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Smart Inorganic Polymers

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Polymers have a broad range of properties and play an essential and ubiquitous role in everyday life. Most of these materials are organic polymers, incorporating in their structure carbon and hydrogen, and also, in most cases, nitrogen and oxygen. Inorganic polymers – that we define as polymers incorporating inorganic elements in their backbone, either alone or in combination with carbon – are much less known, with the notable exception of polysiloxanes, also known as silicones. Inorganic polymers are a hot topic that has attracted broad and persistent interest from both academic and industrial researchers due to their special chemical and physical properties, and potential applications. A current EU-COST Action (CM1302) is dedicated to Smart Inorganic Polymers (SIPs); 7 contributions to this special issue are written by members of this network. This special issue will cover in 5 Tutorial Review and 6 Reviews, contributions about polymers including in their structure main group elements (P, B, Sn, Si) and/or metal frameworks, in particular transition metals. The vast development and rapid expansion of inorganic polymer research, from syntheses to applications, especially in nanotechnologies and for biomedical uses are emphasized in many of these reviews.

Polyphosphazenes are inorganic polymers with a phosphorus-nitrogen backbone, and have a long history: they were first reported as early as the 1890s. Currently, there are significant ongoing developments of polyphosphazenes for uses as flame retardant, as soft materials, or in the biomedical field. The tutorial review by Ian Teasdale et al. provide an introduction to the basics of the synthetic chemistry of polyphosphazenes, with some of the recent advances in their chemical synthesis. This includes not only the synthesis of polyphosphazenes with controlled molecular weights and polydispersities, but also the synthesis of branched structures, block copolymers, and supramolecular architectures.

π-Conjugated polymers and oligomers incorporating heteroatoms, such as polythiophenes, have emerged as promising materials to build electronic flexible devices such as organic light emitting diodes (OLEDs), organic field effect transistors (OFETs) or organic photovoltaic cells (OPV). New types of π-conjugated moieties incorporating phosphorus derivatives, in particular phospholes, should further expand this field. The review article authored by Muriel Hissler et al. describes the synthesis of π-conjugated phospholes and their incorporation into devices for organic electronic materials.

Icosahedral boron clusters display many peculiar characteristics, such as unique stabilities and geometric features. The development of hybrid organic-inorganic π-conjugated polymers, and of silane, siloxane and coordination polymers incorporating icosahedral boron clusters has received considerable academic and technological interest, as emphasized in the tutorial review proposed by Clara Viñas et al.. The inclusion of boron clusters both in π-conjugated and non-conjugated polymers, as doping agents in conducting organic polymers, or as a doping agent bonded to the main chain of the polymer for self-repairing are among the key features already reported. The particular properties of boron clusters may impart unconventional properties to polymers, if clusters are incorporated either non-covalently, or as part of the main chain of the polymer, or as pendant groups from the main chain.

Dendrimers are hyperbranched macromolecules, reminiscent of conventional polymers, as they are constituted of repetitive monomeric units. However, they are synthesized step-by-step, and not by polymerization reactions, hence ensuring a perfectly defined 3D structure. The tutorial review by Anne-Marie Caminade concerns inorganic dendrimers, and more precisely dendrimers incorporating either phosphorus or silicon at each branching point, in particular polyphosphorhydrazone and polycarbosilane dendrimers. It describes the main properties of both families of dendrimers in the fields of catalysis, materials and biology/nanomedicine, with emphasis on the most recent and promising properties.

Ferrocenes are prototypical metallocenes that undergo a reversible one-electron oxidation at a low potential. Incorporating covalently ferrocenes into a polymer can deeply modify its physical and chemical properties. This can be done in two ways, by incorporation into the main chain of the polymer (backbone) or by attachment as pendant groups to the polymer backbone. Two reviews discuss these topics independently. The review by Ian Manners et al. covers in depth polyferrocenylsilanes, main chain organosilicon metallopolymers consisting of alternating ferrocene and organosilane units. Synthetic pathways towards polyferrocenylsilane homopolymers and polyferrocenylsilane block copolymers are shown, essentially by ring-opening polymerisations of suitable precursors. For both homo- and co-polymers, the properties and applications are largely discussed, such as high refractive index materials, electro-actuated redox-active gels, fibres, films, nanoporous membranes, precursors to nanostructured magnetic ceramics, and etch resists to plasmas and other radiation. Applications in nanolithography, nanotemplating, and nanocatalysis, as functional micelles with core-shell structures, for ‘‘living crystallisation-driven self-assembly’’ in solution – a controlled method of assembling block copolymers into 1D or 2D structures –, are also given. Polymers bearing pendant ferrocenes, with potential applications in electrochemistry, electronics, optoelectronics, catalysis, and sensing, as precursors for patterned metal oxides and alloys, and for biology constitute the topic of the tutorial review by Rudolf Pietschnig. It is also shown in this review that the redox properties of the pendant ferrocenyl units may modify the charge, polarity, colour and hydrophilicity of the polymers, and of polymer functionalized interfaces and networks.

Polystannanes are the only type of polymers comprising a backbone exclusively constituted of covalently bound metal atoms, based on SnR_2 units. In his tutorial review, Walter Caseri describes first the synthesis and the chemical and physical characterization of the polystannanes, in particular with ^{119}Sn NMR spectroscopy. Delocalized s-electrons are a rare phenomenon, observed in polystannanes, which is responsible of their characteristic yellow colour. Polystannanes offer a valuable and rare mixture of materials properties, such as for instance, combination of semiconductivity and adequate thermal stability with ease of processing, polymer orientation and film formation.

Metallopolymers are constituted of metal centers incorporated into the backbone of polymers. Three reviews discuss several aspects of the broad range of metallopolymers. The basic concepts, design and synthetic strategies leading to various types of metallopolymers are gathered in the review authored by Ulrich S. Schubert et al.. A large part of the review also concerns the overview and scope of the techniques available for characterizing these organometallic and coordination polymers which potentially possess dynamic behaviour. Metallopolymers have many properties; the review by Cheuk-Lam Ho, Zhen-Qiang Yu and Wai-Yeung Wong discuss the properties of a special class of metallopolymers, the polymetallaynes, in which metal atoms (mainly transition metals) are embedded into π-conjugated polymer chains. This review summarizes the structure-property-function relationships of polymetallaynes, in particular in the fields of electrical semi-conductivity, photo-/electroluminescence, photovoltaics, non-linear optics, liquid crystallinity, and chemo-sensing, depending on the transition metals and the structure of the ligands used. The most recent progress concerning biomedical applications of metallopolymers are gathered in the review by Yi Yan, Chuanbing Tang et al.. Inspired by the advances of metal-containing small molecular drugs, about 30 different metals, most of them transition metals, have been introduced into polymeric frameworks. This review summarizes biomedical applications of metal-containing polymers, in particular as drug delivery vehicles, as drugs (anticancer, photodynamic therapy and radiotherapy) and biocides (antimicrobial and antiviral agents), as biosensors, and for bioimaging.

A further step forward for metallopolymers concerns metal-organic frameworks (MOFs). MOFs are a subclass of coordination polymers, organized in (2D) 3D structures containing potential voids. Single crystals of some types of MOFs may control photoexcitation under the influence of light, being nonlinear and quantum metamaterials, as shown in the review by Evamarie Hey-Hawkins, Alexandr V. Vinogradov et al.. The review begins with an introduction to nonlinear optics (NLO), in particular applied to the case of materials. Based on these data, the nonlinear optical properties of metal-organic structures are studied. Synthetic approaches used for obtaining MOFs with improved quality and the desired properties in the field of non-linear optics are also described.

Taken altogether the reviews and tutorial reviews of this special issue about smart inorganic polymers draw an impressionist (and impressive) picture, with an infinite number of chemical structures, and an already huge number of properties. With this special issue, we hope to stimulate further research and yet more innovative applications for these highly interesting multifaceted materials.