Rapid polymerisation of S_2N_2 within Na-ZSM-5 channels†‡

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Reaction of S_2N_2 vapour with Na-ZSM-5 results in rapid polymerisation and inclusion of the resulting $(SN)_x$ within the zeolite channels.

Upon the discovery of the fascinating conductivity properties of polymeric $(SN)_x$, the four-membered ring system S_2N_2 became the subject of intense interest.[1] This interest stemmed primarily from the fact that conversion of the dinitride to the polymer occurs spontaneously over a period of days, making it an ideal precursor to a material which proved to be the first example of a metal-free superconductor. Although it is some three decades since these first observations, interest continues, and recent work has included X-ray crystallographic investigation of the polymerisation process,[2a] detailed computational investigations into the bonding within the dinitride[2b] and, within our group, identification of a source of the selenium analogue, Se_2N_2.[2c] Although some success at incorporating the polymer into functional systems has been achieved, examples of chemical derivatisation of the polymer or growth of the polymer within new environments have been limited. On the first front, partially oxidised materials such as $(SNBr_{0.4})_x$ have been prepared,[3] while shortly after the discovery of the properties of $(SN)_x$, efforts were made to incorporate it into clathrate and zeolitic systems.[4a] In the latter work Love *et al.* observed filamental type growth of, presumably, $(SN)_x$, along the fibre axis of perhydrotriphenylene (PHTP) crystals, resulting from its prolonged exposure to a thf solution of S_2N_2. They also observed interactions with benzophenone and thiourea matrices, though attempts to induce polymerisation within the channels of a crystal of the natural zeolite mordenite proved apparently unrewarding. In this case some yellow coloration was observed when the crystal was exposed to S_2N_2 vapour, and after a few days some dark filaments were noted "along the needle axis". It is not clear, however, that this was indicative of polymer formation within the zeolitic channels. More recently, Langley and Hulliger reported that similar investigations into the reaction of S_2N_2 with PHTP had proved fruitless.[4b]

Given the advances within zeolite chemistry since these initial attempts, and in the light of the intense current interest in so-called "insulated molecular wires",[5a] reconsideration of the ability of S_2N_2 to polymerise within porous systems becomes germane, especially given that conducting materials such as polyacetylene have been successfully incorporated into zeolite hosts.[5b] Introducing the intrinsically conducting $(SN)_x$ wire into such a host is a conceptually obvious modification that thus far has proven to be synthetically impractical. Here we present the first successful identification of such chemistry within a zeolitic system. The zeolite used for this study, Na-ZSM-5, is of the MFI framework type and was chosen as a suitable host as its 10 T pores (5.5 Å diameter) were judged to be of suitable size for S_2N_2 inclusion, and the presence of infinite channels along the *b*-axis,[6] ideal hosts for subsequent polymerisation.

Exposure of Na-ZSM-5 to S_2N_2 vapour§ can be readily effected by adding a sample vial containing the zeolite to the trap in which the nitride has been freshly collected and then sealing the system under vacuum. S_2N_2 is volatile enough to quickly diffuse onto the zeolite sample and in this case the result is dramatic. If the sample is placed close to the source of the vapour, a visible effect is almost instantaneous, with darkening progressing along the bulk of the sample as the vapour interacts. In such cases, a sample of *ca.* 50–100 mg of zeolite darkens completely to the black colour shown in Fig. 1 (upper) within a minute or so. If the sample is exposed *via* a side-arm to the trap, with the vapour having further to travel, the progress of the interaction may be captured by video (see ESI†). In the accompanying file the timeframe has been speeded up eight-fold; note how darkening of the sample from right to left (*i.e.* from the nearest end to the S_2N_2 source) proceeds very noticeably. Even in such circumstances—with the sample maybe 10 cm away from the bulk of the solid S_2N_2—reaction appears complete in less than 10 min.

The colour of the resulting material is very similar to bulk samples of $(SN)_x$ (which can be generated by leaving the S_2N_2 to stand at ambient temperatures for a number of days)—if anything, it is an even darker blue/black (and also lacks the bronze lustre that $(SN)_x$ can display from certain viewing angles). This strongly suggests the presence of the polymer (as within S–N chemistry as a whole there are few other examples of such dark blue/black chromophores)[7] and this can be confirmed through Raman spectroscopy. As Fig. 2 shows, bands observed in the spectrum of the free polymer are also observed within the zeolitic product. Crucially, there is a small, but significant, change in their exact frequency, a fact which suggests incorporation *within* the zeolite channels rather than simply deposition on the zeolite surface (a conclusion backed up by other observations, *vide infra*). IR spectroscopy proves less useful, unfortunately, due to the masking of most potential S–N bands by the broad aluminosilicate stretches (in the 300–1250 cm^{-1} region). The solitary S–N band which is visible *via* IR (694 cm^{-1}) does, though, coincide with that reported by Banister and Hauptman for "free" polymer.[8]

Further characterisation can be achieved in a number of ways (NB all techniques were performed on samples which had been well washed with CH_2Cl_2 to remove variable amounts of S_4N_4 which crystallise on the zeolite surface). Powder X-ray diffraction

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† This paper is dedicated to the memory of Dr Judith Corker (1967–98) who provided many of the initial ideas behind this work.

‡ Electronic supplementary information (ESI) available: Video of the interaction of S_2N_2 with Na-ZSM-5. See DOI: 10.1039/b711290d

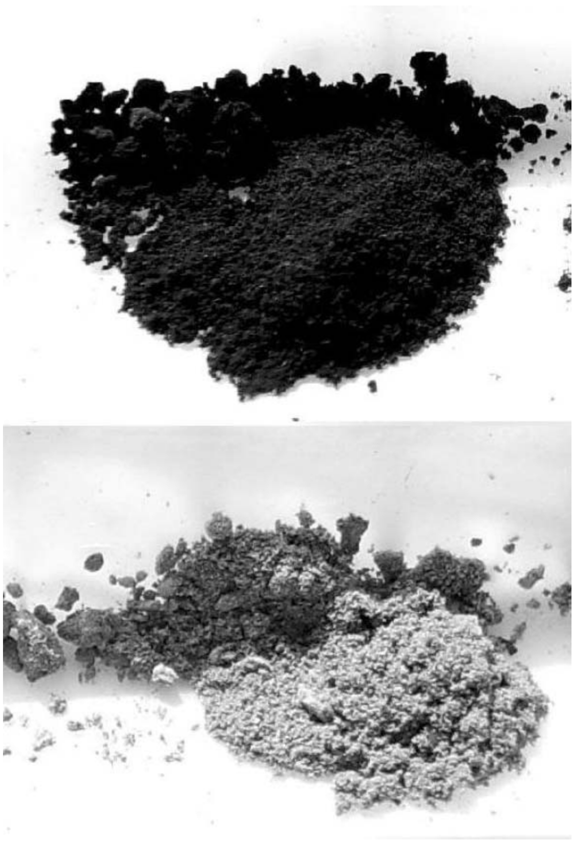


Fig. 1 The products obtained when Na-ZSM-5 (upper) and TPA-ZSM-5 (lower) are exposed to S_2N_2 vapour. Full darkening of the Na system is complete within a few minutes while the TPA sample shown had been exposed overnight. Note that Na-ZSM-5 itself is colourless.

was used to assess the zeolite before and after exposure to S_2N_2 and the powder diffraction data are given in Fig. 3. A significant change in relative intensities of the zeolite reflections can be observed and reflections characteristic of S_2N_2 or the polymer are absent from the pattern. The broadening of the zeolite reflections is indicative of loss of periodicity in the structure associated with disordered occlusion of a host species. This conclusion is further bolstered by the fact that weight change experiments reveal that calcination of the product at 300 °C leads to removal of the incorporated polymer. After this has been achieved, the X-ray powder pattern reverts to exactly that of Na-ZSM-5 *i.e.* the changes shown in Fig. 3 are not simply indicative of breakdown in material crystallinity. Further evidence of internal $(SN)_x$ inclusion is obtained by reacting TPA-ZSM-5 (which contains bulky tetrapropylammonium cations within the channels rather than the small Na^+ cations) with S_2N_2 vapour, in an identical manner to that of the sodium analogue. Even after prolonged exposure, the result is a product that has an off-white colour (Fig. 1, lower), and no Raman active peaks. It appears, in this case, that although the framework of the two zeolites is identical and the surfaces are the same, the difference in reactivity is the result of the cation within the pore. The bulky TPA cation appears to obstruct the ability of the S_2N_2 to enter the pores, whereas the smaller Na^+ ion has no hindering effect. All that we see, therefore, is a small degree of surface polymer formation, which results in the very slight darkening of the colour of the solid.

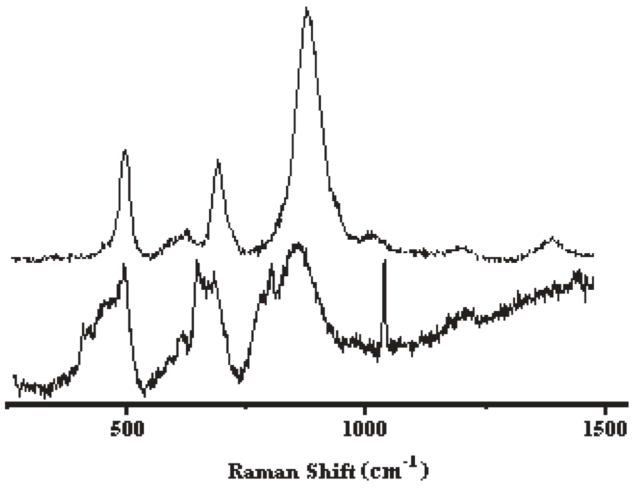


Fig. 2 Comparison of the Raman spectrum of $(SN)_x$ (lower) with that of the product of Na-ZSM-5 exposure to S_2N_2 (upper).

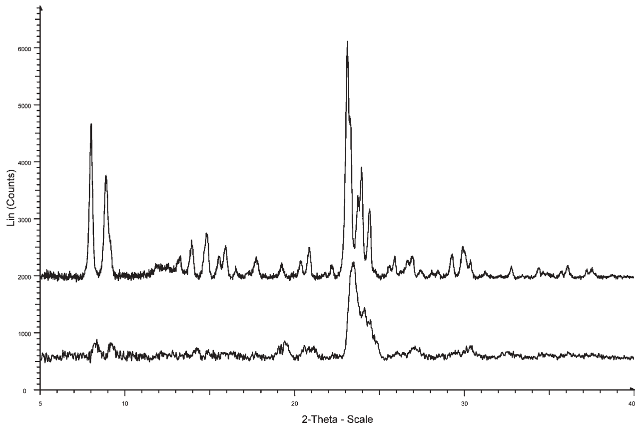


Fig. 3 Comparison of the X-ray powder diffraction patterns of Na-ZSM-5 (upper) and the material obtained upon exposure of the zeolite to S_2N_2. Note that upon heating the latter product to 300 °C, the powder pattern of the resulting material reverts back to that of Na-ZSM-5.

Further confirmation of the inclusion of $(SN)_x$ comes from chemical reactivity of the system. In contrast to other S–N species such as S_4N_4, the use of $(SN)_x$ as a synthon in, for example, transition metal reactions, has been little studied. As part of this investigation we have shown that a stirred suspension of the polymer in thf slowly dissolves as it reacts with the Pt(0) species $Pt(PPh_3)_3$ to generate $Pt(S_2N_2)(PPh_3)_2$ (as revealed by ^{31}P NMR). The latter is a well known example of a metal S–N complex and also forms in the analogous reaction with S_4N_4;[9] a more detailed report of this result will be presented in due course. Crucially for this study, however, the zeolite/S_2N_2 product does *not* react in the same manner—even stirring for many days does not result in loss of the dark black colour. Had this material simply been zeolite coated with $(SN)_x$ on its surface then it would be expected to react in effectively the same manner as "free" polymer. That it does not, confirms that the $(SN)_x$ is present within the zeolite structure, protected from reaction with the platinum species.

The question of the degree of loading of $(SN)_x$ into the cavities of the zeolite can be at least partially addressed through elemental analysis results. A typical sample of the zeolite after overnight exposure to S_2N_2, and then washing with CH_2Cl_2 to remove surface S_4N_4, reveals a nitrogen content of 4.4%. Assuming no surface bound $(SN)_x$ is present, this equates to *ca.* 21 SN units per unit cell of Na-ZSM-5. Within "free" $(SN)_x$ the length taken up by the repeat S_2N_2 unit is *ca.* 2.9 Å and so 21 SN units would amount to an overall length of some 30.5 Å. This relates to a *b*-axis pore length of 19.9 Å within the zeolite, which with two channels per unit cell results in an effective channel length available of 39.8 Å. Taken at face value this calculation would suggest 77% of available pore length has been taken up by polymer; in reality this is a very approximate figure as it of course takes no account of the exact spatial arrangement of the polymer within the channels. We have thus far been unable to generate crystalline material of sufficient size to attempt full characterisation by single-crystal X-ray diffraction.

Unfortunately, attempts made to analyse conductivity changes following polymeric inclusion into Na-ZSM-5 have, thus far, been unsuccessful. We attribute the lack of bulk conductivity to the likely disorder and increased amount of defects along the S–N backbone, once encapsulated within the small crystallites of the zeolite. Work to address this issue is underway. However, it is clear that the reaction of S_2N_2 with Na-ZSM-5 constitutes the first example of a conceptually obvious means of modifying conducting $(SN)_x$ and as such the results should stimulate interest in the (re)investigation of similar systems. Indeed, it is worth noting that preliminary investigations on our part indicate colour changes occur when kaolinite and silica sodalite are exposed to S_2N_2 in a similar manner, suggesting that many more solid-state structures may be capable of incorporating the polymer.

We are grateful to Prof. Derek Woollins, University of St. Andrews, for very helpful advice on S_2N_2 generation and to John Spray, Loughborough University, for the preparation of the custom apparatus used to achieve this.

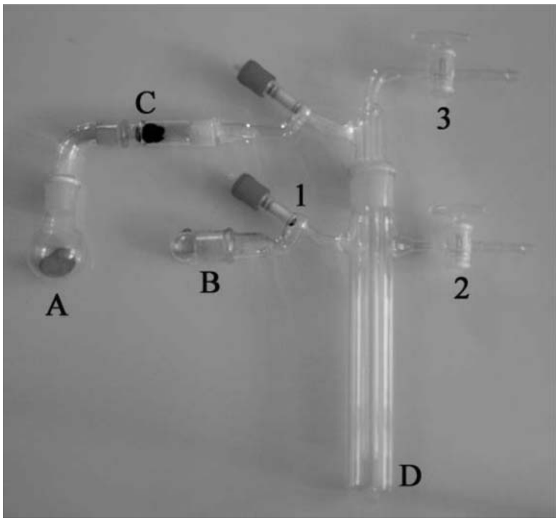
Notes and references

§ **Safety note!** In the pure form both S_4N_4 and S_2N_2 are pernicious explosives, the latter having been reported to spontaneously detonate at ambient temperatures. Although we have not encountered the latter problem, all work involving this material must be carried out with appropriate blast screening.

Prior to its use, Na-ZSM-5[10] was dried in an oven at 110 °C for a minimum of 3 h. S_4N_4 was freshly recrystallised from toluene prior to use. CH_2Cl_2 was dried over, and distilled from, calcium hydride; all washings were performed under a nitrogen atmosphere.

Preparation of S_2N_2 and exposure to Na-ZSM-5: S_2N_2 was prepared using a modification of the traditional route (the cracking of S_4N_4 vapour over heated silver wool),[11] using a tailored, compact variation on the previous apparatus, as shown below. Flask A was charged with S_4N_4 (0.70 g), flask B with Na-ZSM-5 (100 mg) and silver wool (1.00 g) was placed in connection tube C; with taps 1 and 2 closed, the whole of the remainder of the apparatus was then evacuated under dynamic high vacuum *via* tap 3. Heating tape (0.5 m, Isopad S45 tape with an Isopad ML10 thermal controller) was wrapped around tube C, and its temperature raised to 300 °C. With a liquid-nitrogen trap in place over flask D, a thermostatically controlled oil-bath (90–100 °C) was raised so that it submerged the entirety of flask A. (***N.B.*** A maximum gap of *ca.* 0.5 cm from the top of the oil-bath to the beginning of the heating tape was ensured). S_2N_2, formed as clear/white crystals within the collection vessel. The typical reaction time to use up all the S_4N_4 was *ca.* 4 h.

Tap 1 was then opened and after evacuation of the whole apparatus tap 3 was closed and the liquid-nitrogen trap removed. Upon warming, the volatile S_2N_2 was then able to diffuse into flask B and react with the Na-ZSM-5. An intense colour change from the white Na-ZSM5 to a dark blue–black product ensued over the course of several minutes. The reaction was left overnight to ensure completion. To remove S_4N_4, the product was washed with CH_2Cl_2 until the washings ran clear (*ca.* 50 cm^3).



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