Thematic issue on functional polymers

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Polymer chemistry has made a lasting impact on materials science through innovative monomer design as well as improvements in catalysts, and a whole range of strategies for the controlled polymerisation of a wide variety of monomers. At the same time, polymers are indispensable building blocks for nanotechnology. Primarily of course, because of their widespread use as photoresists and as materials for e-beam and nano-imprint lithography, but more and more so as active components in hybrid polymer–silicon devices, sensors, and diagnostic devices. For future applications to have a much greater degree of functionality, the polymers must not only provide a structural support at the nanometer level, but also introduce a chemical complexity that is far greater than accessible using inorganic materials alone. This issue of *Chemical Society Reviews* highlights a number of areas of polymer science where the polymerisation of monomers as such is not necessarily the key aim of the research, but where subsequent modifications or non-covalent interactions like H-bonding and metal–ligand coordination chemistry, are new design rules in the synthesis of 'Functional Polymers'.

Hillmyer and co-workers review recent progress in the modification of polyolefins as a route to materials with new properties. Polyolefins are the largest sector of polymers produced, yet their properties are limited in terms of chemical functionality and compatibility with other, polar materials. Therefore, new strategies which offer mild routes to surface modification of polyolefins are highly desirable and this review discusses in detail catalytic oxidation as a versatile and environmentally friendly route.

Cameron Alexander and co-workers exploit non-covalent interactions *between* polymer chains as a means to generate responsive materials, highlighting the Lower Critical Solution Temperature (LCST) as unique polymer property, which can be exploited in controlled release applications. In short, the solubility of certain polymers (*e.g.* poly(*N*-isopropyl acrylamide)) is strongly dependent on temperature: at low temperature, the polymer is soluble due to H-bonding with water, but at higher temperatures the backbone is not sufficiently 'screened' and the polymers aggregate and precipitate. By introducing different (charged, acidic/basic) co-monomers, the precise temperature of the LCST can be tuned, and pH or salt sensitivity introduced.

Using non-covalent interactions greatly extends the range of structures that can be generated. Marcus Weck and co-workers discuss metal–ligand interactions as a sufficiently strong 'glue' to allow functional groups to be 'clipped on'. These interactions can be tuned by small variations in ligand structures, allowing reversible decoration of polymers with functional groups, and thereby obviating the need to devise and optimise new synthetic routes for every new monomer. By combining different non-covalent interactions, it becomes possible to precisely position different functional groups along the polymer backbone (creating blocks copolymers, random copolymers, comb polymers, *etc.*)

Rint Sijbesma takes non-covalent interactions one step further, building up whole polymers by self-assembly of cleverly designed small molecules. As a result, the polymer's 'existence' is based on the strength and extent to which self-assembly (mostly H-bonding) occurs. Solutions containing such polymers will show dramatic changes in properties such as viscosity, transparency *etc.*, depending on whether the assembly is 'on' or 'off'. Possible applications of self-assembled polymers are obviously in the area of 'smart' materials but also in optoelectronics where the use of organic building blocks must be combined with very high degrees of order to overcome the inherently low conductivity of the materials used.

The paper by Xiong and co-workers reviews an inorganic analogue of the H-bonded organic polymers mentioned above. In the paper, Cu-complexes and their coordination oligomers and polymers, their structures and potential applications as solids possessing unusual physical functional properties such as electrochemical, chiral separation, fluorescent sensing and ferroelectricity are discussed.

We hope that these five reviews provide a stimulating insight into recent progress at some of the frontiers of polymer science. It is clear that by merging polymer science with supramolecular chemistry and materials science, fascinating new chemistry is learned and we are looking forward to progress in the challenging new areas of application that are lying ahead.

Wilhelm Huck

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