A passion for POLYMERS

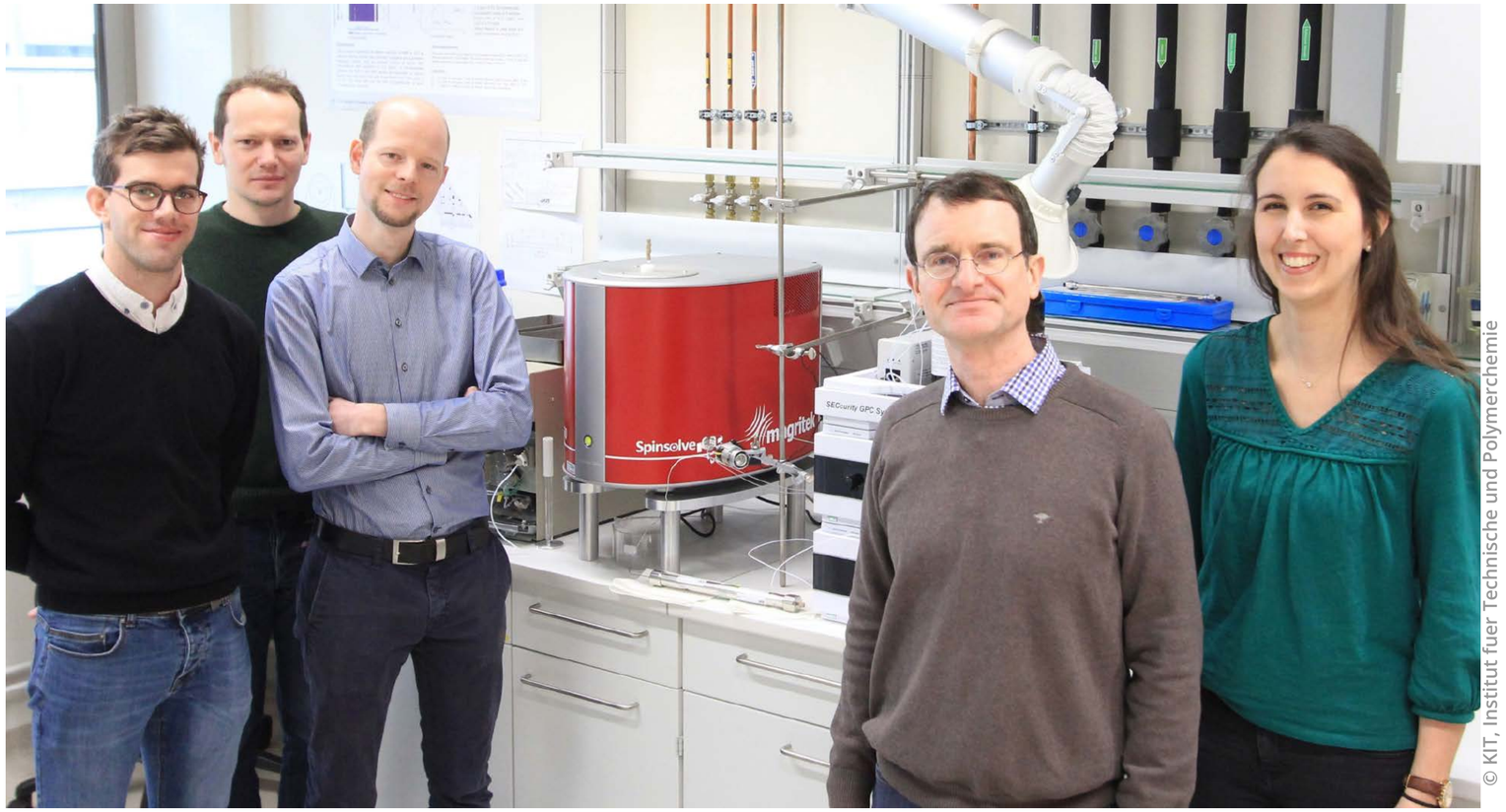
Professor Manfred Wilhelm's ingenious methods to study the molecular structure of polymers have changed the way scientists and industry work with these complex materials, reports Rebecca Pool.

The SEC-NMR systems from Professor Manfred Wilhelm's team at KIT. [KIT, Institut fuer Technische und Polymerchemie]

By his own admission, Manfred Wilhelm, Professor of Polymeric Materials and developer of numerous ingenious methods to analyze polymers at the molecular level, was fascinated by chemical reactions from childhood. Growing up on a wine farm in Maikammer, on the German Wine Route close to Mainz, he was familiar with Erlenmeyer flasks and Bunsen burners long before secondary school. As he recalls: “As a child, I did a lot of my own experiments and came close to burning the house down at least once.”

Thankfully, he didn't, and surviving his unorthodox early years, pursued his passion for Chemistry at the University of Mainz, becoming the first in his family to attend higher education. It was the late 1980s, and while the field of polymer science was beginning to gather momentum, Mainz was a step ahead and already a well-known entity in research circles.

“Mainz has a strong focus on polymers, and one of my school friends studied chemistry in Mainz so I simply decided to do the same,” highlights Wilhelm. “Polymers also have a practical application – if you come from an agricultural background then you don't study History of Art, you study something that you can get a job in.”



Professor Manfred Wilhelm and colleagues with the Magritek Spinsolve 60 spectrometer.

From word go, Wilhelm enjoyed Polymer Chemistry and was taught by some of the field's finest scientists, including Helmut Ringsdorf, renowned for his breakthroughs in polymer self-assembly, and Hans Sillescu, who was the pioneer NMR spectroscopy to study slow, molecular dynamics. Come the third year of his studies, Wilhelm jumped at the chance to join the laboratory of Professor Mitchell A Winnik, at the University of Toronto, Canada, as an exchange student, an opportunity organized by Ringsdorf.

“Ringsdorf was extremely well-connected and for me, coming from the countryside and having never been abroad before, this was really something that I still like to give him credit for,” highlights Wilhelm “I actually lived in Chinatown, in Toronto – which was so very different from where I came from.”

Arriving in Winnik's group, Wilhelm was tasked with working out how to use fluorescence to detect the critical micelle concentration (CMC) in block copolymers, an endeavor that he describes as 'extremely complicated'. “After our first meeting, I left Winnik's office thinking, 'I have no clue what the boss wants' but realized that I was working for him for free, so if I did something it was okay, and if I did nothing, that would also be okay,” he says.

Wilhelm spent the next few weeks obtaining spectra after spectra after spectra of micelle formation in poly(styrene-ethylene oxide), in water, and deliberating over his data, devised a practical theory that changed the way in which researchers everywhere would measure this molecule aggregation. Winnik was thrilled and made Wilhelm the first author of the published research, who then happily returned to Mainz, never to study fluorescence again. Their paper – 'Poly(styrene-ethylene oxide) block copolymer micelle formation in water: a fluorescence probe study' – now has more than 1400 citations.

Doctorate days

Wilhelm embarked on a doctorate with Professor Hans-Wolfgang Spiess, in 1992, at the Max Planck Institute for Polymer Research, in Mainz. Here, in his words, he was 'exposed to so many things' and Spiess had a profound influence on the way he has since approached research.

"When it came to polymers, this was the top-notch institution and I was working in one of the best groups in the world," says Wilhelm "Spiess was this big researcher and I was surrounded by very smart guys – we had a lot of research funds, worked a minimum 60 h a week and it was competitive but in a positive sense – it was all so inspiring and stimulating."

For his PhD, Wilhelm was working with solid-state NMR to study the chemical structure of inorganic and organic polymers. As an analysis tool, NMR was being widely used in medical applications and also to study liquids, but the solid-state version was relatively new and didn't yet rival existing methods, such as X-ray and neutron scattering, and light and electron microscopy. During this time, and over later years, Wilhelm and Spiess were to put solid-state NMR on the analytical map, and hone a range of related techniques while studying molecular orientation distributions and molecule dynamics in many polymers. Meanwhile, during his doctorate, Wilhelm was to also spend a short six-month stint at the University of California Santa Barbara, working with Professor Bradley Chmelka and developing multi-dimensional solid-state NMR to study zeolites.

Here, the young researcher yet again demonstrated his innate ability for the practical, devising an ingenious NMR method to measure the rapid spinning dynamics of benzene rings within these 3D crystalline minerals. "This was really cool and later helped me to get a job offer at Shell in Amsterdam – I didn't take it but instead went to the Weizmann Institute in Israel after my PhD," he says.

Professor Manfred Wilhelm leads Polymeric Materials at the Karlsruhe Institute of Technology.

At the Weizmann Institute, Wilhelm set to work with renowned polymer scientist, Professor Jacob Klein, on something quite different – measuring surface forces in polymers. As always, Wilhelm wanted to better understand exactly how polymer molecules behaved, in this case, under oscillatory shear stress. However, he noticed that when measuring shear in his polymeric liquids, higher harmonic frequencies emerged, which he just couldn't explain.

With his interest well and truly piqued, he asked many colleagues, including several big names back in Mainz, if they were familiar with this phenomenon, and received a resounding no.

Fully aware he had an 'open ticket' to continue postdoctoral research back in Spiess's group, when the time came to leave Weizmann, he returned to MPI Polymer Research, to study these high harmonics investigations, and polymer melt rheology, apace.

“I have to give credit to Spiess here,” highlights Wilhelm. “He thought I would come back to Mainz to do NMR spectroscopy, but when I suggested this new idea, he told me this would be even better as it was different from what he was doing and the outside scientific world would recognize this as my own scientific achievement.”

And the wonderful world of polymer science did. Used to performing many a Fourier transform in solid-state NMR, Wilhelm decided to do the same with his polymer rheology research. In 1998, he, Spiess, and colleague Daniel Maring published 'Fourier-transform rheology' in Rheologica Acta, which showed exactly how the higher harmonic contributions in polymer melts under shear stress could be analyzed in Fourier space. Wilhelm coined the term 'FT-rheology', in the Summer of 1998 and today FTR is widely used in processes such as plastic production, food processing, pharmaceutical, and cosmetic production to characterize the morphology and determine the properties of polymer blends and emulsions.

Winning combinations

Come 2004, Wilhelm was ready to move on and accepted a 5-year contract as an Assistant Professor at Technical University Darmstadt (TUD), in joint cooperation with MPI Polymer Research. Here, he was Head of the Max-Planck research group, Mechanical Polymer in the engineering mechanics department. But as a chemist, he never felt entirely at home in mechanical engineering.

“I'm a guy who thinks in molecules so if I think of a fiber and how to make it stronger, I'll think of the hydrogen bonds, orientation, all-trans configurations, glass transition point, and so on,” he says.

So, when he was offered a full tenure as Professor of Polymeric Materials at the University of Karlsruhe, Institute for Chemical Technology and Polymer Chemistry, in 2006, he cut his TUD contract short and moved on.

He swiftly set to building up a chemistry lab, hiring more and more PhD students and postdoctoral researchers to further the solid-state NMR and FT-Rheology research he had embarked on with Spiess, Klein and colleagues.

Over time, synthesis and characterization of special polymers became a key research strand, with comb structures and rubber materials being just two examples studied. Not surprisingly, from the beginning, his group also developed novel practical applications for polymers.

For example, they worked out how to use hydrogels, typically used in diapers, as a separation agent in water desalination and also to translate osmotic pressure to mechanical force in osmotic motors. Entropy motors, which transform waste heat into mechanical energy, were also constructed from elastomers. “My students working on hydrogels all got cool jobs afterward – BASF, Evonik, and Proctor & Gamble all need people to understand diapers,” he laughs.

The Group also combined rheology methods in unique ways, including rheology-NMR, rheology-dielectric spectroscopy, and rheology-infrared were developed. Indeed, work on the rheology-NMR go

Early on, Wilhelm also got to work combining methods to better characterize polymers in solution, with a key success being his combination of NMR and size exclusion chromatography (SEC). When Wilhelm first joined the Karlsruhe Institute of Technology, he was using SEC to characterize his materials, but quickly discovered that the detectors did not provide sufficient data on the eluting polymers. Given this, he and his team spent the next 10 years developing a chemically-sensitive SEC detector based on FTIR spectroscopy and also combined this with bench-top NMR, using the setup to glean highly detailed information on separated polymer molecules. The researchers have collaborated with Germany-based company Magritek, and one of Wilhelm's students, Markus Matz, won the 2022 Herbert Knauer Science Award for improving bench-top NMR resolution and sensitivity. Their unique HPLC detector helps to make the method more tangible for standard laboratories.

For his part, Wilhelm has turned down many opportunities to take on a Professorship at several other research institutions but has remained faithful to KIT, becoming Dean of the Faculty of Chemistry and Life Sciences from 2019 to 2021. He was also appointed a member of the Academy of Sciences and Literature in Mainz earlier this year.

Looking back, Wilhelm highlights how he has never taken on research that he isn't interested in. “If it doesn't interest me, I don't do it,” he says. “And I also say to my students, we want to be five to ten years ahead of the industry – we are not their laboratory but we want to do something they that can use later.”

So what next for the Professor of Polymeric Materials? He intends to keep working on research that will solve industry problems, and top of his list is recycling polyolefins, a family of thermoplastics that include polyethylene and polypropylene. “We should reduce our plastics consumption but not everyone wants to do this,” he points out. “So recycling is a big topic I would like to work on now.”

And practical as always, Wilhelm would also like to do this sooner rather than later. Admitting he will retire in around ten years, he will now work on new projects that can be completed within this time frame. “I won't live forever and I now have to work on shorter-term projects or else I just cannot succeed,” he says.