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Paul F. Kelly, Roberto S. P. King and Roger J. Mortimer

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Paul F. Kelly,* Roberto S. P. King and Roger J. Mortimer

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Exposure of fingerprints to S_2N_2 vapour results in the prints being visually imaged by polymeric $(SN)_x$ on an unprecedented range of media; in addition, the polymer forms in response to the interaction of S_2N_2 with traces of inkjet inks, for example the minute amounts left by the contact between printed paper and an envelope.

Some three decades ago, the discovery of the fascinating conductivity properties of $(SN)_x$ stimulated much interest in both the polymer itself and in its precursor, the four-membered square molecule S_2N_2.[1] Interest in both species continues to this day; thus recent work has, for example, probed the structure of both the monomer[2] and of the polymer,[3] and investigated the polymerisation process.[4] Work in our group has looked at polymerisation within the confinement of a zeolitic system[5] and at preparation of selenium analogues.[6] For all this interest, however, and despite the intensity of the initial work prompted by the first observations of superconductivity,[7] practical applications of the polymerisation process, and utilisation of the polymer, have largely remained elusive. Although some success at incorporating the polymer into functional systems has been recorded (see examples quoted in ref. 1), the efficiency and stability of such arrangements appears to have mitigated against realistic applications. Here we report an unexpected observation regarding the interaction of S_2N_2 with forensically pertinent materials, and show that polymerisation may be induced and visualisation of the material effected through the resulting dark blue/black polymer.

Disulfur dinitride, S_2N_2, can be generated by the thermal cracking of S_4N_4 through silver wool,† and in the course of previous work on loading this material into zeolite cavities, we reported a modified apparatus that allowed its production efficiently and safely.[5] The latter reactions were brought about by introducing the zeolite into vacuum systems containing S_2N_2, the volatile nature of the latter then meaning that simply warming the system to ambient temperature under reduced pressure allowed the nitride to diffuse into the samples. During the course of such work it became apparent that the nitride interacted with fingerprints that were randomly present on sample vials containing the zeolite samples. This serendipitous observation lead to a more systematic evaluation of this process.

Samples containing fingerprints on a range of media were introduced to S_2N_2 atmospheres using the same reaction vessels previously employed in the zeolite work.[5] Fig. 1 illustrates examples of prints obtained from six different media, chosen to represent as wide a variety of porosity, chemical composition and morphology as possible. In all cases it is apparent that interaction of S_2N_2 with the fingerprints has induced polymerisation, which has then progressed with time (typical exposure time was 2–3 h), eventually imaging the print. It is important to note a number of points about this effect. Firstly, the materials in question were not primed or cleaned in any way—simply used "as received". Secondly, prints placed on the materials were not deliberately charged with excess secretions by deliberate loading, they were merely performed as straightforward thumb prints, from a number of individuals, in a manner consistent with the everyday deposition of prints pertinent to forensic application. Finally, because the polymer is a dark blue/black colour, all the prints shown are immediately apparent to the naked eye—those in Fig. 1 have simply been photographed (with magnification in the case of the paper sample, to give an indication of the level of resolution achieved) and the colour removed.

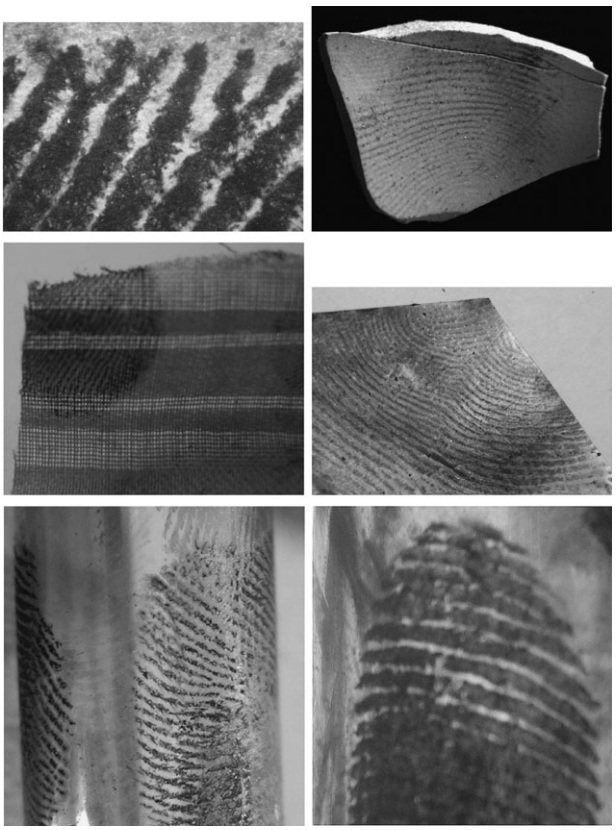

Fig. 1 The induced growth of $(SN)_x$ over latent fingermark residues on various sample surfaces (Clockwise from top left: paper, pottery, aluminium foil, clingfilm, glass, cotton).

Department of Chemistry, Loughborough University, Leics, UK LE11 3TU. E-mail: P.F.Kelly@lboro.ac.uk; Tel: +44(0)1509222578

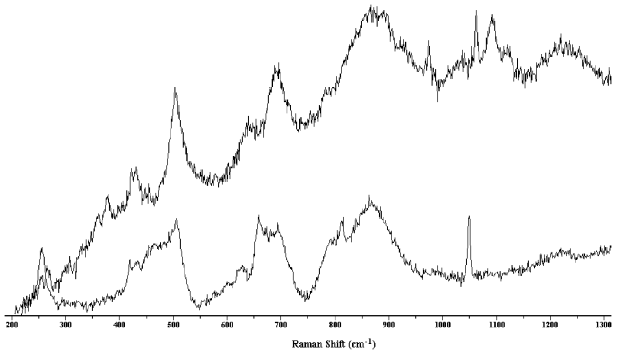

Fig. 2 Comparison of the Raman spectrum of $(SN)_x$ (lower) with that grown on the latent fingermarks (upper), obtained through *in situ* Raman microscopy.

The presence of the polymer in the ''developed'' prints is strongly hinted at by the colour of the material (dark blue/black, though golden in strong reflected light) as there are few chromophores of this nature within sulfur–nitrogen chemistry.[8] It can be confirmed, though, by the use of Raman microscopy (Fig. 2). The developed prints appear air stable, for many days (at least) and, if anything, are even more stable to aerial hydrolysis than bulk samples of the pure polymer. All samples are indefinitely stable under an inert atmosphere, however. The nature of the initial interaction between the S_2N_2 and the materials present in the print has yet to be fully elucidated. Interestingly, prints can be obtained from paper which (after placement of the fingerprint) has been soaked under water or under ether, and then dried. Different components of the print would be expected to be removed in each case, but either residue appears to still be amenable to this technique, suggesting that more than one class of component can interact with the nitride.

In light of the above success, the interaction of S_2N_2 with other substrates was investigated. One of these was inkjet ink, the assumption being that it might act as a nucleation site for polymer growth, and indeed preliminary results indicated that the latter did indeed form around the small amount of ink present in ''washed out'' images.[9] In fact, subsequent work revealed that S_2N_2 is exceptionally sensitive to components of this ink, so much so that invisible traces left by direct contact can be enhanced. This is illustrated in Fig. 3; here, text has been printed, allowed to dry and then placed in an envelope. This was left overnight (with a small book placed on the envelope to ensure constant contact) and then the envelope opened, the contents removed, and the patch of envelope that had been in contact with the print was cut out. At this stage this area appeared completely blank; upon exposure to S_2N_2, however, the text transferred from printed paper to envelope, *via* the small amount of ink diffusion, is ''developed''. Upon being removed from the vacuum apparatus and photographed the presence of text is clearly visible (in, of course, a mirror image).

The interaction of S_2N_2 with traces of inkjet components is so sensitive that the minute amounts diffusing through an entire sheet of paper can be detected. Thus, in Fig. 4, an image was printed and placed in an envelope; a sheet of paper was placed onto the envelope and the combination weighted to keep the components in place. After a number of days the external sheet was removed and the area adjacent to the image within the envelope cut out and exposed to S_2N_2 in the usual manner. Although rather poorly resolved, the image from inside the envelope is nevertheless clearly visible (in this case the image has been contrast enhanced).

Fig. 3 Close-up of the image obtained when a sample area (*ca.* 1″ width) from the inside of an envelope, which had been in contact with 12-point inkjet text, was exposed to S_2N_2. Note that before exposure the area appeared completely blank and that the above is the raw image, with no processing to the original digital photograph, save colour removal from the paper. Of course this is a mirror image of the original text; subsequent digital processing can correct this, and further resolve the text *via* simple contrast enhancement.

This result clearly indicates that initial interaction of S_2N_2 with a component of the inkjet ink can be initiated at extremely small quantities of the latter; presumably then further crystallisation of the polymer occurs over this initial product, and thus the image is built up. This diffusion experiment also shows that it must be a liquid component of the ink that is responsible for the effect. Direct contact of printed paper to blank sheets could transfer small amounts of solid material which could, conceivably, act as nucleation sites for polymer growth. However, this could not produce results such as those illustrated in Fig. 4. Thus it is some mobile component of the ink which is responsible, and future work will attempt to determine the nature of this component.

The results with fingerprints and with inkjet clearly highlight and unexpected forensic promise associated with the S_2N_2/$(SN)_x$ system. This is particularly true in the fingerprints case

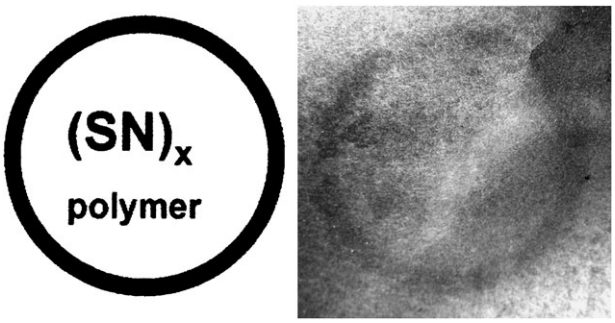

Fig. 4 (left) Original image printed out in inkjet and then placed in an envelope; (right) image (contrast enhanced) obtained without opening the envelope, *via* enhancement (using S_2N_2) of the minute amount of inkjet diffusing through the envelope and on to an external sheet of paper (*n.b.* the mirror image is shown here for easier comparison with the original).

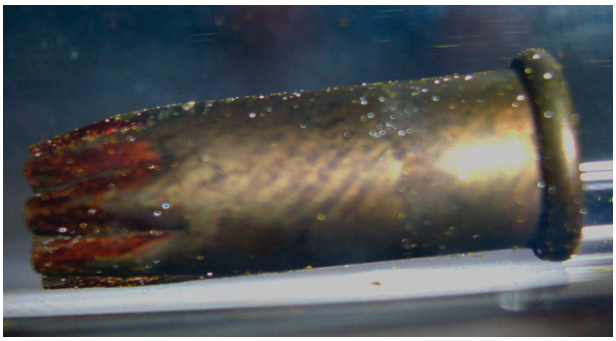

Fig. 5 Fingerprints (deposited before firing) developing on a spent blank gun cartridge, photographed *in situ* during exposure to S_2N_2.

as, despite the long history of print analysis, there is still a keen and active interest in the development of new techniques for latent fingermark enhancement/imaging.[11–17] Of all types of fingermark evidence, the latent print is not only the most commonplace, but also the most difficult to detect since they are largely invisible and typically require either chemical (ninhydrin, DFO, *etc.*), optical (luminescence, UV, *etc.*), or physical (powdering, vacuum metal deposition (VMD), multi-metal deposition (MMD), *etc.*) treatment to differentiate them from the substrate material to which they are bound. Unfortunately, due to the ever increasing array of surface types and materials (porous, non-porous, semi-porous, textured, recycled *etc.*) many detection techniques are effective on some substrates, but not others. Often, therefore, multi-step sequencing of detection techniques is essential for optimised clarity of results.[18] Intriguingly, it appears that $(SN)_x$ growth across fingermark residues is not affected by surface type. We have shown good detection is possible on both porous, semi-porous and non-porous substrates. Common problematic samples, such as aluminium, cotton (Fig. 1) and detonated cartridge shells (Fig. 5) (where the heat generated through firing can deplete/disrupt fingermarks on the shell casing) have all provided positive results.

The use of an inexpensive, non destructive, solvent free, self imaging material could be considered the ideal technique for latent fingerprint detection; especially if its use could be extended to various surface types. In many ways S_2N_2 fits the bill very effectively, thanks to the versatility of the media upon which prints can be developed, the fact that clearly visible images are generated, the fact that exposure times are quite low (prints start to develop within minutes of exposure) and that it is non destructive and non solvent based. Clearly there are limitations to the technique, thanks to the fact that the apparatus required for the generation of S_2N_2 would, in its current guise, preclude portability; in addition, care is required in the handling of the S_4N_4 starting material. That said, the continued requirement for new fingerprint imaging methods means that the versatility of the technique could make it viable, alongside other vacuum deposition techniques currently in practice. When the unusual results with inkjet interactions are also considered, it is clear that the venerable S_2N_2/$(SN)_x$ system still has plenty of potential to surprise us.

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. We are endebted to Dr Helen Reid of Loughborough University for very helpful discussions during the early stages of this work.

Notes and references

† **Safety note!** In the pure form both S_4N_4 and S_2N_2 are friction sensitive.

For fingerprint detection attempts, all sample surfaces were contaminated with fingermarks from various individuals. For ink transfer detection attempts, images/script were printed onto paper (Epson Stylus Photo R26 inkjet printer)), allowed to dry and then placed in contact with the appropriate media. Contact between the two surfaces was initially ensured through use of a paperweight. In such cases all contact surfaces were visibly image free prior to S_2N_2 exposure.

Preparation of S_2N_2 and exposure to materials.

S_2N_2 was prepared using a modification of the traditional route (the cracking of S_4N_4 vapour over heated silver wool),[10] using a tailored, compact variation on the previous apparatus, as described previously,[5] and the target sample(s) (fingerprint or ink contaminated) were placed in the sidearm. Upon warming, the volatile S_2N_2 was then able to diffuse over the target sample. In the case of fingerprints, a faint red colouration was noted along the ridges of the print within just a few minutes of exposure. Further exposure for *ca.* 2–3 h allowed for full "development" of the image as dark blue/black polymer. In the case of inkjet traces, a longer exposure time was required, with samples typically left overnight under the vacuum/S_2N_2 atmosphere.

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