

Conference Report

Conference report of the 43rd Chemistry CUSO Summer School Villars 2012: Inorganic and Metallosupramolecular Polymers

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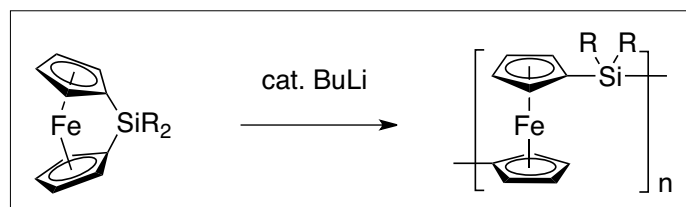
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The 43rd CUSO Summer School in Inorganic Chemistry took place in Villars sur Ollon, Switzerland, from August 13–17, organized by *Corinne Vebert-Nardin* and *Andreas Zumbuehl* from the University of Geneva. The 36 participants from Western Swiss universities had the unique possibility to obtain first-hand information about the topic of inorganic and organometallic polymers. The Victoria Eurotel in Villars provided the ideal setting for a week of exciting talks, stimulating discussions and attractive poster sessions.

The start of the lecture series was made by *Ian Manners* from the University of Bristol, United Kingdom. Before getting into the main topic, he first ensured that all participants had background knowledge in polymer chemistry and polymer physics by giving an introduction, starting from the definitions of polymers and molecular weight distributions all the way to tacticities and crystallinities. Manners was careful to underline each polymerization-type with many relevant examples: The audience was introduced to the concepts of chain and step growth polymerization, their mechanisms and their advantages/disadvantages. Special cases like *Ziegler-Natta* polymerization and living polymerizations were discussed separately. Pointing out that controlled and living polymerizations offer an elegant and basic route for the synthesis of block copolymers, Manners explained the concept of structure formation by self-assembly of block copolymers and their morphological varieties. Focusing on the applications of these block copolymers in photonics, drug delivery and lithography, he finished his introduction with an overview about block copolymers used in nanotechnology, specifically through formation of micelles or hollow structures.

Switching to inorganic polymers, Manners highlighted silicon-based polymers. He presented different established strategies to synthesize polysiloxanes, such as the polycondensation of dihydroxy end-capped siloxanes and the thermal anionic ring-opening polymerization of cyclic siloxanes. The excellent thermal and oxidative stability of these polysiloxanes as well as their high flexibility allow numerous applications in industry. Polysilanes and polycarbosilanes were presented as a second major class of silicon-based polymers. The main route to polysilanes is the *Wurtz* coupling of dichlorosilanes which also offers the possibility of copolymerization. Manners clarified that, due to the delocalization of the σ -electrons in polysilanes, they have a high conductivity and can be used as an analogue to polyacetylene. Also, polysilane and polycarbosilanes can be used as precursors for ceramics.

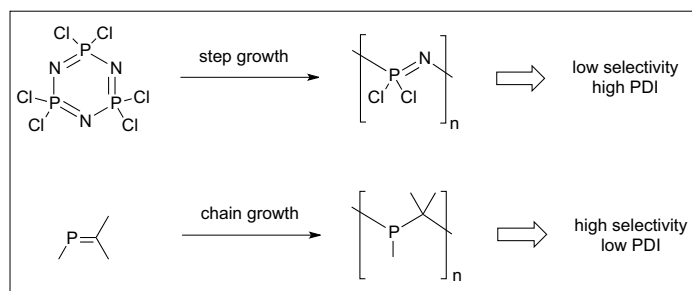
In his second lecture Manners focused on metallopolymers, mainly poly(ferrocenyl)silanes (PFS). Different main and side chain metallopolymers were presented, *e.g.* as sensors for NO or O₂. Manners emphasized that the metallosupramolecular coordination is reversible and can be used in self-healing materials, for example. Being one of the leading scientists in the field of PFS, Manners especially highlighted the on-going research and challenges in this area. The route of synthesizing PFS by living (anionic) ring-opening polymerization of strained ferrocenophane metallorings (see Scheme 1) can also be used for other metallopolymers. Manners also pointed out possible applications of PFS based on their redox activity, like redox-active gels or capsules, precursors of magnetic and catalytically active ceramics, and as a template for the growth of single-wall carbon nanotubes (SWCNT). Another example for the use of PFS was the synthesis of redox-responsive photonic crystals based on PFS gels. In this approach a PFS gel and monodispersed microspheres are combined, resulting in a responsive composite. PFS are also used in polymerization, mainly in block polymerization. Depending on the added monomer(s), a variety of interesting structures can be obtained by self-assembly. For example, a polyisoprene-PFS block copolymer led to the formation of cylinders with a crystalline polyferrocenyl core and a polyisoprene corona.



Scheme 1. Synthesis of poly(ferrocenyl)silanes (PFS).

Professor *Derek P. Gates* from the University of British Columbia, Canada, was invited to cover the field of other inorganic main group element polymers. Gates turned the attention of the audience to the question “Why are there so few examples of inorganic polymers?” Usually, chain growth polymerizations are favored in order to get polymers with low polydispersity indices (PDI) and little cross-linking. For inorganic polymers, however, ring-opening polymerizations are typical and Gates pointed out that due to the nature of the Si–Si double bond, chain growth polymerizations are considered impossible for Si-based inorganic molecules. Searching for solutions for this synthetic challenge, Gates made the distinction between inorganic main chain and side chain polymers. Polymers with inorganic side chains are easier to synthesize than the ones with inorganic backbones, using conventional polymerization methods such as Reversible Addition-Fragmentation Chain Transfer Polymerization (RAFT). Inorganic main chain polymers, such as stannanes, phosphinoboranes and aminoboranes can be produced *via* catalytic dehydrocoupling. Gates pointed out that hybrid organic–inorganic polymers are easier to prepare because conventional organic chemistry can be used, like hydroboration and addition to vinyl groups. Still, the polymer properties are unique due to the presence of the inorganic element in the backbone.

Another example of inorganic main group polymers are polyphosphazenes (Scheme 2). These polymers can be obtained by different synthetic routes, such as polycondensation, ring-opening polymerization and also in living cationic polymerization, which offers the possibility to prepare block copolymers. Furthermore, changing the substituents at the phosphorous atom offers a means to tune the polymer properties. Due to their good biocompatibility, polyphosphazenes might find their way into medicine as biodegradable microcapsules in drug delivery and tissue engineering.



Scheme 2. Step growth mechanism with polyphosphazenes vs. chain growth mechanism for poly(methylenephosphine) (PMP).

Focusing further on phosphorus containing polymers, Gates started his second lecture with phosphorus-based polymers containing π -bonds. First examples were phosphole polymers which have shown novel luminescent properties. The range of π -containing phosphorus polymers is indeed broad: Poly(vinylphosphines) and poly(*p*-phenylene phosphines) for example reveal interesting electronic properties. Gates clearly indicated that the P atom is not directly involved in any π -conjugation in either of these polymers. Since $P=C$ and $P=P$ bonds can be incorporated into polymer backbones, inorganic analogs of poly(phenylenevinyls) are accessible.

At the end of his second lecture Gates closed the circle by returning to his question "Can addition polymerization be applied to inorganic monomers?" Because the direct approach of addition polymerization of inorganic for Si-Si double bonds failed, he now pointed out alternatives, like the use of 'masked disilenes' as monomers. Gates especially highlighted the possibility to polymerize substituted $P=C$ bonds by living anionic polymerization (see Scheme 2). This novel approach opens up a simple and highly selective pathway to functional linear polyphosphines and copolymer systems with low PDIs that can also be used as ligands for metals.

Professor **Jean-François Gohy** from the Catholic University of Louvain in Belgium started off with the topic of metallo-supramolecular polymers, based on terpyridines (Fig. 1). He first explained how terpyridines can be synthesized *via* ring assembly or cross coupling and how the pyridine rings can be functionalized. The terpyridine units can bind metal ions leading to chelate complexes which can be characterized by single crystal X-ray diffraction. Depending on the metal cation, the ratio of terpyridine to metal cation, and the functionalization of the

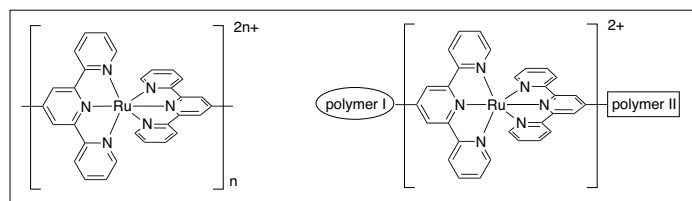


Fig. 1. Terpyridine ruthenium complexes as building blocks for homopolymers (left) or as linkers (right).

terpyridine, various supramolecular architectures with different properties, such as luminescence, can be obtained. By switching to multipyridines or by including more nitrogen moieties in the ring systems, the variety of architectures increases further leading to a big playground for coordination chemists. Even helical structures, rotaxanes and catenanes are accessible this way.

Gohy then introduced di-terpyridine end-capped polymers for building up coordination polymers *via* step growth polymerization. Another possibility is the functionalization of polymer side chains with terpyridines and sequential cross-linking of the chains by addition of metal cations.

In general, different kinds of complexes are accessible: mono-, bis-, homoleptic and heteroleptic complexes. Gohy's approach for the synthesis of heteroleptic complexes: In the first step the mono(terpyridyl)complex is formed and then a second, derivatized ligand is added to form the bis(terpyridyl)complex. The metal cation determines the stability of these complexes. By functionalizing RAFT or Nitroxide Mediated Polymerization (NMP) initiators with a terpyridine unit, terpyridine functionalized block copolymers are accessible and their self-assembly to micelles or gels can be studied. These micelles have tunable properties, such as their diameter, which can be controlled by addition of metal salts to bind any free terpyridine moieties on the outer shell of the micelle.

After this series of lectures on synthetic chemistry, **Julius Vancso** from the University of Twente, Netherlands, acted as a counterbalance; his two lectures about structure, properties and materials science of organometallic polymers were focused on their physical characteristics. Organic polymers on the one side and inorganic and organometallic polymers on the other side show a different spectrum of possible intermolecular interactions. Vancso showed how the strength of certain interactions can be measured using atomic force microscopy (AFM) to investigate polymer surfaces. A highlight in this context was his method to probe supramolecular interactions between a functional group on the AFM tip and a polymer surface (Fig. 2). For example, coordination polymers with hydrogen bonding motifs, like ureido-pyrimidinone (UPy) units, require a force of around 200 pN to be depolymerized whereas it requires only about 100 pN to break up a terpyridine-Ru coordination polymer.

Switching to the possible applications of the fascinating properties of organometallic polymers, Vancso gave a general survey of this field and he especially accentuated the use of polymers in photolithography as positive and negative photoresists.

In his presentation, Professor **Alan Williams**, University of Geneva, set out on a journey through the fascinating world of dendrimers. Starting from the very basics – the definition, synthesis and the requirements for the applied chemical reactions – he continued with chemoselective methods for dendrimer preparation. He emphasized that complex mesogenic structures with different behaviors can be formed using diverse dendrons.

Pointing out the "disadvantages of organic chemistry" (lack of selectivity, incomplete conversion) he suggested the use of phosphorous-based reactions to connect the different generations of a dendrimer. Controlled metal-ligand coordination is another

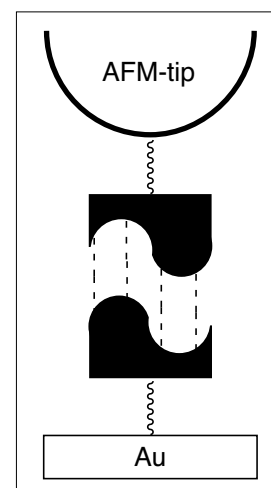


Fig. 2. Concept of a functionalized AFM tip in contact with a functionalized Au surface.

possibility for the assembly of dendrimers. A highlighted example was the electro-active, functionalized G4 dendrimer of Astruc *et al.* in which ferrocenyl units were grafted onto the dendrimer. This ‘outer shell’ of the dendrimer can then be completely and reversibly oxidized. Dendrimers also show good efficiency in catalysis, for example in the ring-opening metathesis polymerization of norbornene. The range of applications for dendrimers is growing, such as in gel formation, as more efficient magnetic resonance imaging contrast agents and for synthesizing nanoparticles inside a dendrimer. With his wonderful comparisons and quotations Williams always kept the whole audience captivated.

Professor **Katharina M. Fromm**, University of Fribourg, immersed her audience deeper into the field of coordination polymers. In the introduction, she explained the difference between common coordination polymers and metal–organic frameworks (MOFs). MOFs are a special case in the field of coordination polymers, namely porous 3D structures composed of metal ions or clusters linked to organic molecules. The structure of the MOFs varies and even chain interpenetration is possible.

In her own research group, nicotinic

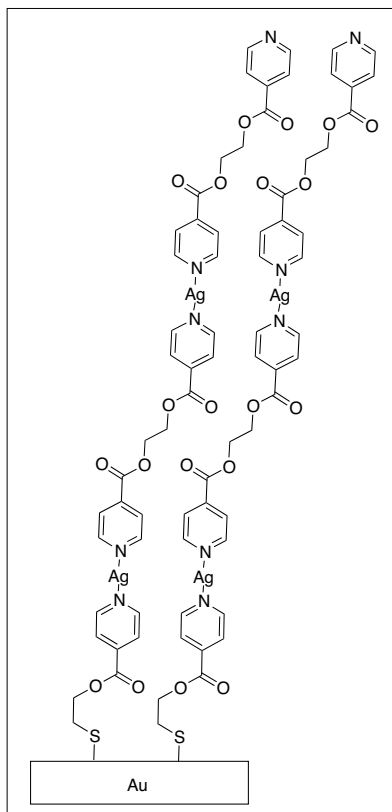


Fig. 3. Silver coordination polymer grafted from a gold surface.

and isonicotinic end-capped oligoethylene glycols were synthesized as ligands for silver cations. Using this example, Fromm elucidated how small changes in the ligand to metal ratio or the oligoethylene glycol chain length lead to major changes in the crystal structure. Without such variations, several coordination polymers would form polymorphic crystal structures.

A highlight in Fromm’s presentation was a silver coordination polymer grafted from a gold surface (Fig. 3). The silver cations in the polymer coating still show antimicrobial and antibacterial properties whereas fibroblast cells survived on the coated surface, a necessity for biomedical applications. Fromm closed the lectures series with an example of oligoethylene glycol complexes with alkaline earth halides which can be used as precursors for oxides.

This lecture concluded the 43rd and final (?) Summer School in Inorganic Chemistry organized by CUSO, a much appreciated program in doctoral education that hopefully will find a continuation in the future. A petition to keep the program alive was signed by the students and will be forwarded to the corresponding authorities.

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The line-up of speakers at the 43rd CUSO summer school in inorganic chemistry: Ian Manners, Derek P. Gates, Jean-François Gohy, G. Julius Vancso, Alan Williams, and Katharina M. Fromm.