

## Intrazeolite Assembly and Pyrolysis of Polyacrylonitrile

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Radical polymerization of acrylonitrile within the pores of zeolites Y and mordenite produces intrazeolite polyacrylonitrile that can be pyrolysed to form conducting carbon filaments.

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The understanding and control of electronic conductivity at nanometer dimensions is a subject of current research activity. The influence of microstructure on the conduction mechanism in conducting organic polymers is of particular importance in

this context. We have recently demonstrated the encapsulation of charged conjugated polymers such as polypyrrole, polyaniline and polythiophene in the crystalline channel systems<sup>1</sup> of zeolites.<sup>2</sup> In this communication, we report the first successful polymerization of acrylonitrile as a precursor for intrazeolite, conducting graphite-like filaments. Zeolite Y is an open framework aluminosilicate with 1.3 nm size supercages formed from interconnected sodalite cages, with

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0.75 nm pore openings. Mordenite (MOR) is characterized by a pseudo-one-dimensional twelve-ring channel system with similar window size, while silicalite offers intersecting zigzag and straight channels with pore openings of about 0.55 nm diameter. The polymerization of acrylonitrile in montmorillonite<sup>3</sup> and of aminoacetonitrile in layered metal phosphates<sup>4</sup> has been reported, but these systems contain sheets of macroscopic dimensions different from the nanometer channels of the zeolite hosts.

The degassed (670 K,  $10^{-5}$  Torr) zeolite crystals were loaded with acrylonitrile vapour on a vacuum line for 60 min at 298 K. Acrylonitrile-containing zeolite (1 g) was then suspended in deaerated water (20 cm<sup>3</sup>) at 313 K. To that suspension were added aqueous solutions of potassium peroxydisulfate (0.01 mol dm<sup>-3</sup>) and sodium hydrogen sulfite (0.025 mol dm<sup>-3</sup>) as radical initiators,<sup>‡</sup> and the suspensions were stirred for 12 h. The zeolite frameworks were dissolved with a 25% aqueous solution of 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 to 920 and 970 K with a heating rate of 2 K per minute, for 12 and 24 h.

After vapour saturation, zeolite Y contains 46 molecules of acrylonitrile per unit cell, mordenite 6, and silicalite 9 molecules. However, even though the monomers adsorb into silicalite, no polymerization is observed within the latter host. The diameter of its channel system of approximately 5.5 Å may be too small for the diffusion of radical initiator into the zeolite, or for polymerization to proceed.

IR spectra of the zeolite-polymer inclusions and of PAN extracted from the zeolites show peaks characteristic of the bulk polymer.<sup>5,6</sup> Bands at 2940 and 2869 cm<sup>-1</sup> are assigned to the methylenic C-H stretching vibrations of the backbone, while a band at 2240 cm<sup>-1</sup> is assigned to the pendant nitrile group. The spectra of the extracted intrazeolite polymers are indistinguishable from the spectrum of the bulk polymer. It can be concluded that the polymer formed in the zeolites is polyacrylonitrile.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of the recovered polyacrylonitrile extracted from zeolite Y, and from Na-mordenite in (CD<sub>3</sub>)<sub>2</sub>SO and DCON(CD<sub>3</sub>)<sub>2</sub> are also identical to that of PAN bulk.<sup>7</sup> The <sup>1</sup>H NMR spectra show two broad bands in a ratio of 2:1, one at  $\delta$  2.0 corresponding to the methylenic group in the polymer, and the other at  $\delta$  3.1 in agreement with a methine group. The <sup>13</sup>C NMR data of the zeolite-extracted PAN are identical to those of the bulk material:  $\delta$  27.5 (CH<sub>2</sub>), 32.7 (CH) and 120.1 (-CN).

The molecular weight of the polymer extracted from the zeolites was determined with gel permeation chromatography relative to a PAN broad standard ( $M_w = 86\,000$ ;  $M_n = 23\,000$ ). The complex molecular weight distribution curves are shown in Fig. 1. For PAN extracted from NaY, a peak molecular weight of ca. 19 000 is observed, corresponding to 360 monomer units or about 0.2  $\mu$ m for an extended chain. An additional shoulder appears at lower molecular weight. In Na-mordenite, two groups of two peaks are observed: a smaller fraction with a peak molecular weight of ca 19 000 and a larger fraction with  $M_w$  close to 1000, or about 0.01  $\mu$ m long in a fully extended form. For both hosts, the distributions at the high molecular weight end are quite similar. This could originate from similar pore diameters of the hosts, but details of the polymerization mechanism are not known in these systems. Crystal defects or diffusional constraints might cause the shorter chain length fraction in the one-dimensional mordenite.

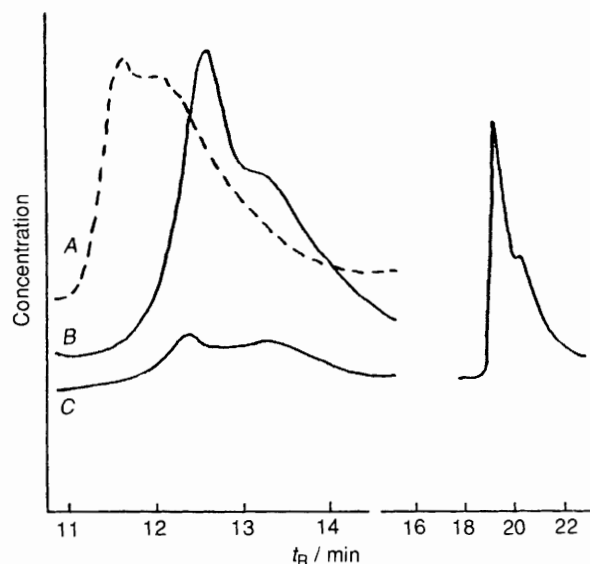


Fig. 1 Molecular weight distribution curves for PAN samples obtained from gel permeation chromatography: (A) PAN broad standard ( $M_w = 86\,000$ ,  $M_n = 23\,000$ ); (B) PAN extracted from NaY-PAN; (C) PAN extracted from NaMOR-PAN

On pyrolysis, the PAN-containing zeolites changed colour from white to grey-black. § The pyrolysed PAN extracted from NaY is insoluble in organic solvents; this suggests that the chain length is substantial even after pyrolysis. The methylenic stretching vibrations of the intrazeolite PAN main chain disappear, together with the characteristic nitrile band. New bands appear in the 1400–1600 cm<sup>-1</sup> region which have been assigned to C=C and C=N double bonds in the pyrolysed bulk PAN,<sup>5</sup> 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<sup>-1</sup> region, similar to the case of pyrolysed PAN (920 K) extracted from the zeolite, suggesting an early stage of graphitization. All the zeolite-PAN samples pyrolysed at different temperatures (920 or 970 K), times (12 or 24 hours) and atmospheres (nitrogen or vacuum) show spectra similar to the spectrum of bulk PAN pyrolysed to 800 K. This result suggests the ability of the zeolite channels to limit formation of an extended graphite-like structure.

The electronic absorption spectrum of pyrolysed 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.<sup>8</sup> The rest of the spectrum is practically structureless and resembles the absorption spectrum of graphite.

Thermal analyses under nitrogen of the zeolite-polyacrylonitrile inclusions show that the zeolite host drastically changes the pyrolysis reactions. Bulk PAN loses weight rapidly above 533 K, accompanied by a sharp exotherm at that temperature. In contrast, the zeolite inclusions show a much slower onset of decomposition with a broad exotherm (NaY-PAN: 518–588 K; NaMOR-PAN: 513–553 K). These observations show that the zeolite host imposes kinetic constraints on the graphitization reaction of intrazeolite PAN.

After dissolution of the NaY host, 30% polymer was recovered based on the amount of monomer loaded into the zeolite. This yield corresponds to an average of 14 polymerized acrylonitrile units per zeolite unit cell. The balance is

‡ For molar ratios of acrylonitrile : peroxydisulfate : hydrogen sulfite of 1 : 0.0027 : 0.0035.

§ X-Ray powder diffraction data demonstrate that the zeolite framework remains intact even after pyrolysis treatments at 970 K for NaY. Scanning electron micrographs show no apparent external bulk polymer coating the zeolite crystals indicating that most of the polymer chains reside in the interior of the zeolite crystals.

assumed to be unreacted monomer. The =CH bands of the monomer disappear after polymerization; thus the unreacted monomer apparently desorbs from the host during the polymerization. For mordenite, the polymer recovery was 18%. This value corresponds to approximately one molecule of acrylonitrile per unit cell of mordenite.

The NaY host containing pyrolysed PAN showed d.c. conductivity¶ smaller than  $10^{-8} \text{ S cm}^{-1}$ , in contrast to  $1.2 \text{ S cm}^{-1}$  with bulk pyrolysed PAN (920 K). The absence of measurable d.c. conductivity in the NaY-pyrolysed PAN samples 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 pyrolysed PAN *extracted* from the zeolite,  $2 \times 10^{-5} \text{ S cm}^{-1}$ , is almost identical with that of bulk PAN pyrolysed at 800 K, and five orders of magnitude smaller than that of the bulk sample pyrolysed 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. The same conductivity value of about  $2 \times 10^{-5} \text{ S cm}^{-1}$  is obtained for extracted pyrolysed PAN, pyrolysed at different temperatures, atmospheres and times. It can be concluded that the spatial limitations within the zeolite channels prevent the formation of more extended, graphitized structures with higher conductivity.

In summary, 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. The effect of larger host pore sizes on polymerization and graphitization of acrylonitrile inclusions and their associated electronic conductivity are presently being explored. These systems are promising candidates for low-field conductivity at nanometer scale dimensions.

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¶ Four-point conductivity measurements of pressed pellets.