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## COMMUNICATION

# Water soluble polymers, solid polymer membranes, and coated fibres as smart sensory materials for the naked eye detection and quantification of TNT in aqueous media.

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**This study developed sensory polymeric materials for the colorimetric sensing of TNT in aqueous media. Solid films and coated fabrics permitted the detection of TNT, through colour change, and its quantification, by taking a picture of the materials and processing their RGB parameters to define the evolved colour.**

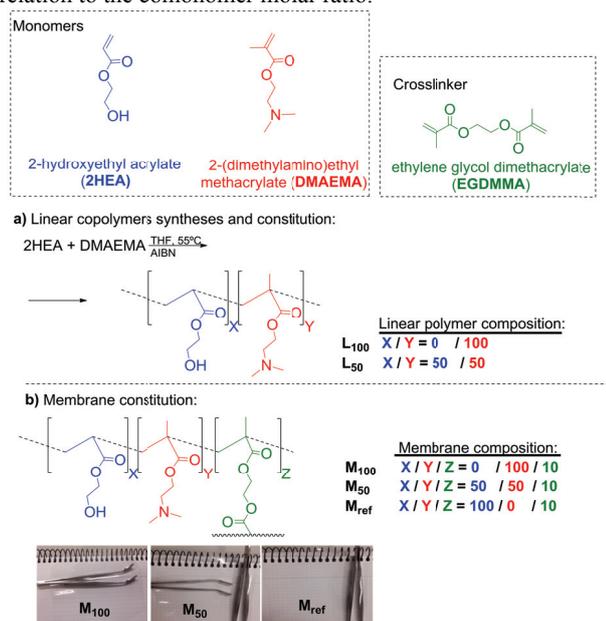
The detection of explosives by non-specialised personnel using rapid, cheap techniques is a challenging issue that has arisen from societal concern about their widespread use in mining industries, military endeavours, and terrorist attacks. The detection and quantification of explosives is twofold, through vapour detection and in solution. The former is related to homeland security and humanitarian efforts such as demining, for instance, and the latter with forensic and criminal investigations and environmental control and remediation. Among the broad set of explosives, 2,4,6-trinitrotoluene (TNT) is one of the most widely used in civil and military applications, and its detection in solution in groundwater or extraction from soil is necessary for the control and remediation of abandoned military sites, industrial waste, and spills by explosive-related industries because nitroaromatics are blood and liver toxins that can be absorbed by the skin or gastrointestinal tract.<sup>1</sup> In the same way, TNT's detection in solutions of washed scrap-metals and residues are essential in terrorist strike investigations. With these needs in mind, we undertook the preparation of water-soluble polymers, solid sensory polymer membranes with gel behaviour, and smart fibres made from polymer-coated yarns as colorimetric chemosensing materials for the naked eye detection of TNT in aqueous solutions.<sup>2-6</sup>

The well-known formation of highly coloured complexes of the electron-deficient aromatic ring of TNT with Lewis bases, such as amines, alkoxy, and hydroxyl groups, under mild conditions, also called the Meisenheimer complexes,<sup>7-11</sup> has been exploited for the detection of nitroaromatics using colour changes through UV/Vis spectroscopy. Following this approach, we engaged in the preparation of colorimetric chemosensory polymeric materials using a costless commercial acrylic monomer, 2-(dimethylamino)ethyl methacrylate (DMAEMA), which contains an amine group as a colorimetric sensory moiety for TNT. This was a different methodology than that usually followed to achieve sensitivity and the selectivity challenges encountered in explosive

sensing, which is usually carried out using conjugative polymers and is typically based on fluorescence quenching,<sup>12,13,14,15</sup> and not in colour variations. Both the thermally initiated radical homopolymerisation of DMAEMA and copolymerisation of DMAEMA with the hydrophilic co-monomer 2-hydroxyethyl acrylate (2HEA) rendered water soluble linear polymers, L<sub>100</sub> and L<sub>50</sub>, respectively (Scheme 1), whose colourless solution in water containing organic solvents developed red colours in the presence of TNT. The addition of a crosslinker to DMAEMA or to a mixture of DMAEMA/DMAEMA permitted the preparation of film shaped solid membranes with thicknesses of 110 µm, both lipophilic and hydrophilic and with gel and organogel behaviour, named M<sub>100</sub> and M<sub>50</sub>, respectively (Scheme 1). The membranes were colourless and transparent and were cut with an office puncher into easily handled sensory discs with diameters of 5 mm. The immersion of the sensory discs in solutions containing TNT turned them reddish in minutes. Moreover, the coating of white cotton fibres and yarns allowed for the preparation of intelligent garment pieces that turned reddish upon coming into contact with organic/aqueous solutions containing TNT. Apart from the visual detection of TNT and its quantification by the UV/Vis technique, the solid materials also permitted its quantification using the colour definition, or the RGB parameters, of a digital picture taken with a conventional camera or smartphone, avoiding the use of time-consuming techniques requiring operation by skilled, specialised personnel.<sup>16-18</sup> A reference membrane M<sub>ref</sub>, without sensory amine motifs, was also prepared for comparative and control purposes (Scheme 1).

The polymers were characterised as sensory materials prior to testing. Thermal resistance is a key parameter of materials for final applications and was evaluated for the membranes using thermogravimetric analysis (TGA) (Table S1 and Figure S1). The decomposition temperatures of membranes that resulted in 5% loss under a nitrogen atmosphere (*T*<sub>5</sub>) were approximately 250 °C, indicating that the materials had a reasonably good thermal stability for sensing applications. The chemical constitution of the M<sub>ref</sub>, as derived by FTIR spectra (Figure S2), corresponded to the proposed structure ( $\nu_{\text{OH}} = 3033\text{-}3696\text{ cm}^{-1}$ , broad signal;  $\nu_{\text{C=O}} = 1721\text{ cm}^{-1}$ ), and its spectral pattern resembled the structure of the well-known poly(2-hydroxyethyl methacrylate).<sup>19</sup> No significant changes were observed between M<sub>ref</sub> and M<sub>50</sub>; in M<sub>100</sub>, the absence of the hydroxyl group was in accordance with the absence of  $\nu_{\text{OH}}$

approximately  $3400\text{ cm}^{-1}$ . The solvent-swelling percentage (SSP) or solvent uptake, i.e., the hydrophilicity and lipophilicity, is a strategic parameter in the design of solid sensory materials because the target molecules enter the membrane, which is where the sensing event takes place, by diffusion into the solvent-rich membrane gel or organogel phase. The SSPs of the membranes in water were 61% and 54%, and in acetone they were 41% and 38% for  $M_{100}$  and  $M_{50}$ , respectively. It has been proven that a SSP higher than 40% and lower than 100% is appropriate for both the rapid diffusion of chemicals into the membrane and maintaining the tractability, in terms of mechanical properties, of the water-swelled materials. Furthermore, these data showed that the constitution of the material provided it with an amphiphilic character useful for detection in both organic and aqueous environments. In relation to the linear polymers  $L_{100}$  and  $L_{50}$ , the characterisation data were in full agreement with those of the membranes (Figures S3-S5 and Table S2). The NMR data confirmed the structure and composition of the copolymer  $L_{50}$  in relation to the comonomer molar ratio.



**Scheme 1.** Sensory material preparation and codes: a) linear copolymer and b) membranes, with pictures showing the materials' colourlessness and transparency.

After characterisation, the material's performance as a chemosensors was evaluated. It is known that the interaction of an amine with TNT leads to the development of a reddish colour, as was the case with the sensing acrylic monomer **DMAEMA**. However, the sensing was highly specific and no colour change was observed upon the addition of other nitroaromatic compounds, such as 2,4-dinitrotoluene (2,4-DNT) and 4-nitrotoluene (4-NT) (Figure S6). This interaction is based on the Meisenheimer-like complexes, which are species in equilibrium, including charged species, and the partial transfer of electronic charge from an amine group, behaving as a Lewis base, to the aromatic nucleus of the nitro-compounds.<sup>8,20</sup> Figure S7 reveals a gradual shift in the proton resonances for the methyl groups of tertiary amine and the methylene group (N-CH<sub>2</sub>-) to a lower field, along with the downfield shift of the TNT's aromatic proton resonance, confirming the interaction of **DMAEMA** with the TNT.<sup>21,22</sup> Forensic and environmental samples prepared upon extraction with organic solvents usually contain water, and consequently, the ideal testing media in lab proof-of-concept sensory systems for this purpose are organic solvents enriched with water. However, the Meisenheimer complex formation is described to be

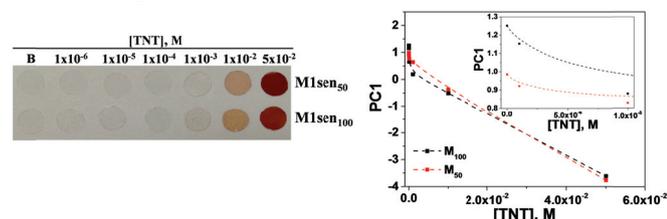
strongly affected by the presence of water,<sup>11,23</sup> so we analysed the behaviour of the monomer in dry acetone and in acetone:water (80:20, v:v), resulting in an enhanced response in the latter (Figure S8). We chose acetone because it is a common solvent for extraction and forensic applications, it is cheap, samples can be rapidly concentrated at low temperature, it does not present important environmental concerns, and it gave satisfactory TNT titration curves (Figure S9) using the UV/Vis technique, with a limit of detection (LOD) and limit of quantification (LOQ) of  $5.7 \times 10^{-5}$  M and  $1.7 \times 10^{-4}$  M, respectively.<sup>24</sup>

In a similar fashion, stock water solutions of  $L_{100}$  and  $L_{50}$  were used to prepare sensory acetone:water (80:20, v:v) solutions with a sensory dimethylamino motif concentration of 1.2 mEq/L. The UV/Vis titration curves (Figures S10 and S11) allowed for the detection of TNT with a LOD/LOQ of  $4.2 \times 10^{-5}/1.3 \times 10^{-4}$  M and  $9.0 \times 10^{-5}/2.7 \times 10^{-4}$  M for  $L_{50}$  and  $L_{100}$ , respectively. These limits were reasonably good for the detection of TNT in solutions according to previously reported data.<sup>11,25</sup> Moreover, the aqueous solutions of  $L_{100}$  and  $L_{50}$  were an environmental friendly tool for preparing sprays with which to detect *in situ* the presence of TNT on surfaces, as demonstrated in the detection of cotton fibres that had been in contact with TNT (shown in the video provided as ESI).

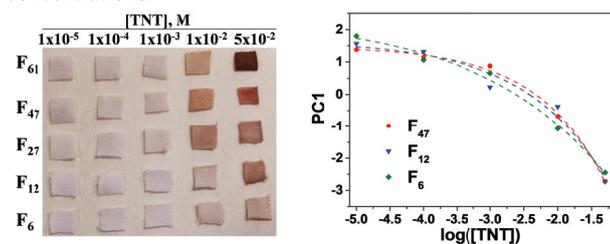
The solid sensory kits were manufactured from the  $M_{100}$  and  $M_{50}$  using a conventional office sheet paper punch to cut out discs 5 mm in diameter. Colour changes were visible to the naked eye after immersing the discs in an acetone:water (80:20, v:v) solution of TNT for 2-3 minutes, indicating the efficient formation of Meisenheimer complexes. Moreover, the rapid visual detection of TNT was highly selective, with the materials remaining silent with other nitroaromatic compounds, such as 2,4-DNT and 4-NT (Figure S12) when following the same behaviour that exhibited the sensory monomer **DMAEMA** in solution. To determine the response time of the two sensory membranes, sensory discs of  $M_{100}$  and  $M_{50}$  were immersed in a quartz cuvette containing a solution of TNT ( $1 \times 10^{-2}$  M) in an acetone:water solution (80:20, v:v), and the spectra were recorded periodically every 45 s (Figure S13). A detection time of 25-30 min was adequate, and the optimal time for the sensing experiments was considered to be 1 h when accounting for the instability of Meisenheimer complexes under ambient conditions and the decomposition of TNT in solution.<sup>10</sup> A naked eye titration of the TNT acetone:water (80:20, v:v) solution was carried out by dipping the colourless discs into the solution for 1 h and observing the colour development (Figure 1). A visual colour change was observed at a TNT concentration of  $1 \times 10^{-3}$  M. After photographing the discs, the three RGB parameters of each disc were processed using principal component analysis (PCA), extracting one principal component (PC1), which gave an account of > 96% of the information on the three RGB parameters, thus permitting the simple elaboration of 2D titration curves ([TNT] vs. CP1) with a concomitant noise reduction (the principal component parameters are shown in Table S3-S13). The procedure is shown in a cartoon in Figure S14 and described in depth in recent publications by our Research Group.<sup>26,27</sup> The LOD/LOQ were  $1.1 \times 10^{-4}/3.5 \times 10^{-4}$  M for the sensory material  $M_{100}$  and  $1.4 \times 10^{-4}/4.3 \times 10^{-4}$  M for  $M_{50}$ . In light of previously reported data, these were concluded to be extremely sensitive sensory materials for the detection of TNT. This conclusion was especially true considering that the quantification was carried out with costless materials, *in situ*, and using the hardware and software of a smartphone/laptop.

We extended our study to the preparation of smart fibres for the colorimetric detection of TNT, as an attractive class of substrate for fabricating wearable chemical polymeric sensors. Fibres from white cotton fabric were coated with the sensory polymer prepared from **DMAEMA** and **EGDMMA**. 1x1 cm cotton fabrics were coated with

61, 47, 27, 12 and 6%, by weight, of the sensory polymer to render smart fabrics with references  $F_{61}$ ,  $F_{47}$ ,  $F_{27}$ ,  $F_{12}$ , and  $F_6$ , respectively (see picture in Figure S15). Following the procedure described for the sensory disc, the fabrics were immersed in acetone:water (80:20, v/v) containing concentrations of TNT ranging from  $1 \times 10^{-5}$  to  $5 \times 10^{-2}$  M. The colour changes were observed in minutes and could be visually related with the TNT concentration and the fabric's sensory polymer content (Figure 2). Similarly, the TNT concentration could be quantified with the colour definition of each fabric taken from a digital picture, giving rise, for instance, to LOD values of  $1.1 \times 10^{-3}$ ,  $2.4 \times 10^{-3}$  and  $1.8 \times 10^{-3}$  M for the coated fabrics  $F_{47}$ ,  $F_{12}$ , and  $F_6$ , respectively. The picture shown in Figure 2 was taken after immersing the coated fabrics in the media containing TNT for only two minutes, an impressive response time. This time was shorter than that corresponding to the sensory membranes, most likely because of the coated fibres' high sensory surface and the time needed for the diffusion of TNT into the sensory membranes, which was highly diminished when reducing the cross section of the sensory material from one hundred of microns to a thin coating. The coating increased the rigidity of the cotton fabric, with a concomitant loss of garment comfort, though this increase was not apparent to the touch with the lower polymer containing fabrics,  $F_{12}$  and  $F_6$ , from which full garments could be prepared. On the other hand, all of the coated fabrics could be used to sew small TNT sensory labels into conventional garments.



**Figure 1.** Titration of TNT using the RGB parameters from digital photographs of the sensory discs. These pictures of the sensory films,  $M_{100}$  and  $M_{50}$ , were taken after immersing the discs in acetone:water (80:20, v/v) for 1 h, and the reduction of the three parameters (R, G, B) to one principal component (PC1) was achieved via principal component analysis. The pictures of the discs depict the colour variations caused by differences in the TNT concentrations.



**Figure 2.** Digital picture taken from squares of lab coat fabric dipped for 2 minutes in TNT solutions of concentrations ranging from  $1 \times 10^{-5}$  M to  $5 \times 10^{-2}$  M, using acetone as a solvent (left), and titration curve using the single principal component (PC1) obtained from the three digital colour parameters via principal component analysis.

In summary, we prepared sensory polymeric materials, both as linear soluble polymers and solid-film shaped networks, and coated fabrics that permitted the colorimetric detection of TNT in solution. Upon putting the sensors into contact with solutions containing TNT, colour development was observed in minutes. Pictures of the sensory films and coated fabrics permitted the explosive's quantification by processing the RGB parameters that defined the digital colours, with limits of detection between the micro and millimolar ranges.

Applications in the forensic and environmental remediation fields can be envisaged from these results. However, we are working in the improvement of the sensitivity of the materials by using monomers having primary instead of tertiary amines.

## Notes and references

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† Electronic Supplementary Information (ESI) available: experimental preparation and characterisation of the materials, complementary details of the colorimetric sensory of TNT with linear polymers and with membranes, principal component analysis procedure and data, and demonstrating video. See DOI: 10.1039/c000000x/

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