Biobased pyrazines

Impact paragraph

As mentioned in the Introduction, this work is mostly driven by curiosity but fits well in a larger framework of sustainability efforts towards a *"green"* economy. However, science is not a system on its own, science is part of society in general and as such it is important to address the impact science has or might have on society. This Chapter intends to provide insight in the impact of the work described in this thesis at a scientific and at a more societal level.

The main aim of my work was to find which pyrazine containing monomers could be made from biomass and what properties these monomers might provide to corresponding polymers. Concerning the first part, it was shown that a number of functional pyrazine monomers can be easily synthesized from amino acids in a scalable fashion using the Dakin-West reaction. The developed procedure is generally applicable under safe conditions allowing scale-up to useful amounts. As a result, the Dakin-West reaction can now be considered a viable option to use in pharma and material science. Next to this, the work also showed the large potential that amino acids have as a, currently underutilized, renewable biobased starting material.

In the second part of my thesis work, a new class of pyrazine containing polymers was developed using two of these versatile building blocks. The resulting new type of polyesters show very interesting thermal behavior. One of the monomers showed melting temperatures far exceeding the other, although their structures are quite similar. By systematically changing the structure of other close analogues, I could demonstrate that the observed thermal properties are unique to this pyrazine monomer. The polymer crystal structure was determined, which showed specific interactions at the basis of the thermal properties. These non-classical or weak hydrogen bonding interactions are commonly not considered in the design of new materials. My work thus shows the importance of physical interactions in designing new materials and should provide a basis for further work in this direction using these type of biobased monomers.

Another interesting result of the work, which may deliver broader societal impact was the ability to post-modify the developed monomers and polymers. This post-modification showed that these materials have an added benefit in, that their properties can be tuned after synthesis. Next to this, the post-modification again revealed that weak physical interactions can have a large influence on material properties. In this case by showing that one fully modified material went from low melting to high melting and by showing that the surface properties of the polymers can also be modified.

All of this work is only a first step into exploring pyrazine containing polymers and their unique chemistry. Further work will be necessary to show the overall safety profile of these materials and to find their societal added benefit. If these monomers and polymers turn out to be environmental toxins they will never be commercialized. If they are found to be benign and show great benefits, for instance biodegradability or tunable properties, these materials might be very promising in numerous applications. The initial mechanical properties indicate that the materials could be used as engineering plastics, potentially replacing poly(ethylene terephthalate), poly(butylene terephthalate) or isotactic poly(propylene) while providing extra tunablity. The major challenge for any new material will remain adaptation by the market. Having published most of this work, academic-, material- and pharmaceutical-scientists can use the results in their own research and might find inspiration in the new building blocks.

Overall, the work described in this Thesis provides an insight in different materials from biomass and how little we sometimes know about physical interactions. Although not directly applicable as a replacement for fossil and unsustainable materials, the reported polymer can inspire other scientists to think more outside of the box. The work also shows how powerful a multi-disciplinary approach to new materials is. It is not only a case of synthesizing a new monomer and testing what properties the resulting polymers has but also providing a deeper understanding of those properties that provides the most scientific merit.

Next to this, I believe this work is a very good example of underappreciated blue-sky research. Work of this nature does not easily receive funding in the current funding schemes, especially since there was no earlier work in this direction. The funding provided by the Dutch Province of Limburg without any prerequisites or demands for societal impact has provided an ideal platform for the new and interesting results. Although the work has little societal impact right now, there was none at Bell laboratories or the Philips NatLab and without those institutes, we would not have cell phones, cd’s or computers. I see a bright future for (biobased) pyrazines in material science.