A Polymer Magician: Professor Charlotte K. Williams

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At *Organometallics*, the Editorial Team has been highlighting a number of scientists that we feel have had profound impact on the field, and perhaps also on ourselves. In this editorial, I wish to introduce another of our Pioneers and Influencers, Professor Charlotte K. Williams from Oxford University. Professor Williams works on three things I love: Homogeneous metal catalysts, carbon dioxide, and selectivity. With these ingredients, she is developing impressive protocols for making versatile and sustainable polymers.

Figure 1. Professor Charlotte K. Williams.

As a small-molecule chemist, I am in awe of scientists who embark on making polymers. Polymers often referred to as "plastics," are large molecules, composed of repeating subunits, and they have favorable properties, such as macroscale toughness, which shorter molecules are unable to provide. The current worldwide production of polymers is 360 million tons/year.[1] However, developing a polymerization catalyst that can produce polymers with exactly the desired physical-chemical properties is a magician's work. As Williams and Nozaki write: "*In contrast to small-molecule catalysts, polymerization catalysts also control the polymerization rate, selectivity, and productivity that govern the resulting materials' crystallinity, decomposition temperature, viscosity, rheology, and mechanical performance. Catalyst selection may also be used to tune the polymer molecular weight, dispersity, chain composition, chain architecture, and regio- and/or stereochemistry*."[2]

Charlotte Williams was born in 1975 and studied Chemistry at Imperial College London, from where she received a Bachelor's Degree in 1998. During her PhD studies (1998 - 2001), Williams worked with Vernon Gibson and Nicholas Long, initially embarking on classic organometallic chemistry with focus on ferrocenediyl ligands.[3] In fact, the first scientific article coauthored by Williams appeared in *Organometallics*, with the title "*Hang-gliding with Ferrocenes: Unusual Coordination Chemistry of 1,1'-Bis(mesitylthio)ferrocene*" (Figure 2).[3a]

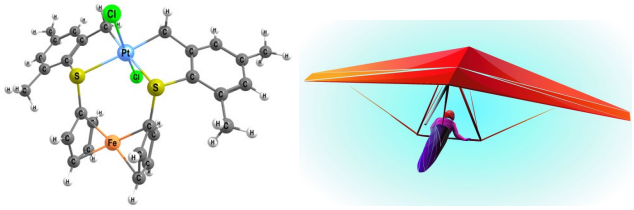

Figure 2. X-ray structure of the hang-glider-like C,S-cyclometalated Pt^{IV} complex formed from 1,1'-bis-(mesitylthio)ferrocene (*left*)[3a] and a hang-glider (*right*).[4]

The ferrocenediyl complexes were tested in Suzuki coupling and olefin polymerization catalysis.[3c,e] From then on the use of homogeneous catalysts in polymerization reactions became a defining topic in Williams' work. During 2001-2002, she was a postdoctoral fellow, first studying lactide ring-opening polymerization (ROP) with William B. Tolman and Marc Hillmyer at the University of Minnesota, USA.[5] Subsequently she worked with organometallic light-emitting polymers, with Andrew Holmes and Richard Friend at the University of Cambridge, UK.[6]

In 2003, Williams returned to her Alma Mater, Imperial College, as a lecturer. Here she started her independent career, with focus on developing new homogeneous catalysts for polymerization reactions, initially focusing on yttrium complexes.[7] In 2004, CO_2 entered into her research as a potential polymer ingredient, due to William's interest to develop polymers from sustainable feedstocks. However, initially all her attempts to develop an efficient catalyst for copolymerization of CO_2 failed, and several years without success passed by before her team finally could report a major breakthrough in 2009 (patented in 2008): A dizinc catalyst with a reduced Robson type macrocycle, which is able to copolymerize CO_2 and cyclohexene oxide (Figure 3).[8] Williams was not the first to copolymerize CO_2 and epoxides; indeed, the first reaction of this type, mediated by $ZnEt_2$, was

developed in 1969 by Inoue and coworkers.[9] This was followed by seminal studies leading to well-defined homogeneous zinc catalysts reported by the groups of Darensbourg,[10] Coates,[11] and Lee,[12] among others.[13] However, Williams' catalyst was a remarkable step forward for its properties: robust, airstable, with high end-group fidelity, and most important, the first well-defined zinc catalyst that was highly active at only 1 atm CO_2 pressure.[8]

The Williams group reported a bimetallic cobalt analogue in 2010 (Figure 3, right), which is even more active and selective than the zinc catalyst, producing no cyclic carbonate as an undesired byproduct.[14] This was later followed by the first homogeneous heterodinuclear Zn/Mg catalyst with improved performance for CO_2-epoxide copolymerization, still with the reduced Robson ligand.[15] If Williams' initial work is described as involving the synthesis of a hang-glider complex (Figure 2), then I suggest considering these beautiful macrocyclic catalysts as her follow-up jet planes (Figure 3). The catalysts' excellent performance may be due to the two metals in proximity, as the polymer chain growth is expected to occur through a shuttle mechanism involving both metal centers (Figure 4).[15]

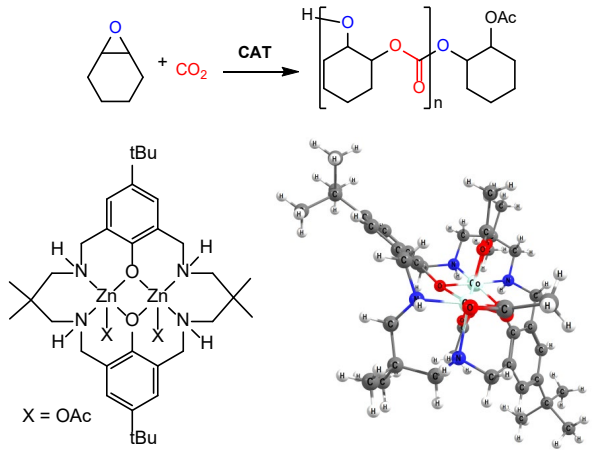

Figure 3. *Top*: Copolymerization of CO_2 and cyclohexene oxide (CAT = catalyst). *Bottom*: Bimetallic Zn catalyst reported by Williams in 2009 (*left*)[8] and X-ray structure of the Co analogue reported in 2010 (*right*).[14]

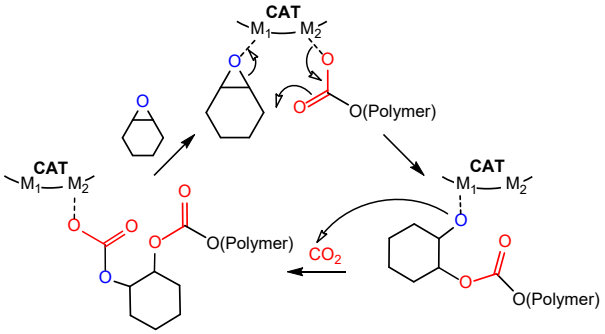

Figure 4. Proposed bimetallic shuttle mechanism for ring-opening copolymerization (ROCOP) of cyclohexene oxide and CO_2 (based on mechanism shown in ref. 15).

In 2009, Williams became Reader at Imperial College, which can be considered equivalent to an Associate Professor. In 2011, she received the *Bio-environmental Polymer Society Outstanding Young Scientist Award* for her work,[16] and in 2012 she became Professor of Catalysis and Polymer Chemistry at Imperial College.[17]

Prof. Williams continued to perform polymer magic and reported in 2014 a novel control mechanism that allows switching a single catalyst between ROP of lactones and ring-opening copolymerization (ROCOP) of epoxides and CO_2 in one pot (Figure 5).[18] The catalytic system involved the zinc species in Figure 3, known to be active in ROCOP to form polycarbonates.[8] Williams's group showed that this catalyst is inactive for ROP of lactones to form polyesters, unless an epoxide is added as an initiator, which converts the zinc carboxylate into an active zinc alkoxide. The truly magical discovery was that the ROP reaction could be turned off again by adding CO_2. By adding or removing CO_2, ROCOP and ROP can be alternated, resulting in an unprecedented one-pot formation of copoly(ester-carbonates) (Fig. 5).

Subsequently, Williams reported that anhydrides also could be used as monomer feedstock in the chemoselective polymerization approach, and thus a large variety of copolymers can be formed in a highly selective manner.[19] In recent years, Prof. Williams has extended the portfolio of catalysts and (sustainable) monomers that can be employed, and in particular, has shown the controlled production of many new polymers with highly promising properties.[20] The use of CO_2 as a non-fossil carbon feedstock remains a major focus in her work. This is a topic that is gaining increased attention, as highlighted in the *Organometallics* Special Issue on CO_2 Utilization, where Williams reported the isolation of a rare anionic Ti(IV) complex, assumed to be a model of the catalytic alkoxide intermediate.[21] Recently,

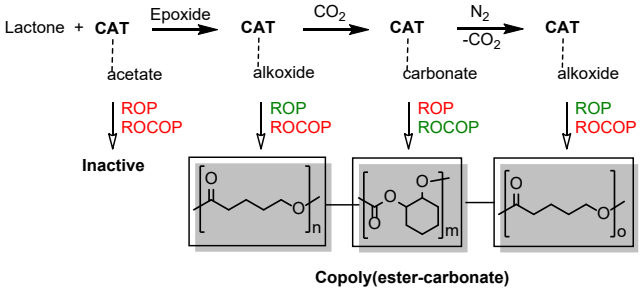

Figure 5. Chemoselective polymerization control[18]: If the bimetallic Zn catalyst (Fig. 3) is mixed with caprolactone, no reaction takes place. Addition of epoxide activates ROP. If CO_2 is added, ROP is suppressed, but ROCOP is activated. Removal of CO_2 reactivates ROP (green: active, red: inactive).

her group showed how the combination of metals, chosen based on their role in the catalytic cycle, can improve heterodinuclear catalysts for CO_2/epoxide copolymerization: In a reported Mg/Co complex, the magnesium center improves epoxide coordination and the cobalt center accelerates carbonate attack.[20f]

It is particularly impressive to me when academics become innovators and company founders: In 2011, Williams founded Econic Technologies, a company focusing on catalysts to make polymers from CO_2. She commented in an interview: "*Our first major catalyst discovery was in 2008. We filed a patent and continued to develop the science while exploring options for the technology and eventually formed Econic in 2011*."[22] For her industrial entrepreneurship, Prof. Williams was awarded the *WISE Tech Start-up Award* in 2015.[23] The catalysts developed by Econic are sold to polyol producers whose carbon dioxide-based polyols then are used to make polyurethanes for applications, for example soft foams for house-hold goods, automotive components, adhesives, elastomers and home insulation foams.

In 2016, Williams became Professor of Inorganic Chemistry at Oxford University. The same year, she received the *Corday-Morgan Prize*, recognizing her contributions to using renewable resources to make polymers.[24] In 2018, she received the *Otto Roelen Medal* by Dechema and the German Catalysis Society, in recognition of her developments of highly active catalysts for CO_2 copolymerization.[25]

There is no doubt that Williams has contributed fundamental breakthroughs in the field of homogeneous polymer catalysis and CO_2 utilization, and she is also a role model as an inventor and entrepreneur. Her impressive scientific record counts around 140 publications and 30 patents, many licensed industrially. In addition to her scientific achievements, she is a dedicated group leader and has mentored numerous postdocs, PhD students and undergraduates. Of her former group members, 16 are in academic positions worldwide. Besides chemistry, she has a love for the wilderness and for fossil hunting, alongside other hobbies, including swimming, cycling and hiking. With her famliy she is regularly going on biking adventures and crossed Scotland by bike in 2019.

To me, Prof. Williams is both a scientific and a personal role model. I have never worked with her, but just reading her articles has inspired me many times. I am a female chemist and although I have performed research in academia for 20 years, my sense of belonging is small, which appears common for women in STEM fields.[26] Over the years, I have monitored my feeling of belonging and I have realized what makes it spike: Inspiring female chemists, whose work and achievements remind me that women have a natural place in science and in academia. On days where the feeling of not belonging weighs particularly heavy on my shoulders, I look toward my role models, and it helps me calm my inner critic and carry on. Professor Charlotte Williams is such a role model to me, and I am sure, also to many others.

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Notes

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REFERENCES

[1] *Plastics – the Facts 2019*, downloaded on 24.07.2019 from https://www.plasticseurope.org/application/files/1115/7236/4388/FINAL_web_version_Plastics_the_facts2019_14102019.pdf

[2] Nozaki, K.; Williams, C. K., Metal Complexes for Catalytic Polymerizations, *Inorg. Chem.* **2020**, *59*, 957.

[3] a) Gibson, V. C.; Long, N. J. ; White, A. J. P.; Williams, C. K.; Williams, D. J., Hang-Gliding with Ferrocenes: Unusual Coordination Chemistry of 1,1'-Bis (Mesitylthio)Ferrocene *Organometallics*, **2000**, 19, 4425, b) Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, C. K.; Williams, D. J., New Unsymmetrical Thioether- and Thiolate-Substituted Ferrocene Ligands and an Unusual Bridged-Pd Dimer Complex *Chem. Commun.*, **2000**, 2359, c) Williams, C. K.; Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, D. J., Novel Ferrocenediyl Ligands, Their Metal Complexes, and Potential to Catalyze Olefin Polymerization, *Abstr. Pap. Am. Chem. Soc.* **2001**, *221*, U679, d) Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, C. K.; Williams, D. J., The Synthesis and Metal Coordination Chemistry of a Novel Phosphine- and Thiolate-Substituted Ferrocenediyl Ligand, *Organometallics*, **2002**, *21*, 770, e) Gibson, V. C.; Long, N. J.; White, A. J. P.; Williams, C. K.; Williams, D. J.; Fontani, M.; Zanello, P., Synthesis, Characterisation and Catalytic Activity of Metal Complexes of Neutral, Unsymmetrical P/S Ferrocenediyl Ligands, *J. Chem. Soc., Dalton Trans.* **2002**, 3280.

[4] Hang glider image licensed from Dmytro Hrynchak/shutterstock.com.

[5] a) Williams, C. K.; Brooks, N. R.; Hillmyer, M. A.; Tolman, W. B., Metalloenzyme Inspired Dizinc Catalyst for the Polymerization of Lactide, *Chem. Commun.*, **2002**, 2132, b) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B., A Highly Active Zinc Catalyst for the Controlled Polymerization of Lactide, *J. Am. Chem. Soc.*, **2003**, *125*, 11350.

[6] Sandee, A. J.; Williams, C. K.; Evans, N. R.; Davies, J. E.; Boothby, C. E.; Kohler, A.; Friend; R. H.; Holmes, A. B., Solution-Processible Conjugated Electrophosphorescent Polymers, *J. Am. Chem. Soc.*, **2004**, *126*, 7041.

[7] a) Hodgson, L. M.; White, A. J. P.; Williams, C. K., Yttrium(III) Complex as a Highly Active Catalyst for Lactide Polymerization, *J. Polym. Sci., Polym. Chem.*, **2006**, *44*, 6646, b) Platel, R. H.; Hodgson, L. M.; White; A. J. P.; Williams, C. K., Synthesis and Characterization of a Series of Bis(Oxo/Thiophosphinic)Diamido Yttrium Complexes and Their Application as Initiators for Lactide Ring-Opening Polymerization, *Organometallics*, **2007**, *26,* 4955.

[8] Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K., Highly Active Dizinc Catalyst for the Copolymerization of Carbon Dioxide and Cyclohexene Oxide at One Atmosphere Pressure, *Angew. Chem. Int. Ed.*, **2009**, *48*, 931.

[9] Inoue, S.; Koinuma, H.; Tsuruta, T., Copolymerization of carbon dioxide and epoxide with organometallic compounds, *Makromol. Chem.* **1969**, *130*, 21.

[10] a) Darensbourg; D. J.; Holtcamp, M. W., Catalytic Activity of Zinc(II) Phenoxides Which Possess Readily Accessible Coordination Sites. Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide, *Macromolecules* **1995**, *28*, 7577, b) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. A.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H., Catalytic Activity of a Series of Zn(II) Phenoxides for the Copolymerization of Epoxides and Carbon Dioxide, *J. Am. Chem. Soc*. **1999**, *121*, 107.

[11] a) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. Catalytic Reactions Involving C1 Feedstocks: New High-Activity Zn(II)-Based Catalysts for the Alternating Copolymerization of Carbon Dioxide and Epoxides *J. Am. Chem. Soc.* **1998**, *120*, 11018, b) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky E. B.; Coates, G. W. Single-site beta-diiminate zinc catalysts for the alternating copolymerization of CO_2 and epoxides: catalyst synthesis and unprecedented polymerization activity, *J. Am. Chem. Soc.* **2001**, *123*, 8738.

[12] Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S. I., Yun, H. S.; Lee; Park, Y. W., Bimetallic Anilido-Aldimine Zinc Complexes for Epoxide/CO_2 Copolymerization, *J. Am. Chem. Soc*. **2005**, *127*, 3031.

[13] Kember, M. R.; Buchard, A.; Williams, C. K., Catalysts for CO_2/Epoxide Copolymerisation*, Chem. Commun.* **2011**, *47*, 141.

[14] Kember, M. R.; White, A. J. P.; Williams, C. K., Highly Active Di- and Trimetallic Cobalt Catalysts for the Copolymerization of CHO and CO_2 at Atmospheric Pressure, Macromolecules **2010**, *43*, 2291.

[15] Saini, P. K.; Romain, C.; Williams, C. K., Dinuclear metal catalysts: improved performance of heterodinuclear mixed catalysts for CO_2–epoxide copolymerization, *Chem. Commun.* **2014**, *50*, 4164.

[16] https://www.imperial.ac.uk/news/103269/dr-charlotte-williams-wins-outstanding-young, accessed on 28.07.2020.

[17] https://www.imperial.ac.uk/news/113929/promotions-celebrated-across-imperial, accessed on 28.07.2020.

[18] Romain, C.; Williams, C. K., Chemoselective Polymerization Control: From Mixed-Monomer Feedstock to Copolymers*, Angew. Chem. Int. Ed.* **2014**, *53*, 1607

[19] Romain, C.; Zhu, Y.; Dingwall, P.; Paul, S.; Rzepa, H. S.; Buchard, A.; Williams, C. K., Chemoselective Polymerizations from Mixtures of Epoxide, Lactone, Anhydride, and Carbon Dioxide, *J. Am. Chem. Soc.* **2016**, *138*, 4120.

[20] a) Stößer, T.; Mulryan, D.; Williams, C. K., Switch Catalysis To Deliver Multi-Block Polyesters from Mixtures of Propene Oxide, Lactide, and Phthalic Anhydride, *Angew. Chem. Int. Ed.* **2018**, *57*, 16893, b) Stößer, T.; Williams, C. K., Selective Polymerization Catalysis from Monomer Mixtures: Using a Commercial Cr-Salen Catalyst To Access ABA Block Polyesters, *Angew. Chem. Int. Ed.* **2018**, 57, 6337, c) Stößer, T.; Sulley, G. S.; Gregory, G. L.; Williams*,* C. K., Easy access to oxygenated block polymers via switchable catalysis, *Nat. Commun.,* **2019***, 10,* 2668, d) Raman, S.; Raja, R.; Arnold, P. L.; Davidson, M. G.; Williams*,* C. K.; Waste not, want not: CO_2 (re)cycling into block polymers, *Chem. Comm.* **2019***, 55,* 7315, e) Sulley, G. S.; Gregory, G. L.; Chen, T. T. D.; Carrodeguas, L. P.; Trott, G.; Santmarti, A.; Lee, K.; Terrill, N. J.; Williams, C. K., Switchable Catalysis Improves the Properties of CO_2-Derived Polymers: Poly(cyclohexene carbonate-b-ε-decalactone-b-cyclohexene carbonate) Adhesives, Elastomers, and Toughened Plastics, *J. Am. Chem. Soc*, **2020**, *142*, 4367, f) Deacy, A. C.; Kilpatrick, A. F. R.; Regoutz, A.; Williams, C. K., Understanding metal synergy in heterodinuclear catalysts for the copolymerization of CO_2 and epoxides, *Nat. Chem.* **2020**, *12*, 372.

[21] Raman, S. K.; Deacy, A. C.; Carrodeguas, L. P.; Reis, N. V.; Kerr, R. W. F.; Phanopoulos, A.; Morton, S.; Davidson, M. G., Williams, C. K. Ti(IV)–Tris(phenolate) Catalyst Systems for the Ring-Opening Copolymerization of Cyclohexene Oxide and Carbon Dioxide, *Organometallics*, **2020**, *39*, 1619.

[22] https://www.imperial.ac.uk/news/164912/profile-innovator-professor-charlotte-williams accessed 28.07.2020.

[23] https://wise.statementcms.com/uploads/wise/files/WISE_Awards_Role_Model_Booklet.pdf accessed 28.07.2020.

[24] https://www.rsc.org/ScienceAndTechnology/Awards/CordayMorganPrizes/2016-Winner-Williams.asp accessed 28.07.2020.

[25] https://analyticalscience.wiley.com/do/10.1002/gitlab.16457/full accessed on 28.07.2020.

[26] Smith, J. L.; Lewis, K. L.; Hawthorne, L.; Hodges, S. D., When trying hard isn't natural: Women's belonging with and motivation for male-dominated STEM fields as a function of effort expenditure concerns, *Personality and Social Psychology Bulletin* **2012**, *39*, 131.