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ZEOLITES AND RELATED MICROPOROUS MATERIALS: STATE OF THE ART 1994

PART C

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Conducting Polymer Wires in Mesopore Hosts

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Nanometer-size conducting structures are of great interest in view of fundamental issues and potential applications. We explore the inclusion chemistry of conjugated polymers and graphite-like materials as a means to create such structures. Novel mesoporous materials with pore diameters in the 3 nm range (MCM-41) are used as hosts. Monomer molecules are introduced *via* vapor or solution transfer and polymerized either by included or external reagents. The properties of the conjugated systems are studied while encapsulated or after dissolution of the host. In the case of polyaniline formed on oxidation of aniline with persulfate, microwave absorption shows the presence of *conducting filaments* in the host channels. The above systems are compared with graphite-type material encapsulated in MCM-41 by first forming a precursor polymer such as polyacrylonitrile that is pyrolyzed at 500-800°C. These polymer chains are the first nanometer-size conducting filaments stabilized in a well-defined channel host.

1. INTRODUCTION

Intensive efforts are directed at the reduction of the size of electronic components, in order to increase storage capacity and speed in information processing. At the culmination of this development one could envisage devices with components of *molecular size*.[1] While still mostly at the conceptual stage, "molecular electronics" has inspired much interesting research directed at building devices from molecular assemblies. Organic conducting polymers[2] with their characteristic quasi one-dimensional chain structure and good conductivity might offer the best potential to control charge transport at molecular dimensions.

We have demonstrated the preparation of nanometer-size polymer filaments such as polypyrrole, polyaniline, polythiophene, and pyrolyzed polyacrylonitrile in zeolites with channels smaller than about one nanometer.[3] Precursor monomers are introduced into the zeolite host and are subsequently polymerized by appropriate oxidants in the pore system. Using microwave absorption measurements, it was found that *charged* polymers encapsulated in these narrow pores are not conducting, apparently because the charge carriers are trapped by the channel walls.[4]

Encapsulation of conducting polymer filaments in various host structures has recently been developed. For example, polypyrrole and polythiophene fibers of about 0.1-1 μm in width have been grown electrochemically within microporous membranes, such as Anopore alumina filtration membranes[5]. Methylacetylene gas reacts with the acid sites in various zeolites to form conjugated oligomers,[6] and polyacetylene was formed in different forms of mordenite.[7]

We have now extended our studies of polyaniline and pyrolyzed polyacrylonitrile to the newly developed mesoporous aluminosilicate hosts, MCM-41, which offer much larger channel diameters than classical zeolites.[8]

2. EXPERIMENTAL

The MCM-41 host was synthesized with $C_{16}H_{33}N(CH_3)_3OH$ according to ref. 8, with a Si/Al ratio of 18, and calcined at 580 °C. Before loading with monomers, the hosts used in this study were pretreated with oxygen and vacuum at high temperature (12 h at 400°C, 10^{-5} torr) to remove water and trace amounts of absorbed organic molecules. To load with copper ions, 1.00 g of the calcined MCM was stirred for 3 h at 25 °C with 100 mL of 0.1 M Cu(II)nitrate (aq), filtered, and washed with water. These steps were repeated four times. Slight decreases in crystallinity were observed.

Polyaniline was formed by adsorbing dried and vacuum-distilled aniline into the host from the vapor phase at 40 °C for 24 h; a maximum of 0.3 g aniline adsorbed in 1.0 g of CuMCM host (Sample AN-CuMCM). The saturated host was then immersed in an aqueous solution of peroxodisulfate at 0 °C for 4 h (mole ratio of oxidant vs. aniline 1:1, 1 g of AN-CuMCM in 50 ml 0.2 M HCl) and a drastic color change to dark green was observed. After thorough washing with water, the materials were dried under vacuum (Sample PANI-CuMCM). A typical polymer loading is 0.16 g per 1.00 g of CuMCM host.

Polyacrylonitrile was introduced as follows. MCM-41 was contacted with degassed (three cycles of freeze-pump-thaw) acrylonitrile vapor at room temperature for 4 hours. The acrylonitrile loaded MCM-41 (ANZ) was evacuated to remove the molecules absorbed on the surface of the host. Under nitrogen, ANZ was mixed with distilled H_2O (typically 1.00 g of ANZ with 20 ml of water). The temperature was raised to 40°C, then $K_2S_2O_8$(aq) and $NaHSO_3$(aq) were added. The mixture was stirred at 40°C under nitrogen for 20 hours; the solids were filtered off, washed with water and dried under vacuum. The resulting white solid (PANZ) was pyrolyzed under nitrogen at different temperatures between 500°C and 800°C for 24 hours (PPANZ).

3. RESULTS AND DISCUSSION

3.1. Polyaniline in mesoporous hosts

The conductivity of polyaniline is not only controlled by the degree of chain oxidation, but also by the level of protonation in $\{[(\text{-B-NH-B-NH-})_y(\text{-B-N=Q=N-})_{1-y}]\ (HA)_x\}_n$.[9] In the emeraldine salt (PANI), y is close to 0.5; B, Q are C_6H_4 rings in the benzenoid and quinoid states, and HA is an acid.

Here we will discuss a representative preparation, using a copper-exchanged MCM host that was equilibrated with aniline and contacted with peroxodisulfate. The copper ion content in CuMCM is rather low (0.21 Cu/Al). Therefore there may not be sufficient oxidant to polymerize large amounts of polyaniline inside the host. By carrying out the reaction in air, oxygen could be the indirect oxidant which continues to oxidize the Cu^{+1} to Cu^{+2} during the reaction. However, we find that such conditions will produce non-conducting leucoemeraldine or mixtures of products, but not the conducting emeraldine salt.

When the exposure to aniline vapor is carried out under vacuum, no polymer is formed (sample AN-CuMCM). The pink products may contain some radicals and cations of aniline or its oligomers, as indicated by an electronic absorption peak at 410 nm, suggesting the presence of nitrenium cations ($C_6H_5NH^+$) or nitrenium radicals ($C_6H_5NH\cdot$).[10] The cations and radicals are quite reactive; upon contact with air, the color turns brown.

If the pink material is reacted with $(NH_4)_2S_2O_8$/HCl aqueous solution under exclusion of air, the resulting dark green product, PANI-CuMCM, contains the *emeraldine salt form* (diagnostic IR peaks at 1581, 1497, 1300, and 1230 cm^{-1}).[11] The electronic absorption spectrum of PANI-CuMCM shows peaks at 3.4 and 1.6 eV, typical for the band-gap and polaron transitions of emeraldine salt.[12] The encapsulated, evacuated

polymer exhibits a single fairly broad (8 G) ESR line at g=2.0057. The rather large linewidth could suggest slightly lower protonation levels than in emeraldine salt,[13] or dipolar interactions with the MCM channel walls.

Thermogravimetric experiments in oxygen show that the stability of PANI-CuMCM is higher (decomposition between 350-600 °C) than that of bulk PANI (rapid decomposition between 300-400 °C) (Figure 1). This indicates hindered diffusion of reactants and products during the pyrolysis reactions. In contrast, with AN-CuMCM the major weight loss occurs below 200 °C.

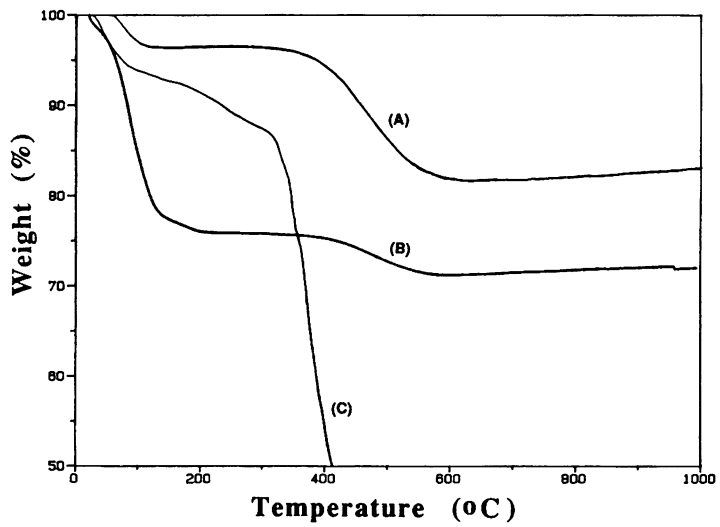

Figure 1. Thermogravimetric analysis in oxygen of (A) PANI-CuMCM, (B) AN-CuMCM, and (C) bulk PANI. Heating rate: 5 °C/min with 100 mL/min oxygen.

The location of the polymer (inside vs. outside of the channels) is an important aspect of these systems. Infrared spectra of the hydroxyl region of CuMCM before aniline loading show a single peak at 3691 cm^{-1} (in Nujol), which disappears on contact with aniline. This indicates complete coverage of the intrachannel surface with aniline. The intrachannel volume reduction after polymerization was probed with

nitrogen sorption. The nitrogen sorption isotherm of PANI-CuMCM shows a residual pore volume of 0.43 ml per g of CuMCM host, compared with 0.64 ml pore volume in the empty host. If a polymer density of unity is assumed, the loading of 0.16 g/(g host) is close to the expected change in porosity probed with nitrogen sorption. Even after loading with polymer, the tubular structure of the channels is maintained as indicated by a similar isotherm shape. The shift of the saturation transition to lower partial pressure shows that the channels are now narrowed.

What is the conductivity of the encapsulated PANI? Transport studies of bulk emeraldine salt have led to the model of a granular metal where charge hopping in amorphous regions between metallic bundles dominates the macroscopic conductivity.[14] The d.c. conductivity of a compressed pellet of PANI-CuMCM is in the range of 10^{-8} S/cm. This is not more than the conductivity of unloaded CuMCM, and many orders of magnitude lower than bulk PANI, demonstrating that no significant conducting paths develop on the crystal surfaces. The microwave cavity perturbation technique[15] was used to probe the charge transport of PANI filaments in the MCM host. The microwave conductivity (at 2.63 GHz) of dry PANI-CuMCM is *only 10 times less than that of as-synthesized bulk PANI* (d.c. conductivity of 0.2 S/cm), after correction for the volume fraction of the polymer in the host. This significant conductivity is striking evidence that conjugated polymers can be encapsulated in nanometer channels and still support mobile charge carriers. The channels of the CuMCM host provide enough space for important polyaniline interchain contacts.

3.2. Pyrolyzed polyacrylonitrile in mesoporous hosts

Pyrolyzed polyacrylonitrile (PAN) was chosen as an alternative example for intrachannel conducting materials. Polymerization of acrylonitrile proceeds in the presence of free radical or anionic initiators, and pyrolysis produces a ladder polymer by cyclization through the nitrile pendant group. At higher temperature, a graphite-like structure with increased conductivity is formed, in which the delocalized electrons contribute to the charge transport.[16] The polymerization of acrylonitrile in montmorillonite[17] has been reported, but these systems contain sheets of micrometer dimensions, different from the nanometer channels of the MCM hosts.

The vapor transfer of acrylonitrile into the host can be easily achieved at room temperature. The terminal hydroxyl groups of MCM-41 are still observed after inserting acrylonitrile, but at the same time a significant peak at 2244 cm^{-1}, which is the characteristic vibration of

CN, appears. The acid-base interaction between guest and host observed in the above aniline/CuMCM-41 system was not detected here, due to the weaker basicity of acrylonitrile compared to aniline. X-ray diffraction data show that the crystallinity of the host is intact after insertion of polyacrylonitrile, and even after pyrolysis at 800°C.

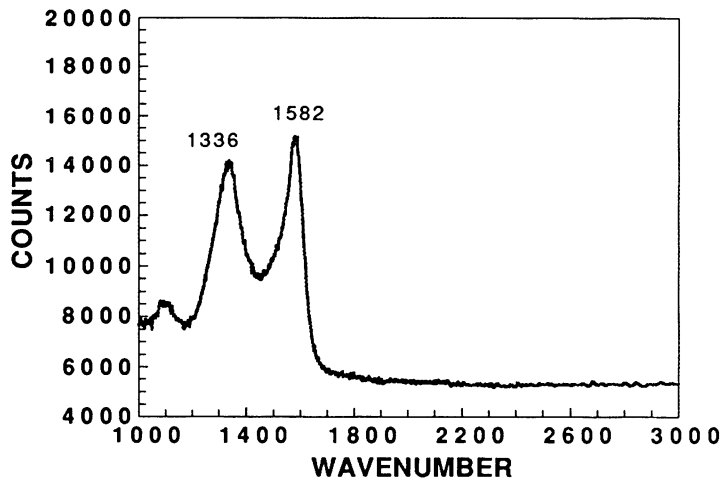

Figure 2. Raman spectrum of sample PPANZ (800 °C, 24 h). Excitation with ca. 50 mW at 514.5 nm.

The IR spectrum of polyacrylonitrile pyrolyzed at 800°C is featureless, however the Raman spectrum shows two distinct peaks at relative wavenumbers of 1582 cm^{-1} and 1336 cm^{-1} which are similar to the characteristic vibrations of graphite[16] (Figure 2). The diffuse reflectance UV spectrum of pyrolyzed polyacrylonitrile/MCM between 200 and 800 nm is also similar to that of graphite.

The nitrogen content of pyrolyzed polyacrylonitrile not only depends on the pyrolysis temperature but also on the polymer environment. In general, for the same pyrolysis temperature, polyacrylonitrile in MCM-41 has a higher C/N ratio compared to bulk polymer (Table 1).

The normalized microwave conductivity of PPANZ (with ca.12 wt% of CH_x) is higher than that of the bulk polymer. This is consistent with the formation of graphite-like material in the polyacrylonitrile/MCM system. The microwave conductivity also increases with the pyrolysis temperature as shown in Table 1. Furthermore, the formation of

graphite-like material *inside* the channels of the MCM-41 host is supported by the volume decrease observed in nitrogen sorption isotherms.

In conclusion, we have achieved the fabrication of 'molecular wires' based on conducting polymers in nanometer channels. This type of stabilized conducting systems will be important for the development and understanding of nanometer-size electronic devices.

Table 1.
The C/N ratio and AC conductivity at 2.63 GHz of bulk polyacrylonitrile and polyacrylonitrile/MCM pyrolyzed at different temperatures.

Sample	Pyrolysis conditions	C/N ratio	AC conductivity (S/cm)[a]
Polymer/MCM	800°C 24 hr.	9.86	1.4×10^{-1}
Bulk polymer	800°C 24 hr.	8.87	4.8×10^{-3}
Polymer/MCM	650°C 24 hr.	5.15	1.7×10^{-2}
Bulk polymer	650°C 24 hr.	4.50	4.4×10^{-3}
Polymer/MCM	500°C 24 hr.	3.92	2.0×10^{-3}
Bulk polymer	500°C 24 hr.	3.79	1.2×10^{-3}

[a]The density of pyrolyzed polyacrylonitrile was assumed to be 2.0 g/cm^3.

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