

# Hydrogen-Bond Acidic Polyhedral Oligosilsesquioxane Filled Polymer Coatings for Surface Acoustic Wave Sensors

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**ABSTRACT:** A series of novel polyhedral oligosilsesquioxane nanofiller compounds functionalized with hydrogen-bond acidic sensor groups was prepared, characterized by IR, <sup>1</sup>H-, <sup>13</sup>C- and <sup>29</sup>Si-NMR, and MALDI-TOF MS, and formulated into polymer coatings for 500 MHz surface acoustic wave sensor platforms. Sensor responses to the explosives simulant dinitrotoluene and to the nerve agent simulant dimethyl methylphosphonate were studied, and the performances of the polyhedral oligosilsesquioxane formulations were compared with those of conventional hydrogen-bond acidic linear surface acoustic wave sensor

polymers carrying the same sensor groups. The polyhedral oligosilsesquioxane formulations gave good initial responses to the simulants, maintained 40–65% of their original response over a period of 6 months and maintained their sensitivity down to a simulant vapor concentration of 1 ppb v. The surface compositions of the surface acoustic wave sensor coatings were characterized by sum frequency generation spectroscopy. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3171–3182, 2007

**Key words:** sensors; fillers; coatings

## INTRODUCTION

In order for array-based gravimetric chemical vapor sensors such as surface acoustic wave (SAW) sensors to collect the most chemical information, each element in the array needs to be coated with a different polymer.<sup>1,2</sup> The collection of polymers must cover the full range of solubility interactions (dispersion, dipole–dipole, and hydrogen-bonding), and needs to include nonpolar, polarizable, dipolar, hydrogen-bond basic, and hydrogen-bond acidic polymers.<sup>3–7</sup> Most polymers exhibiting these types of interactions are commercially available, except for the key class of hydrogen-bond acidic polymers, which are essential for the detection of hydrogen-bond basic entities, such as nerve agents<sup>8–15</sup> (Fig. 1) and nitroaromatic explosives in security and defense applications.<sup>15–20</sup> Hydrogen-bond acidity may be introduced into a polymer by functionalizing it with phenol or fluorinated alcohol groups<sup>4,7,13–15,19,21–25</sup> (Fig. 2). Because these groups have high polarity, they increase the glass transition temperature ( $T_g$ ) and lower the rate of vapor diffusion to an undesirable level. Hence silicon-oxygen bonds or silicon-carbon bonds

are introduced into the polymer backbone to lower  $T_g$ .<sup>4,15,16,18,19,22,23</sup>

The use of linear polymers, such as BSP3,<sup>2</sup> SXFA,<sup>4</sup> PSpFA,<sup>13,14</sup> NRL5,<sup>15</sup> and FPOL<sup>10,26</sup> (Fig. 2) as coatings for SAW sensors is well established, and dendritic hydrogen-bond acidic SAW polymers with good initial sensitivity to the nerve agent simulant dimethyl methylphosphonate (DMMP, Fig. 1) have also been reported.<sup>27–29</sup> In addition to carrying the desired hydrogen-bond acidic sensor groups and having good initial sensitivity to species such as DMMP and nitroaromatics, hydrogen-bond acidic SAW sensor polymers must be robust enough to withstand multiple vapor challenges and maintain their sensitivity over time.<sup>29–31</sup> Since the linear and hyperbranched hydrogen-bond acidic polymers discussed earlier have low  $T_g$ s and tend to be fluids at room temperature, it is difficult to attain a combination of good sensor properties and robust coating properties in a single polymeric material, although some attempt has been made to address this issue by crosslinking polysiloxane SAW coatings.<sup>31</sup> In this study, robust nanocomposite SAW coatings that maintain a good response over time<sup>32</sup> when airbrushed onto 500 MHz SAW platforms were prepared by dispersing polyhedral oligosilsesquioxanes (POSS) carrying hydrogen-bond acidic sensor groups within a nonsensing polycarbosilane carrier, and also within linear hydrogen-bond acidic polymer

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