Q sorbate molecules which need not be water. The essential part in the square brackets represents the 4-connected framework which is usually anionic. A simpler formula used for many zeolites is:

$$(M^{n+})_{x/n} [(AlO_2)_x (SiO_2)_y] . zH_2O$$
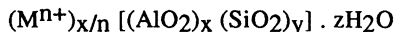
The following Table 1 presents a brief description of important zeolite structure types.[24] Structural building blocks and cage topologies of those zeolites are shown in Figure 1. In Zeolite Y, the framework consists of sodalite cages, connected through four D6R that enclose a supercage with 12.5Å internal diameter. The supercages are accessible through four S12R windows with a free aperture of 7.4Å. Relevant cation locations are the center of the hexagonal prism (site SI) and in the six-membered rings connecting into the sodalite (SI'; SII') and into the supercage (SII). The ions are often slightly displaced from the center plane of the rings. In mordenite (MOR), complex 5-1 units form two major intersecting channels, one defined by windows with oxygen 12-rings (6.5Å x 7.0Å) and one defined by windows with oxygen 8-rings. Mordenite is thermally very stable due to the large number of energetically favored five-membered rings in the framework.

Table 1. Representative Zeolite Structure Types.

Name	Unit Cell/Composition	Cage Type	Main Channels/Å[a]
LTA, Linde A	$Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$ 27 H_2O	a, ß	4.1 ***
FAU, Faujasite	$Na_{58}[(AlO_2)_{58}(SiO_2)_{134}]$ 240 H_2O	ß, 26-hedron(II)	7.4 ***
RHO, Rho	$Na_{12}[(AlO_2)_{12}(SiO_2)_{36}]$ 44 H_2O	a, D8R	3.9x5.1 ***
MOR, Mordenite	$Na_8[(AlO_2)_8(SiO_2)_{40}]$ 24 H_2O	complex 5-1	6.5x7.0* <-> 2.6x5.7*
MFI, ZSM-5	$Na_n[(AlO_2)_n(SiO_2)_{96-n}]$ 16 H_2O	complex 5-1	{5.3x5.6 <-> 5.1x5.5} ***
AFI, AlPO-5	$AlPO_4$	12R	7.3 *

[a] The number of stars (*) at the channel description indicates the dimensionality of channel connections. The cage types are depicted in Figure 1.

3. Poly(2-ethylaniline) in Zeolite Hosts.

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 section 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[25]. The chemical oxidation of aniline in acidic aqueous solution yields the "emeraldine salt" form of bulk PANI as a dark blue-green precipitate[26]. 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[27], probably as diaminobenzene radical cations[28]. 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.
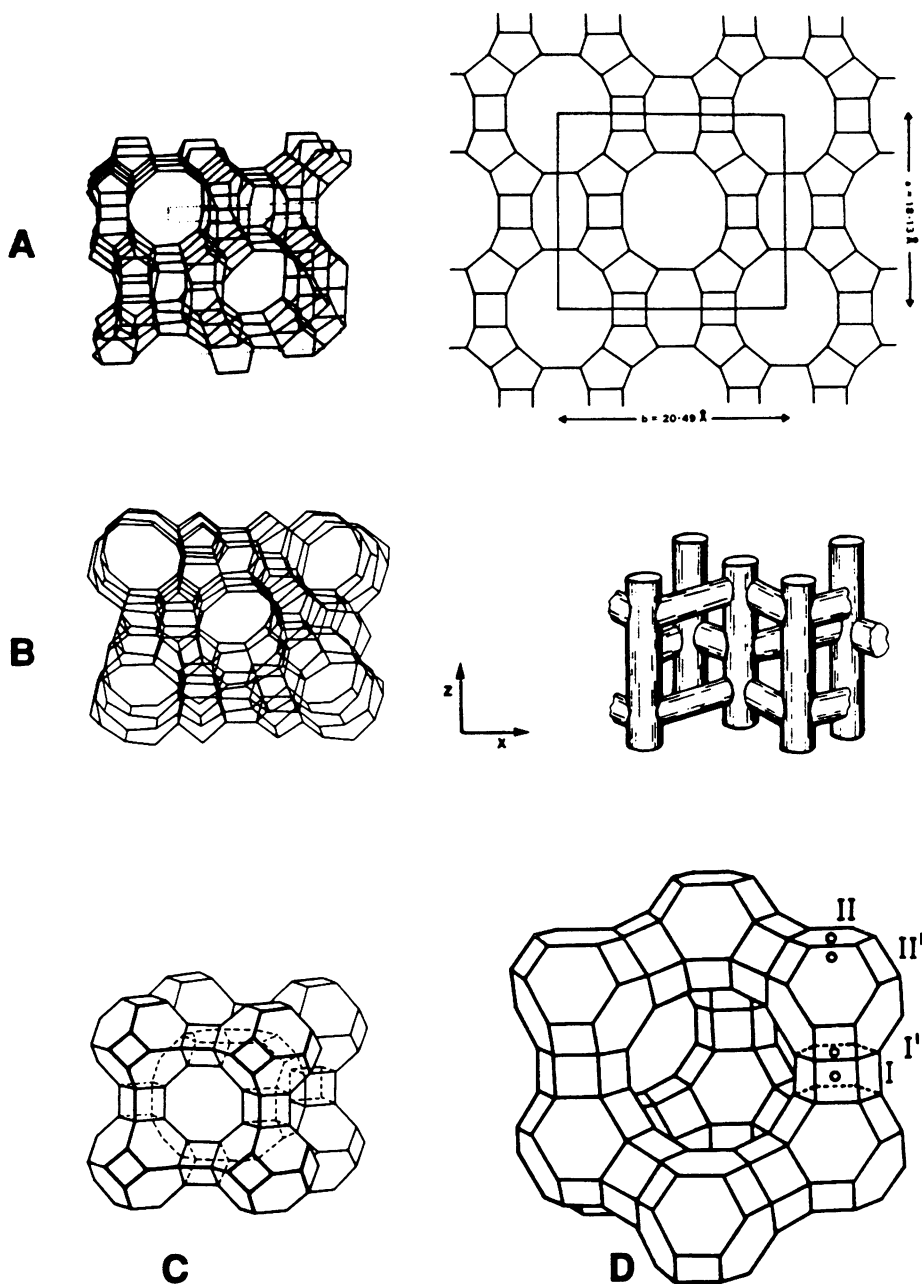
Figure 1.   The structures of zeolites.
A, Mordenite, B, Silicalite, C, zeolite A, and D, Faujasite.

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[29]. 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$_4$OH. 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[30]. 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].

3.1.1. *The Polymerization Reaction as a Function of Host and Oxidant.* Table 2 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.

Table 2: 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$_6$Y-ETAN[c]	27, 32[e] (46)	persulfate	+ blue
		iodate, H$^+$	- white[d]
		H$_2$O$_2$	- 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$_8$M-ETAN[c]	6.5 (8)	persulfate	- bluish
		H$_2$O$_2$	- 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.

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. 2-Ethylaniline did not polymerize in mordenite even though a considerable amount of monomer was loaded into it (Table 2). It can be concluded that the one-dimensional framework of mordenite introduces steric restrictions and precludes polymerization due to geometric constraints.

3.1.2. *Spectroscopic characterization.* IR Band positions and their assignments are summarized in Table 3. 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[31]. The absorption at 1642 cm^{-1} is characteristic of zeolitic water. The spectra of other zeolite samples (Table 3) 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.

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

3.1.3. *Chain length determination.* Gel permeation chromatography (GPC) measurements provided molecular size distribution curves for poly(2-ethylaniline) bulk and the polymer extracted from H_6Y-ETAN (calibrated with polystyrene standards). The distributions are

Table 3. 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	υ_{as} CH$_3$
2934	2933	2936	υ_{as} CH$_2$
2876	2873	2876	υ_s CH$_3$
1642			zeolitic H$_2$O
1593	1598	1594	quinoid
1500	1498	1504	benzenoid
1455	1457	1457	-CH$_2$-C=C- δ_{as} CH$_3$
1404			byproduct
1335	1345	1331	Phenyl-N (quinoid)

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

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.

Since poly(2-ethylaniline) does not have the same structure as polystyrene, a correction factor was applied. For polyaniline, calibration with a tetramer of aniline was suggested[32]. 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 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.

4. Polyacrylonitrile Chains in Zeolite Channels: Polymerization and Pyrolysis.

We discuss the assembly of polyacrylonitrile (PAN) strands in different large-pore zeolites, zeolite Y and mordenite, and explore the pyrolysis reactions of the encapsulated polymer (Figure 2).[33]

Acrylonitrile vapor was adsorbed in the degassed (670 K, 10^{-5} Torr) zeolite crystals at a vacuum line for 60 min at room temperature. To an aqueous suspension of the acrylonitrile-containing zeolite were added aqueous solutions of potassium peroxodisulfate and sodium bisulfite as radical polymerization initiators. The zeolite frameworks could be dissolved with HF to recover the intrazeolite polyacrylonitrile (PAN). IR and NMR data show no damage to the polymers after this treatment. For pyrolysis, the zeolite/PAN adducts were heated under nitrogen or vacuum for extended periods.

Zeolite Y absorbs 46 and mordenite 6 molecules of acrylonitrile per unit cell on saturation. The polymer recovered from the zeolite hosts is identical to bulk PAN as shown by NMR spectroscopy.[34] The ^1H NMR spectra show two bands at a ratio of 2 to 1, one at 2.0 ppm corresponding to the methylenic group in the polymer, and the other at 3.1 ppm confirming a methine group. The ^{13}C NMR data of the zeolite-extracted PAN show CH_2 (27.5 ppm), CH (32.7 ppm), and -CN (120.1 ppm), identical to the bulk material. Infrared spectra of the zeolite/polymer inclusions and of PAN extracted from the zeolites show also peaks characteristic of the bulk polymer,[35,36] including methylenic C-H stretching vibrations of the backbone (2940 cm^{-1} and at 2869 cm^{-1}), and a band at 2240 cm^{-1} due to the pendant nitrile group. The spectra of the extracted intrazeolite polymers are indistinguishable from the spectrum of the bulk polymer. The polymer formed in the zeolites is thus polyacrylonitrile.

The molecular weight of the polymer extracted from the zeolites was determined with gel permeation chromatography, relative to a PAN broad standard (M_w = 86,000; M_n = 23,000). For PAN extracted from NaY, the main molecular weight distribution peaks at 19,000, corresponding to 360 monomer units or about 0.2 μm for an extended chain. For PAN extracted from Na-mordenite, a bimodal molecular weight distribution is observed; a small fraction peaks at 19,000 and a large fraction at about 1,000, corresponsing to a 0.01 μm chain in a fully extended form. The shorter chain length in mordenite might indicate crystal defects or diffusional constraints for the polymerization reaction.

On pyrolysis, the color of the PAN-containing zeolites changes from white to grey-black. The electronic absorption spectrum of pyrolyzed PAN extracted from NaY shows the appearance of a feature at about 350 nm, as in the bulk, probably due to conjugated carbon-nitrogen double bonds in the ladder polymer.[37] The methylenic stretching vibrations and
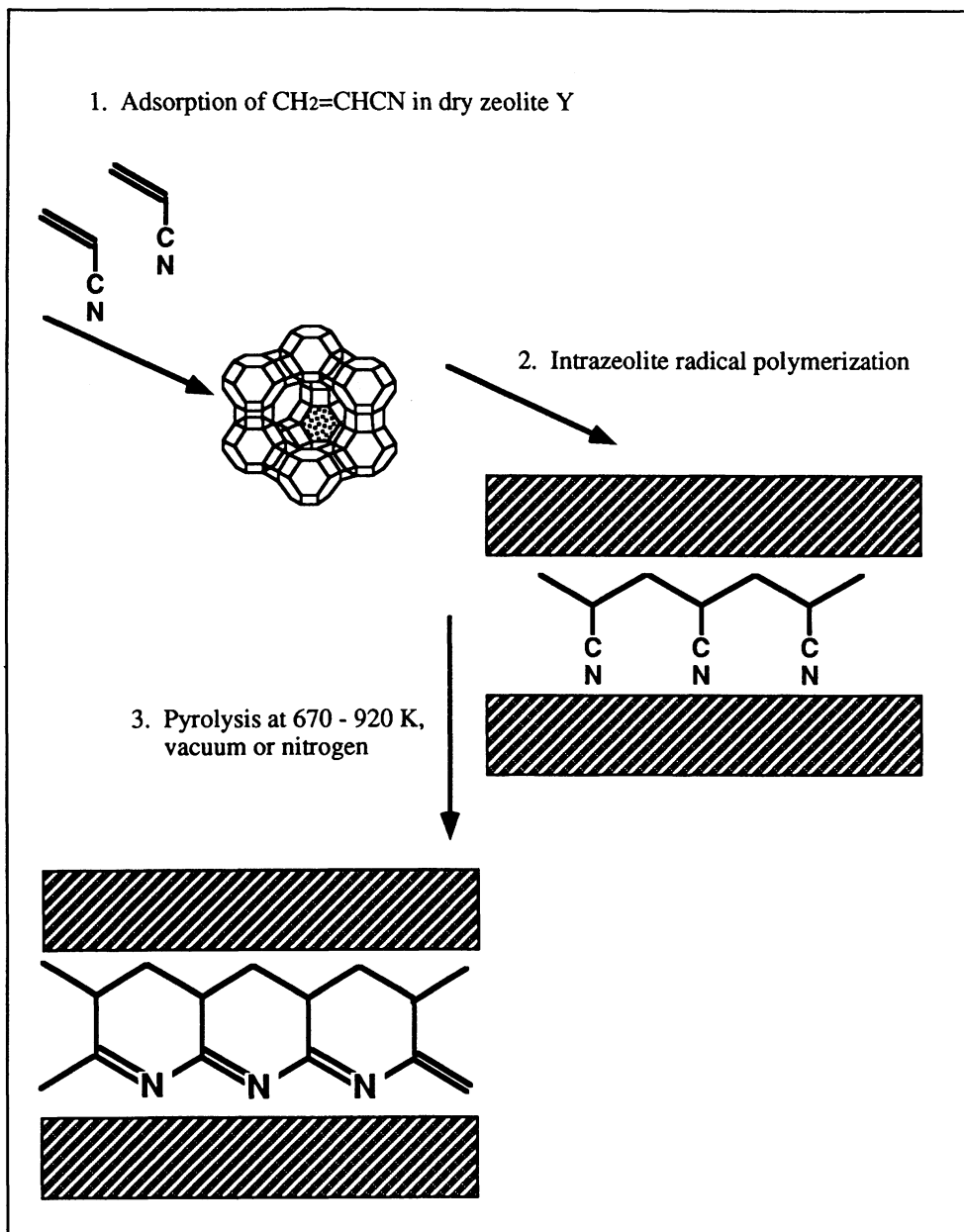
58

Figure 2. Polymerization and pyrolysis of acrylonitrile in zeolite channels

the nitrile band of the intrazeolite PAN main chain disappear. New bands appear in the 1400-1600 cm^{-1} region which have been assigned to C=C and C=N double bonds in the pyrolyzed bulk PAN, as well as the tail of the electronic excitation corresponding to free carrier absorption. A sample of bulk PAN heated to 800 K instead of 920 K shows more defined features in the 1400-1600 cm^{-1} region, similar to the case of pyrolyzed PAN (920 K) extracted from the zeolite. This suggests an early stage of graphitization for the intrazeolitic material. Zeolite/PAN samples pyrolyzed at different temperatures, times, and atmospheres, (nitrogen or vacuum) show spectra similar to the spectrum of bulk PAN pyrolyzed to 800 K.

Samples of NaY with pyrolyzed (920 K) PAN show no measurable dc conductivity. This is not surprising because the polymer is encapsulated completely within the insulating zeolite, and because no external polymer coats the zeolite crystal surfaces. However, the conductivity of the pyrolyzed PAN *extracted* from the zeolite is at the order of 10^{-5} Scm^{-1}, almost identical with that of bulk PAN pyrolyzed at 800 K, and five orders of magnitude smaller than that of the bulk sample pyrolyzed at 920 K. In contrast to the bulk polymer, pyrolysis treatment conditions above about 870 K have little effect on the resulting conductivity of the extracted intrazeolite samples. We conclude that the spatial limitations within the zeolite channels prevent the formation of more extended, graphitized structures with higher conductivity.

This study demonstrates the inclusion synthesis of polyacrylonitrile in the channel systems of NaY and Na-mordenite zeolites, and its pyrolysis to yield a conducting material consisting of nanometer size carbon filaments. Preliminary microwave conductivity measurements show substantial conductivity of these filaments *even when encapsulated in the zeolite*. These and related systems are promising candidates for low-field conductivity at nanometer scale dimensions.

5. Conclusion.

The examples discussed above demonstrate the versatility and great potential of zeolite molecular sieves to encapsulate and stabilize extremely thin filaments of conjugated polymers. The regular arrangement of the cages and their variable connectivity is of great interest for superlattice assembly of electronic and optical materials based on conjugated systems. The conductivity of these and related systems as a function of host structure and pore dimensions is presently being explored in this laboratory.

6. Acknowledgments.

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