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Introduction to hybrid inorganic–organic polymers

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This themed issue of *Polymer Chemistry* highlights the exciting interplay between organic and inorganic structural motifs leading to new fundamental insights and macromolecular function. Organic polymers have revolutionized modern manufacturing due to their low production cost, ease of reprocessing, and light weight. The inclusion of inorganic elements can extend the functionality of materials. For example, inorganic elements can introduce new nuclear properties (e.g. high spin orbit coupling in tellurium (<https://doi.org/10.1039/D5PY00439J>)), new electronic phenomena (e.g. sigma bond conjugation in polysilanes), and new properties such as flame retardancy (phosphorus-containing polymers) or dynamic covalency (sulfur-containing polymers). Many structures that are inaccessible to hydrocarbon monomers due to strain, such as small cages or rings, are also more readily formed by inorganic elements due to their more ionic bonds (e.g. polyhedral oligomeric silsesquioxanes).

As carbon's near neighbour, silicon features prominently in both inorganic and hybrid polymer systems. Polysilanes have a backbone of Si–Si bonds with organic side chains. The first polysilane

was reported in 1924, making this class of hybrid polymer nearly as old as Staudinger's 1920 articulation of the macromolecular hypothesis. In this themed issue, new approaches to the incorporation of Si–Si bonds into polymers are reported (<https://doi.org/10.1039/D5PY00405E>). Su *et al.* focus on the incorporation of silicon clusters as side chain pendants by Ru-initiated ring-opening metathesis polymerization of a novel norbornene, functionalized with a [2.2.2]-bicyclosilane (<https://doi.org/10.1039/D5PY00465A>). Due to its constrained conformation, enabling destructive quantum interference, the [2.2.2]-bicyclosilane-polymer hybrid is appealing as a low dielectric, insulating material.

Polysiloxanes like polydimethylsiloxane (PDMS) are the most widely commercialized hybrid inorganic–organic polymers. Several papers in this themed issue focus on chemical strategies for the introduction of novel, functional organic side chains onto the PDMS backbone (<https://doi.org/10.1039/D5PY00431D>, <https://doi.org/10.1039/D5PY00058K>, <https://doi.org/10.1039/D4PY01316F>). Kaneko *et al.* prepared polysiloxanes containing both methyl side chains and catechol-functionalized pendants, which showed enhanced adhesive properties, including the ability to adhere dissimilar materials (<https://doi.org/10.1039/D5PY00442J>). The design is biomimetic, inspired by the catechol-containing amino acids found in mussels capable of adhering to both organic and inorganic surfaces.

Due to the flexibility of siloxane linkages, cages featuring Si–O bonds are readily accessible *via* condensation, with the most well-studied system in this context being polyhedral oligomeric silsesquioxanes (POSS) (<https://doi.org/10.1039/D4PY01460J>, <https://doi.org/10.1039/D5PY00192G>). These nanometer-sized siloxane cubes with tunable substituents can be used as additives or monomers for onward polymerization. Imoto *et al.* have studied the influence of incorporating POSS side-chains on the thermal stability and ease of crystallization in polymethylenes (<https://doi.org/10.1039/D4PY01222D>). The density of POSS sidechains influences crystallization outcomes with low POSS-density polymethylene exhibiting facile crystallite formation, and high POSS-density polymethylene showing low crystallinity. The results suggest that a dense tethering of bulky cages along a polymer backbone limits mobility, preventing chains from forming well-ordered domains. In contrast, a low density of cages allows greater side-chain mobility and facile organization into larger crystalline aggregates. These fundamental principles are likely transferrable to polymers featuring other inorganic cages such as carboranes and polyhedral phosphazanes.

Illustrating the potential for inorganic molecules as non-covalent additives (fillers), Tanaka *et al.* have studied combinations of luminescent POSS cages with π -conjugated polymers to uncover design principles that lead to effective white light emission in composite films (<https://doi.org/10.1039/D5PY00144G>).

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White emission requires the coexistence of two or more luminophores whose relative emissions remain balanced across the device-relevant temperature range. Films with bulky POSS cages show concerted, monotonic attenuation of emission from both the POSS and π -conjugated polymer components, preserving overall color balance.

Besides silicon, sulfur is perhaps the most prevalent inorganic element incorporated into commodity materials (*e.g.* rubber vulcanization) (<https://doi.org/10.1039/D5PY00478K>). Beyond its use as a crosslinker, sulfur has also been incorporated into polymers in the form of thiophenes, thioethers, sulfides, sulfoxides, and sulfones to exploit unique properties such as dynamic S–S bonds, strong π -conjugation, affinity for soft metal ions, and redox flexibility. Adachi and Ohshita *et al.* have taken sulfur polymers to the next level in their article which reports the synthesis, optical pro-

perties, and calculated electronic structures of polymers featuring thiaborin repeat units (containing S and B atoms) copolymerised with diketopyrrolopyrrole (<https://doi.org/10.1039/D5PY00203F>).

The unique acceptor–acceptor type p – π^* conjugated backbone renders the structures very electron-deficient. Oxidation of the sulfur to sulfone lowers the LUMO further and increases boron's Lewis acidity, resulting in reversible coordination to DMAP, which could give rise to their use in Lewis base sensing.

Also aiming for bifunctionality, Plajer *et al.* report amphiphilic block copolymers which combine a hydrophobic sulfur-rich chain with a hydrophilic polyethylene glycol block (<https://doi.org/10.1039/D4PY01415D>). These structures leverage the soft sulfur ligands to selectively spatially confine the coordination and encapsulation of soft transition-metal species (*e.g.*, PdCl_2) *via* the sulfur lone pairs, as visualised by cryo-TEM

tomography and isolated by SEC. The authors reported a second example of encapsulation, $(\text{bipyridine})_2\text{Ru}(\text{BARF})_2$, which produces uniformly loaded micelles with a red-shifted MLCT emission and preliminary photocatalytic singlet-oxygen generation, demonstrating functional behaviours relevant to metal sequestration, catalyst delivery and photodynamic applications.

As the articles in this issue show, hybrid inorganic–organic polymers represent a rich vein for fundamental and functional discoveries in macromolecular chemistry. While most studies in this issue have focused on the lighter inorganic elements (*e.g.* Si and S), the principles gleaned and properties revealed provide strong motivation for exploring the full elemental diversity of the periodic table in polymer systems. We thank all authors for their contributions and hope that this themed issue invites new researchers to this exciting research area.