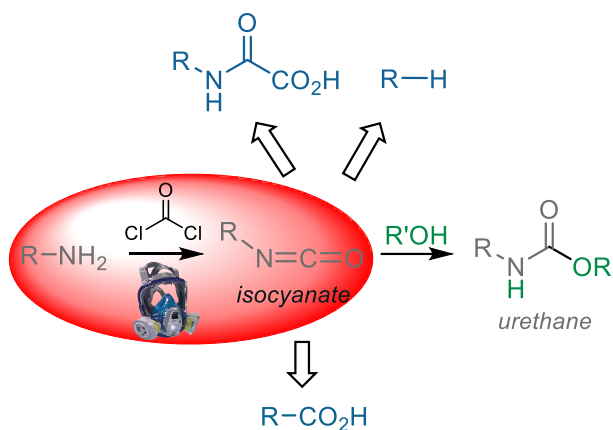


## New Approaches to the synthesis of urethanes and polyurethanes through free-radical processes

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Urethanes display attractive biological activities and constitute key structural motifs in many targets having clinical potential.<sup>1</sup> Urethanes exhibit excellent proteolytic stabilities, and are thus often used as peptide bond surrogates. They are also widely used as amine protecting groups, showing orthogonality and stability towards acids, bases or hydrogenation. The urethane linkage is also found in polyurethanes (PUs), an important class of polymers with a wide range of applications in furniture and interiors, automotive industry, electronics and appliances, packaging and footwear industries.<sup>2</sup> The addition of alcohols (polyols) to (poly)isocyanates is probably the most reliable method to access urethanes and PUs. However, the use of isocyanates in industrial applications is increasingly subjected to international regulations, as they are known to be powerful irritants and are classified as carcinogenic to animals and potentially to humans. Their synthesis also relies on the use of poisonous phosgene. This presentation will describe recent efforts in our laboratory to develop methods to access isocyanates and also directly urethanes without phosgene. Strategies relying on the use of amines,<sup>3</sup> alkanes<sup>4</sup> or carboxylic acids<sup>5</sup> based in particular on photocatalysis and metal catalysis, will be described.



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