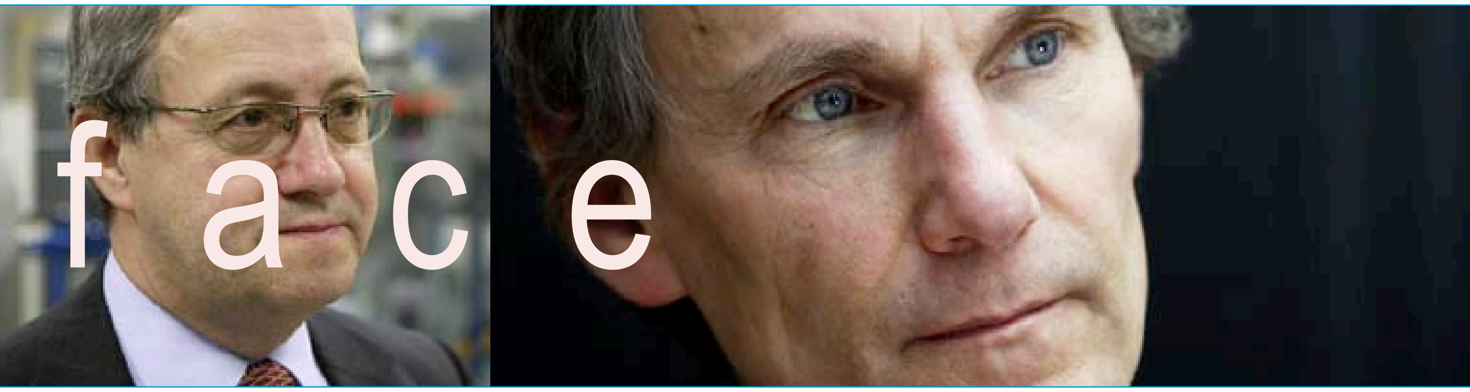
Bringing science to industry

The year we look back on, 2005, closed in December with the DPI Annual Meeting in Marl, Germany, hosted by our industrial partner, Degussa. It was an opportunity for DPI to show its strength: the merging of excellent academic knowledge with the industrial impact of international companies. DPI is the only LTI with a real international character and strategy; that was the opinion expressed in the recently published evaluation report by Technopolis for the Ministry of Economic Affairs. The ambition of the Executive Board of DPI is to strengthen this international dimension, particularly in Europe.



The Ministry of Economic Affairs sees this as a positive element in strengthening the position of the Netherlands as a knowledge-based economy. All large companies (multinationals) in the field of polymers with R&D activities in the Netherlands are DPI partners. "In the relatively new fields of functional and bio-inspired polymers, we still want to convince a number of companies to become partners," Michels says. "And we are also looking at European funding," Joosten adds.

The funding of LTIs will change after 2007 due to a phasing out of the present financial scheme. In response, DPI is already hard at work drafting a new long-term research and business plan which will serve as the basis for the government to determine the manner and level of funding for the coming years.

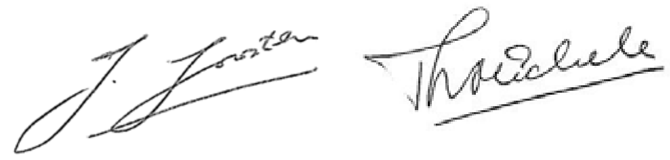
The Dutch Innovation Platform has designated chemistry as a key technology area. Jacques Joosten: "The Netherlands is very strong in chemistry. If we want to maintain that position, we have to invest to make it stronger. DPI is a valuable instrument in this respect, focusing on long-term research. It is a vision that is clear about the need for us in the Netherlands to maintain successful initiatives and ensure that there is cohesion. For the key area Chemistry DPI fits the strategy perfectly."

The main point of criticism in the Technopolis report was the lack of visibility of the results that had been achieved. Since DPI tends to have industrial partners with a substantial capacity for absorption, it sometimes has difficulty in making visible what the research has generated for the marketplace. Visible results can be seen in the growth of the number of DPI partners, the increase in the number of patents and the rise in the number of scientific publications. But that does not show what companies do with the results. Joosten: "It's quite logical that companies don't go around selling to all and sundry what they get from the DPI research. Don't forget, competitors always sit at the same table at DPI. The fact that they are and remain partners indicates that the work we do delivers a return." Michels adds: "We are putting every effort into getting more focus and mass in our programmes. This will enable us to gain more quality in the direction that we have selected together. So we select increasingly those universities and institutes in Europe that are able to contribute to a technologically challenging programme of the highest scientific quality. The choice of programmes is determined by the industry on the basis of scientific recommendations. For this purpose an expert scientific chairman is now in place for every programme committee, and external experts are consulted in the proposal selections. An international advisory panel, the Scientific Reference Committee has also in the past year given its first in-depth evaluations and recommendations on DPI's scientific quality and general direction." The possibility exists that not all the current partners will be able to go along with the chosen directions. Joosten reckons that where one or other partners leave due to this, new companies will join. "A certain dynamic in the partner base doesn't harm the position of DPI."

DPI has a large patents portfolio and, with 52 filed patents, is top of the LTI list. The amended IPR system offers companies the opportunity to decide within 2.5 years whether they want to take over a DPI patent. After that period the knowledge institute will weigh up whether it wishes to reclaim the right or allow the patent to lapse and pass into the public domain. "The call for valorisation is a hot issue in public R&D. Within the existing DPI formula we have few possibilities; we remain restricted to pre-competitive long-term research," Michels says. "But we can stimulate valorisation from knowledge institutes." Joosten: "Our inventions are certainly of interest not only to the SME sector but also to start-ups.

We are looking for a means of making our knowledge available to SMEs, and this is being detailed in our business plan.” Meanwhile, DPI is trying to get the universities aware about boosting inventions and the appropriateness of opting to patent or not. Michels: “The possibilities for new inventions for start-ups are likely to lie more in functional polymer systems, plastic electronics and renewable materials than in polyolefins or engineering plastics.” Joosten adds: “As far as patents go, it is important to make a distinction between ‘nice to have’ and ‘need to have’. We don’t want to be an organisation that exists on the basis of its patents portfolio, even if that were possible. We valorise DPI knowledge via our patents, which are mainly commercialised by our industrial partners. The annual 18 million euro budget that we have available must be used as far as possible on knowledge development. That is the added value of DPI. We will continue to put everything into that. To get our knowledge into the industry. That remains our calling.”

Jacques Joosten, Managing Director *Thijs Michels, Scientific Director*



Annual Report 2005

contents

Jacques Joosten:
“The Netherlands is very strong in chemistry. If we want to maintain that position, we have to invest to make it stronger. DPI is a valuable instrument in this respect.”

Summary of financial data 2005

Income (x EUR million)

Contributions from industrial partners	4.73	27 %
Contributions from knowledge institutes	3.97	23 %
Contributions from Ministry of Economic Affairs	8.87	50 %
Total income	**17.6**	**100 %**

Expenditure (x EUR million)

By nature			By Programme Area		
Personnel costs	13.85	78 %	Organisation and support	1.68	10 %
Depreciation	2.25	13 %	Polyolefins	2.45	14%
Other costs	1.53	9 %	Engineering Plastics	1.84	10 %
			Rubber Technology	0.85	5 %
			Functional Polymer Systems	2.92	17 %
			CoatingsTechnology	1.51	9 %
			High-Throughput Experimentation Key Performance Indicators	2.19	12 %
			Corporate Programme	4.15	23 %
Total expenditure	**17.6**	**100 %**	**Total expenditure**	**17.6**	**100 %**

data 2005

2005 Key Performance Indicators

Number of industrial partners

End 2004: 30
End 2005: 34

Number of partner knowledge institutes (universities etc.)

End 2004: 23
End 2005: 24

Industrial contribution (cash and in-kind) as % of total expenditure

End 2004: 25%
End 2005: 27% EUR 3.782,000 cash + EUR 720,000 in kind

Contribution Ministry of Economic Affairs

End 2005: 50%

Number of patents filed by DPI

In 2004: 10
In 2005: 12

Number of patents licensed or transferred to industrial partners

In 2004: transfers on hold due to legal issues
In 2005: 1

Track record former DPI researchers 2005	Fte
Departed in total	75
Employed by partner knowledge institute	14
Employed by non-partner knowledge institute	14
Employed by industrial partner company	30
Employed by industrial non-partner company	11
Returned to native or foreign country	22
Retired	0
Unknown	1

Industrial follow-up

No information available due to confidentiality

European governmental funding (% of total funding)

In 2004: 0%
In 2005: 0%

Participation of foreign knowledge institutes (% of total expenditure)

In 2004: 6.6%
In 2005: 7.4%

Research output	2004	2005
Scientific publications:	219	186
PhD theses:	15	19

Overhead costs as % of total expenditure

In 2004: 10%
In 2005: 10% personnel costs EUR 961,000
other costs EUR 724,000

Expenditure for knowledge transfer

In 2004: EUR 261,000
In 2005: EUR 400,000 (2.3%)

Partners

Industry

- Accelrys
- Akzo Nobel
- Analytik Jena GmbH
- Agro Technology & Food Innovations
- Astra Zeneca
- Avantium Technologies
- Avery Dennison
- Basell
- Bayer AG
- Borealis AB
- Chemspeed Technologies AG
- Ciba Specialty Chemicals
- Degussa AG
- Dow
- DSM
- ECN
- Forschungs Gesellschaft Kunststoffe e. V.
- Friesland Foods*
- GE Plastics
- Hysitron Inc.
- Kraton Polymers
- Microdrop Technologies GmbH
- Merck KG
- National Petrochemical Company Iran
- NTI Europe
- Océ
- OTB Engineering
- Philips Research
- Sabic
- SEP
- Shell
- Teijin Twaron
- Ticona GmbH
- TNO Science and Industry
- Waters Technologies Corporation

* per 2006

Knowledge Institutes

- Agro Technology & Food Innovations
- University of Amsterdam
- National Technical University of Athens
- University of Birmingham
- Delft University of Technology
- Deutsches Kunststoff Institut
- University of East Anglia
- ECN
- Eindhoven University of Technology
- ESCPE Lyon
- Forschungsinstitut für Pigmente und Lacke
- University of Groningen
- Universität Hamburg
- Universität zu Köln
- University of Leeds
- Leiden University
- Queen Mary University of London
- Maastricht University
- Max Planck Institut für Polymerforschung
- University of Nottingham
- Università degli studi di Napoli Federico II
- NWO / Dubble
- Polymer Technology Group Eindhoven*
- Radboud University Nijmegen
- ESPCI/CNRS Paris
- University of Stellenbosch
- TNO Science and Industry
- University of Twente
- University of Utrecht
- Wageningen University and Research Centre

* per 2006

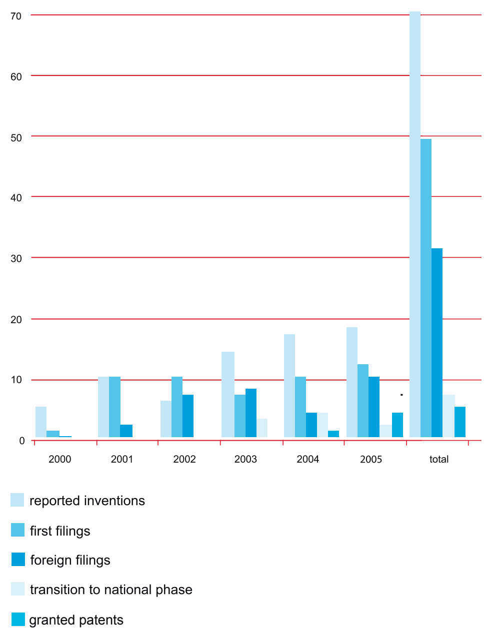
Ministry

Dutch Ministry of Economic Affairs

Intellectual Property

Creating and protecting intellectual property is a constant and growing focus of attention at DPI. In 2004, DPI set up the Contracts & Intellectual Property Affairs department to facilitate this work. As an incentive for inventors, a patent award is granted to any researcher whose invention has been filed as a first filing and then a foreign filing. In 2004 seven inventors received DPI's Patent Award (in the period October 2003 to October 2004). In total 25 patent awards have been granted.

The statistics below show the growth of DPI's patent portfolio. The positive trend evident in the number of reported inventions is reflected accordingly in the growth of first filings, foreign filings and transitions to the national phase. DPI has also granted one licence for a DPI invention to a DPI partner, and has transferred five of its inventions to DPI partners.



Organisation

Supervisory Board

Dr H.M. van Wechem, Shell International, Chairman (from May 2005)
Prof. Dr E. Meijer, DSM Research, Chairman (until May 2005)
Dr.Ing. M. Covezzi, Basell
Prof. M. Dröscher, Degussa AG Prof.Dr Ir C.J. van Duijn, Eindhoven University of Technology
Dr H.-W. Engels, Bayer Material Science
Dr H. van Houten, Philips Research
Drs N.P.J. Kuin, Océ Technologies BV
Prof. Ir K.C.A.M. Luyben, Delft University of Technology
Prof. Dr J. Put, DSM Research
Prof. Dr W.C. Sinke, Energy Research Centre of the Netherlands ECN
Dr Ir E.J. Sol, TNO Science and Industry
Dr Ir M. Steijns, Dow Benelux
Prof. Dr Ir H.Tijdeman, Twente University
Dr Ir J.A.J.M. Vincent, Sabic EuroPetrochemicals
Prof. Dr D.A. Wiersma, Groningen University
Prof. Dr J. de Wit, Akzo Nobel

Scientific Reference Committee

Prof. Dr E. Drent, Leiden University (NL), Chairman
Prof.Dr L. Leibler, Ecole Superieure Physique et Chimie Industrielles, Paris (F)
Prof.Dr H. Sirringhaus, Cavendisch Laboratory, Cambridge (UK)
Prof.Dr B. Voit, Institut für Polymerforschung, Dresden (G)

Executive Board

Prof.Dr Ir J.G.H. Joosten, Managing Director (from May 2005)
Prof. Dr M.A.J. Michels, Scientific Director
Dr Ir H.G.J. de Wilt, acting Managing Director (till May 2005)

Programme Area Coordination

Dr J.A.E.H. van Haare, Functional Polymer Systems, Coatings Technology
Dr. S. Schmatloch, High-Throughput Experimentation, Corporate Research
Dr J.E. Stamhuis, Polyolefins, Engineering Plastics, Rubber Technology

Scientific Programme Chairmen

Prof. Dr V. Busico, Polyolefins
Ir R.P.A. van den Hof, Engineering Plastics
Prof. Dr Ir J.W.M. Noordermeer, Rubber Technology
Prof. Dr. D. Haarer, Functional Polymer Systems
Prof. Dr C.D. Eisenbach, Coatings Technology
Prof. Dr U.S. Schubert, High-Throughput Experimentation
Prof. Dr M.A.J. Michels, Corporate Research

Organisation Staff

A.F.J. van Asperdt, Financial Administrator
Drs M.C.A. van Egmond, Office Manager
I.N.H.M. Hamers, Secretary
P.J.J. Kuppens, AA, Controller
Ir J.G.M. Nieuwkamp, Patent Attorney
S. Koenders, Programme Secretary
L. Robben, Human Resources Management
J.J.D. Tesser, Communication Manager
Ir S.K. de Vries, Trainee Patent Attorney

Breakthrough in lowering viscosity by adding nanoparticles

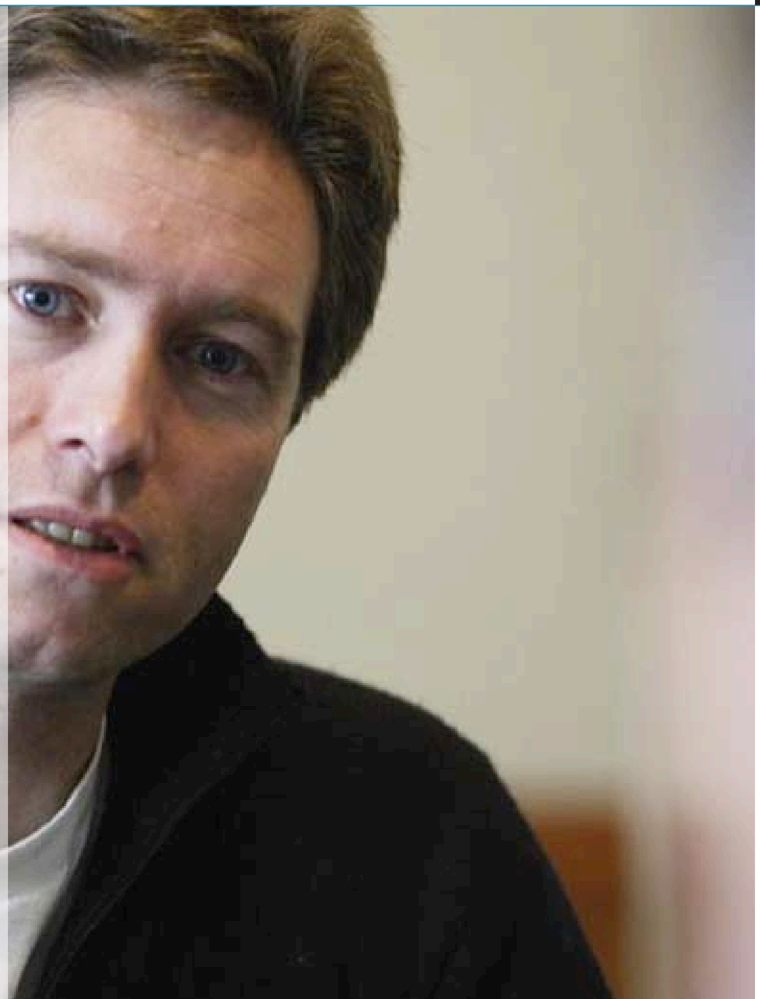
An industrial champion makes the difference

Cooperation between industry and academia, as promoted and supported by the DPI, is most effective if at least one partner is heavily involved and researchers make efforts to establish direct contacts with them on a regular basis.

Serendipity to the rescue

Polymer researchers all over the world expend great efforts to improve the processability of polymers without affecting the chemical and mechanical properties for which a specific material was chosen. Many plastic products are made by injection molding and the ease with which a polymer fills the mold, in more technical terms low viscosity, is of utmost importance in that process. A less viscous material means that the processing temperature, the processing pressure or the time that the polymer is held in the mold can be reduced. All these parameters have a positive influence on the processing costs. Viscosity is lower when the molecular weight of a polymer melt is lower, but its mechanical properties such as impact strength and stiffness improve when the molecular weight increases. A compromise between mechanical and processing properties is usually the result.
To his great surprise, Sachin Jain found during a PhD-project, more or less by accident that the incorporation of low concentrations of silica particles with nanoscale dimensions lowers the viscosity of synthetic polymers by more than one decade, without affecting, even improving in some cases, the other mechanical properties. The serendipity effect came into play when he was investigating the effect of the added particles on the mechanical properties, such as impact strength.
Dr. Markus Gahleitner, New Opportunities Manager & Programme Officer Polymer Design in Borealis, explains: "Small hard particles have been investigated in their role as impact modifiers since the early 80s. Adjustment of the adhesion between sufficiently small hard particles and the matrix would make the material more impact-proof. The change of focus in Jain's research work from improving mechanical properties to improving fluidity appears to me to be a quite normal trend in PhD studies."

When Sachin Jain started his PhD work at the TU/e in 2001 he focused on understanding the material properties of polymer matrices with added particles. That was the main interest of the industrial partners involved in the project at the time. Jain: "We used silica particles in a polypropylene matrix and started with high (20 percent) concentrations mainly for chemical characterizations. However, the concentration of fillers was so high that we ended up with very brittle and degraded material, which was, of course, not useful. It was only when we decreased the particle concentration to a maximum of 2 percent by weight, and made a dispersion without chemical interaction between particles and matrix, that we ended up with useful material albeit with strange properties. It showed no degradation, had the same molecular weight as the original, as well as slightly improved mechanical properties, … and, surprisingly, a lower viscosity. In some cases the process properties were even improved compared to pure polypropylene."
Dr. Han Goossens, assistant professor of Polymer Technology and one of the supervisors of Jain's PhD-thesis work, remembers that Jain, excited as he was about his results which potentially have far reaching consequences for polypropylene processing conditions, wanted to air his results at a conference. "Maybe we should keep it to ourselves for the time being and discuss it first with the DPI partners," he said, disappointing Jain with his suggestion. "For us it is important to work with industrial partners. We can look into phenomena but you have to have input about where and how it can be used."



Jan Stamhuis:
"You need an 'industrial champion' to really benefit from cooperation between universities and industry."

Han Goossens:
"We are very happy when industrial partners show their interest on a regular basis."

Sachin Jain:
"I think the initiative, even the responsibility, to maintain regular contacts with the industrial partners should lie with the researcher."

Markus Gahleitner:
"A practical training period with an industrial partner would help researchers in their contacts."

Reward

Gahleiter agrees: "We wanted to avoid problems associated with publishing papers too early." But there was a reward in the waiting. As soon as the DPI-partners involved in the project heard about these results, they showed their interest. Jain: "There were meetings where everyone showed up, even when that particular project was the only one to be discussed on that day, they all came." "They must have felt that something was going on," is the observation of Dr. Jan Stamhuis, DPI's programme coordinator, who was involved in the project at the very early stages of his present position with the DPI.
Borealis was involved in DPI work on polyolefins at the time, but not specifically in this project. Goossens involved Borealis in the person of Gahleitner. The latter explains his interest: "We focus on the long-term outlook. At the time there was only 20 grams of the modified material made, but if you have kilograms you can do more mechanical tests. And if these turn out well, a world market of hundreds of kilotons is an inviting prospect for a company like ours. How much exactly depends on the most important technical property, and that is … the price," says Gahleitner laughingly. Stamhuis observes: "Although eventually there was a lot of interest from other members, it was clear that only when Borealis in the person of Markus Gahleitner was closely involved, it was possible to turn this project into a real success. You need an 'industrial champion' to really benefit from cooperation between universities and industry. When other companies notice this interest they will join in.

Involvement

Gahleitner proved to be the one that kept 'pushing and pulling' the project members. Goossens appreciates this: "It can be very disappointing for us researchers if the industrial contact persons do not show enough interest, or get involved enough. We were very happy, when Markus became involved." Gahleitner, a bit over-whelmed: "If this works for polypropylene it will also work for polyethylene, since that is a simpler molecule. The market for polyethylene is even bigger that that for polypropylene. But before we can use it in production, we must really understand the system better." Jain, coming back to the involvement of the industrial partners, adds: "The industrial contacts have their own work to contend with on a daily basis, so my project was probably not their top priority. So I think the initiative, even the responsibility, to maintain regular contacts with the industrial partners should lie with the researcher. Researchers who start their work with the DPI should be aware of this." Stamhuis suggests that perhaps a kick-off meeting and scheduled project team meetings, at least once every six months, could help to improve contacts. Galheitner, challenged by this, suggests scheduling a practical training of researchers in one of the companies involved. This could help in several ways: the researcher gets a good opportunity to build up his contacts and the industrial sponsor learns more about the project (and about the researcher!). Moreover, the project staff gets a better appreciation of the possibilities and impossibilities in industrial research.

The involvement of Borealis meant more than the disappointment of not being able to present his results at a conference for Jain, as he observes a bit further in the discussion. "They helped us with the patent application. That was finished in a very short time, so that I could finish my thesis in time. So it had advantages for both of us. This work could probably not have been done inside a company. It would have been stopped at an early stage. And for me it was nice to work with people form different companies. I learned a lot from that, from working with different cultures." Jain now works as a Research Scientist in BASF.

Development

The next step will be to make 50 to 100 kilogram of polypropylene with silica particles and see how the material behaves in a real extrusion pipe. Borealis and the TU/e will continue to work on this together. It will no longer be a DPI project, since it will move out off the pre-competitive research phase. But Borealis will, if it eventually produces the new material, remain dependent on the DPI patent. The development will be done partly in cooperation with others, but the closer it gets to production, the more it will be Borealis on its own. Gahleitner: "There is still a lot of work to be done before you can use the material for piping, for instance. If you show that something works, you are only halfway through the process. Fitting it in the actual production process of existing standard plants will take as much time." Jain adds: "My results will be the starting point for more applied research. The principle will be used in other materials like polyethylene, but also in other polymers. Other particles can be tried." Goossens at the TU/e in the meantime will try to understand the mechanism better.

Improve conductivity by adding nanoparticles

Hidden treasures off the shelf

Big companies with large R&D activities rarely use all of their research results in products. The scope of the company may have shifted or economic conditions may have changed. But that doesn't make the results less interesting, both in a technical and an economic sense. In smaller, specialized companies these results can be put to very good use and thrive. The DPI can help.

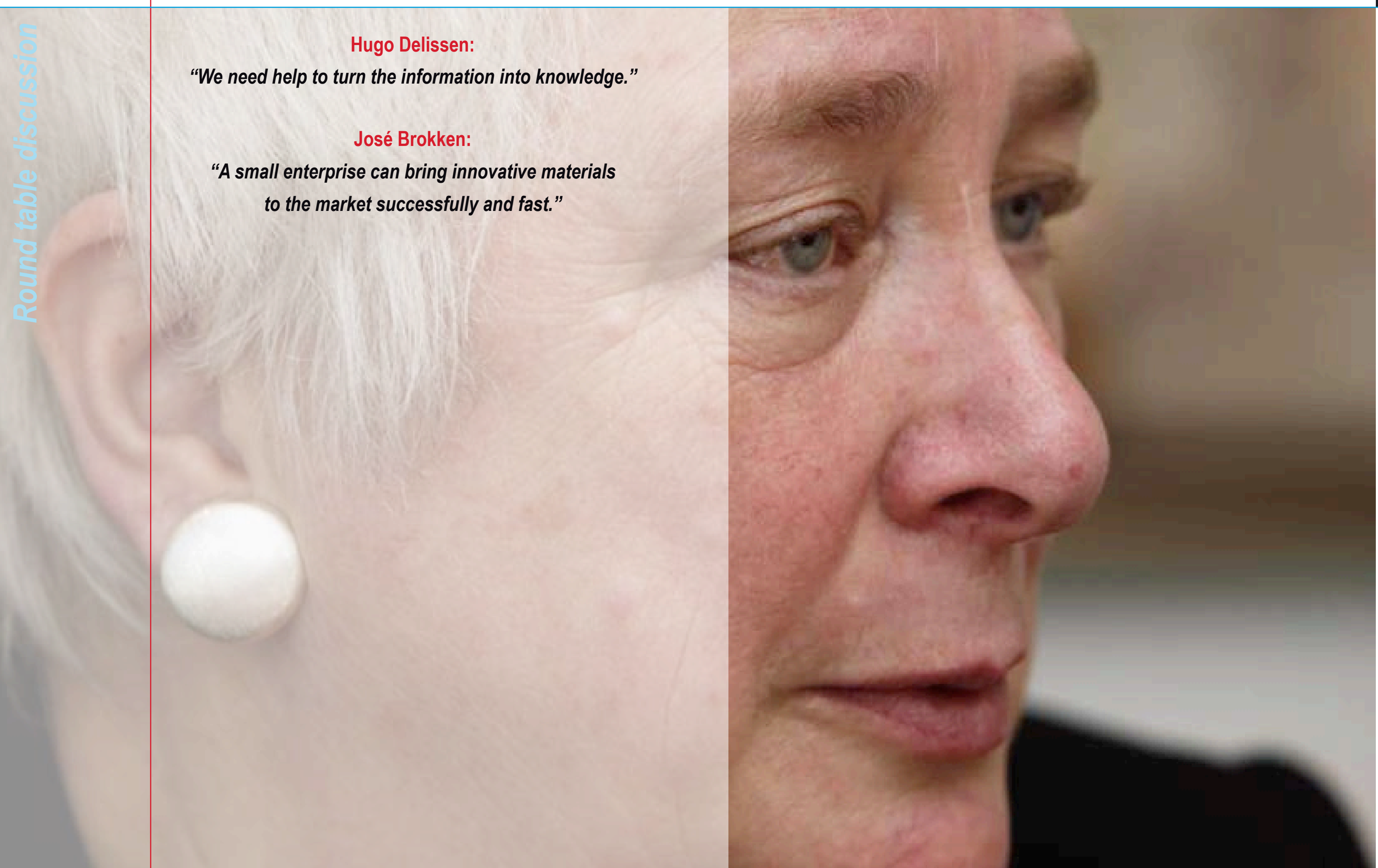
A pinch of conducting material

In many existing applications of polymers it would be very useful if they conducted electricity, even just a little. Static electricity would then be able to flow away thus making polymer packaging materials easier to handle, polymer surfaces less susceptible to attracting dust, and carpets less likely to deliver electric shocks. Even providing electromagnetic interference shielding could be contemplated. But preferably not using completely new materials for which production processes would have to be developed. It would be better to use the existing polymers and just add a pinch of a stable conducting material to realize the desired conductivity without changing the original properties of the polymer. Carbon black is a material which meets these requirements to a certain extent, but … it is expensive and it needs to be used in a concentration of at least 10 percent by weight. Because of this, the processing and the final material properties change. It makes packaging materials non-transparent for example. In the mid 1980s, Shell Research delivered a less expensive pinch in a project started in the mid 1980s, but it was never used because the company changed focus. Now it is a product of Nanospecials, a start-up with experience in nanoparticles and powder technology, but still on the learning curve in polymers.

In the 1980s, Dr. José Brokken, who is now Subcluster Coordinator Conductive Polymer Blends at the DPI, was working at Shell investigating additives to make thermoplastic polymers conductive. In principle three methods are possible: add antistatic agents, use doped conductive polymers, or use a conductive additive as filler in the polymer matrix. "It was a unique project at the time because both the economic and technical aspects were studied. The third possibility was the most promising. We discovered Phthalcon-11, a new highly stable nanoparticle that in principle could be produced cost-efficiently. Less than 1 percent by weight was needed to increase the conductivity to commercially attractive levels." The project was a great success, but in the meantime Shell cut back on its chemicals division and it was stopped. After her retirement from Shell, Brokken resumed the work in the group of Prof. Bert de With at the University of Technology in Eindhoven. "At the DPI we are now interested in understanding the system. What is the minimum amount of additive needed and how is this dispersed? How can we tune the conductivity? We have shown that in thermo-set materials, the area of interest within the DPI, the conductivity is higher and we understand the mechanism behind it. I cannot say more about it at the moment as an application for a patent is being filed."

One wing

The other participant in the discussion, apart from the DPI's programme coordinator John van Haare, is Hugo Delissen, Director of Nanospecials. Nanospecials originated from the business activities within Philips in the field of nanoparticles to make a transparent conductive coating for cathode ray tubes. ATO (antimonium-tinoxide) particles were developed in the 1990s, produced and sold to all the manufacturers of good old cathode ray tubes (monitors and TVs), first by Philips, later by LWB Eindhoven and Nanospecials. "You can't fly on one wing, so we were looking for more products in the field of nanoparticles. Via the contacts that we had with Dr. Brokken's research group at the Eindhoven University of Technology, we heard about Phthalcon-11. The technology to produce it fits in perfectly with fluorescence powder production, a field in which we have a lot of experience. In my view Phtalcon-11 is a very promising material. Big chemical companies are interested. I see large quantities, hundreds of tons a year, being produced in the future. You cannot do that if you have no experience in rushing tons of powder through production plants." Brokken nods affirmatively.



Hugo Delissen:

"We need help to turn the information into knowledge."

José Brokken:

"A small enterprise can bring innovative materials to the market successfully and fast."

Delissen continues: "We now have the Shell-knowledge on the use of Phtalcon-11 in thermoplasts. Shell has been very helpful. But since Nanospecials is not a member of the DPI, we do not have access to all the newly developed knowledge on thermoset materials. We can only use the published data. The ticket to the DPI is too expensive for us, so we cannot contribute in further developments of the material in thermoset matrices and we cannot profit from the results of that work. But many of the DPI partners, large chemical companies among them, know about Phthalcon-11 and that creates a huge potential market for us. So what we are going to do is use the Shell patents and produce Phtalcon-11 under license. In order to produce it we need help to turn the information we get from Shell into knowledge. José Brokken advises us in this process. "

Small enterprises

How could the DPI help, is what Van Haare wants to know. Delissen: "If the DPI helps us, we could do something in return for DPI partners by supplying them with particles for research purposes. And subsequently with commercial quantities, of course." That would be a way for small enterprises to participate in the DPI without paying the full amount. "And why not initiate start-ups in the DPI?" This suggestion by Delissen gives Van Haare food for thought. Brokken enthusiastically adds: "There are numerous research results on the shelves of large companies, even the DPI has findings they do not use. These could be developed with help from the DPI and later result in products by small dedicated companies. However, the research results used already need to be close to the market. And another thing is, why not formalize contacts with small enterprises, give them the opportunity to ask experienced researchers for advice, lower that threshold."

Brokken returns to the project at hand: "A new infrastructure, and new research results in the field of conductive nanoparticles in thermoset materials have resulted from my work both in and outside of the DPI. Nanospecials can use the infrastructure and the non-DPI knowledge in its practical work. The problem is that the DPI is interested in nanotechnology, but since a number of the big companies have 'nano' as their core business they are reluctant to share information in that field. That insight and my conviction that innovative materials can be brought to the market faster and better by a small enterprise, made me turn to Nanospecials."

Generic approach

Delissen says, when asked, that Nanospecials can be up and running at full production capacity in one year from now. "It is our sole and key point of attention and we have to make a success of it. That is not easy though. The building up of networks of nano materials in thermoplastic polymers needs to be studied. The dispersing mechanism has to be understood in detail. My experience is that such a nano composite always has to be made-to-measure." "But," Brokken adds, "the technology to produce dispersions is related to that for ATO, which is a very stable process, which I expect is also of importance for other nanoparticles, even non-conductive nanoparticles. It is of the utmost importance to look at this field from an interdisciplinary point of view. If you want to put a product into the market, it is very useful if you know the properties of the material not for 80 percent, but for 110 percent. Small variations in raw materials, in process conditions may have huge consequences for the end result. A generic approach to nanoparticle technology will help us here." The time-to-market of other products could even be shorter than that for Phthalcon-11.

Microwave-assisted heating added to laboratory robots

A new synthetic strategy

A new development, microwave-assisted synthesis of polymers, has been tried out in the DPI labs over the last two years. It turned out to be a promising strategy and because of the close cooperation with a chemical instruments company a new commercial system has become available in just one year. Now the DPI can use it for research into new materials with promising applications. The short communication lines and the infrastructure in the DPI stimulate and accelerate such win-win situations.

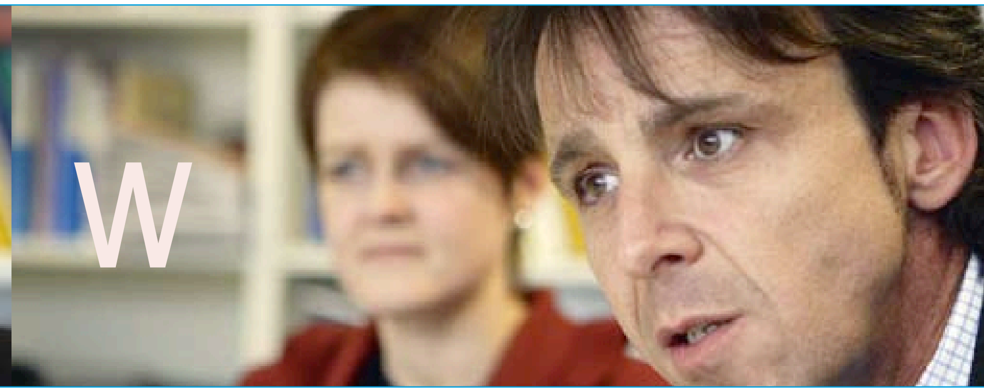
Increase reaction speed

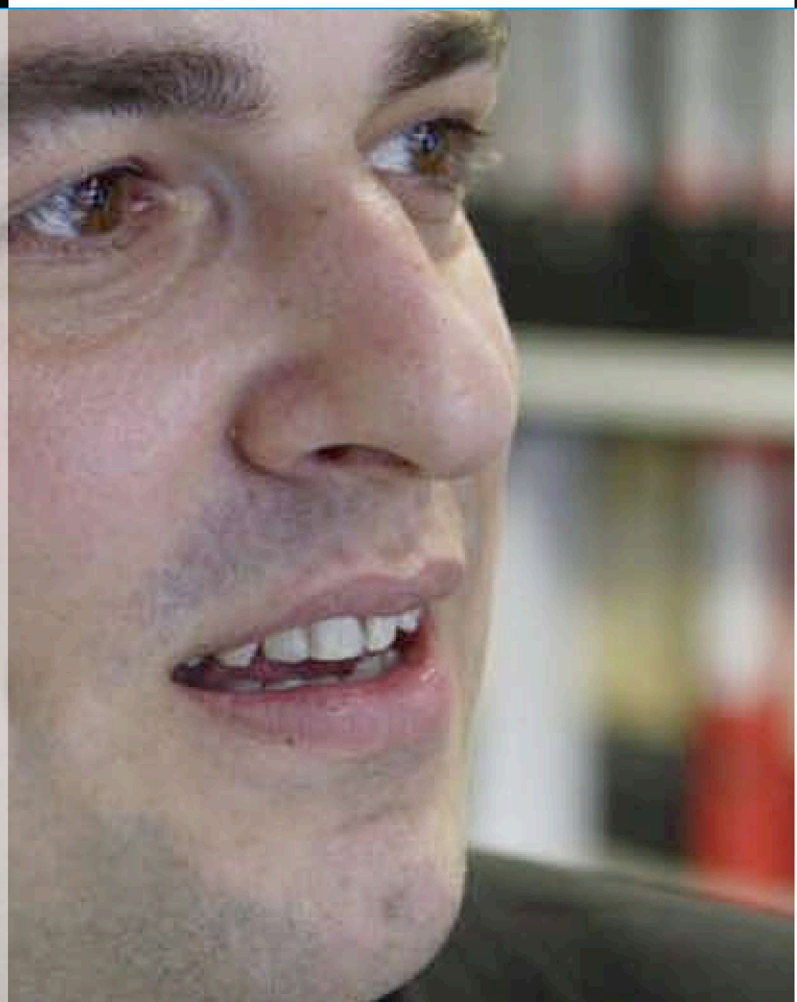
Chemical reactions proceed faster at increased temperatures. An efficient way to heat the reactants in a vessel is by using microwaves. It is efficient because the reactants are heated directly without the intermediary heat transfer steps from heating jacket, to reactor wall and to the reaction mixture. Microwaves are absorbed by polar molecules or ions that will oscillate in step with the microwave field. Collisions and friction between moving molecules result in heating and that, in its turn, either causes the reaction to proceed faster or to suppress side reactions thus facilitating cleaner processes. Selective heating can also activate specific reactions. Microwave-assisted heating has successfully been used for synthesis of organic compounds since the mid 1980s. Only recently it has been used in the synthesis of polymers. The combination of microwave-assisted heating and fully automated high-throughput experimentation methods in one instrument resulted from a fruitful DPI cooperation between the Eindhoven University of Technology and Chemspeed Technologies in Switzerland.

Success

Two years ago the DPI's annual report contained a discussion with participants in the then relatively new cluster High Throughput Experimentation. Professor Ulrich Schubert, leader of the Laboratory of Macromolecular Chemistry and Nanoscience at the Eindhoven University of Technology, ended that discussion by explaining when projects in the cluster would be deemed a success: "For us, success at the end of the day, four years from now when the present projects end, comes when industry takes over the methodology, and the equipment developed together is actually bought and used." Now, only two years later, such a success has already been attained with the SWAVE, in which Chemspeed Technologies combined its flexible platform for automated substance handling, work-up and analytics with microwave-assisted heating.

Stefan Schmatloch, DPI's programme coordinator in the field of High Throughput Experimentation, explains about the project that led to this development: "The project to look into microwave-assisted synthesis started two years ago. The DPI was one of the first to use it in fundamental polymer research. We achieved some good results: chemical synthesis could be accelerated, it proved to be a greener technology because less energy was needed for higher yields, and we got more insight in the chemical reactions. Chemspeed Technologies was technology partner in this project and in March 2005 they expressed the wish to use that technology in their automated platform. As early as January 2006, they introduced a product to the market, the SWAVE. The DPI network was instrumental in that development."





Carine Munsch:
"Feedback from researchers in the field is very important for Chemspeed."

Ulrich Schubert:
"This development is an important step for both fundamental academic and applied industrial research and it reflects the strength of the DPI concept."

Frank Wiesbrock:
"It is a faster, more selective and cleaner synthesis method."

Michael Schneider:
"People are at least as important as the infrastructure."

Richard Hoogenboom:
"Automated microwave assisted synthesis opens a whole new arena of applications."

Trigger

Schubert adds: "We had been working with the automated platform technology of Chemspeed Technologies for five years when we asked ourselves whether microwave-assisted synthesis would work for polymers as well. We very quickly had the first results and saw the huge potential. We wanted to combine it with the equipment we had: the robot systems from Chemspeed Technologies. Our experiments at the time still involved a lot of manual work: fill the vials, cap them, place them in the microwave, take them out again and repeat this procedure several times for multistep syntheses. We successfully collaborated with Chemspeed Technologies to implement microwave assisted heating in their robot system."

In March 2005 the decision to produce a new system was taken. In March 2006 the first system was installed in the lab in Eindhoven. Schubert: "We expect a lot from it. We can perform a large number of new reactions, and can speed up the process of screening properties for new functional polymers enormously."

DPI will use the SWAVE for different applications. For the development of new materials for drug delivery, for instance: compartments that degrade and deliver the embedded drug at the right place and the right time. Fast synthesis of a number of potential materials will increase the insight and help to gather expertise in modelling. Materials for scaffolding that degrade in a predictable way will help research in tissue engineering.

Arena

Dr. Richard Hoogenboom, one of the co-workers of Schubert in the Eindhoven laboratory, is anxious to start: "We were looking into a specific polymerization technique. When we started with it, the polymerization time was about 16 hours. We were disappointed and tried to see whether microwave heating could shorten that time. It turned out that if we fine-tuned the conditions and chose the right parameters, we could bring this down to ten minutes. This allowed us to perform screening experiments and vary the parameters to optimize the syntheses and make new polymers within a day. The idea is to incorporate new monomers with interesting side chains that change or add to the functions of the polymers. Several of these new monomers were difficult to polymerize without the advantages of microwave-assisted heating. We make linear block copolymers, long chains consisting of two different monomers in different combinations, and expand that to triblock and tetrablock copolymers. That opens a whole new arena of applications, which is inaccessible without microwaves."

Schubert: "Now you can programme the SWAVE to incorporate a, b, c, d monomers in a polymer. It was never acceptable to do this manually. And these can be monomers that cannot be included in the classical way. The instrument makes a new synthetic strategy possible." Dr. Frank Wiesbrock, who was working as a postdoc student with Schubert on the microwave-assisted synthesis and has moved to Chemspeed Technologies in the meantime, gives an example of how microwaves help to improve product properties: "For many applications in life sciences such as drug delivery and health care, there is a strict requirement for the polymers to be non-coloured. When you use microwave heating, the side-reactions are suppressed. It is a faster, more selective and cleaner synthesis method.

The SWAVE is the world's first commercial instrument that provides fully automated microwave-assisted synthesis in an inert atmosphere with unique gravimetric dispensing of solids. This eliminates a major bottleneck, particularly in the pharmaceutical industry which frequently uses microwave-assisted synthesis."

Advantages

Dr. Michael Schneider, responsible for business development at Chemspeed Technologies: "In the pharmaceutical industry microwave-assisted synthesis is a mainstream technology now. But with the SWAVE we are also addressing other chemical industries and academia. The key aspects are robotic technology with automated tool exchange and the flexible reactor technology that we offer on the same robotic platform."
Dr. Carine Munch, project manager for the development of the SWAVE at Chemspeed Technologies, adds: "But we are not just a robotics company, we develop our systems with the chemists needs and wishes as a guideline. Like me, all our project leaders have a background in chemistry. Chemspeed Technologies is application-driven and not technology-driven. Feedback from researchers in the field is very important."
Wiesbrock sums up the SWAVE's advantages: "You can go far beyond the boiling point of the solvent. You produce less waste. Two and three-step reactions in particular, go much more quickly." Schneider sees yet other advantages: "To get more experiments done per time unit is one aspect, but the SWAVE releases well qualified human resources from dull work to do more intellectual activities, such as analyzing the results, thinking of better strategies, and doing better science. And then there is the quality: the reproducibility of the reactions is better. Automation allows a reaction to be done or repeated in exactly the same way, something which a human being can't do. The SWAVE can produce quantities exactly as needed. And it works through the night without complaint."

Very quick

Schubert: "Here you have a perfect example of the two DPI objectives: gain more insight in fundamental processes and trigger new technologies. There is something going on in academia, we try things out here, we find the partners, trigger a technology development, they come up with a completely new system that we can use again for R&D purposes. Normally this whole process would have taken much more time. Michael Schneider is member of the programme committee of the DPI, sees what is going on, and can trigger the start of the development of a new product. This approach definitely works in the DPI. Now we have the large industrial members around the table and they can use and implement this new technology directly to screen material properties, develop catalysts, and make new polymers. They could not have developed such a system themselves within this short timeframe and it would have been too expensive for one company on its own. One year is extremely quick."

Schneider adds a slight nuance: "You have to keep in mind that we combined two existing technologies, so we did not have to develop these from scratch. Our modular approach makes it possible to accommodate new technologies quickly, and anticipate emerging technologies. That is an important factor in allowing us to have the SWAVE on the market so rapidly. One plus one is greater than two. But apart from that, the people are at least as important as the infrastructure of DPI. From the beginning we had an open and constructive cooperation, no small talk, very straightforward discussions, with real commitment."

Not the end

Schubert: "I am sure that this is only an intermediate step, there will be a further development. Purification steps could follow, this is not the end of it. Now we can mix, react, analyse, and get a 90 percent yield, but part of the purification is still done in a classical way. That could be the logical next step in the same platform. The end result will be a packaged amount of very pure material, with a bar code attached that will be sent by UPS somewhere where it is needed."
We will see about this in the annual report two years from now.

Polyolefins

Introduction

Present-day industrial processes for polyolefin production are among the most efficient and atom-economical chemical transformations ever implemented, with productivities under mild conditions and selectivities rivalling those typical of the more celebrated enzymatic catalysis. However, at odds with the common belief, the basic understanding of such processes is far from being satisfactory; in particular, the reliable measurement of active site concentrations and of specific chain propagation rates is still – euphemistically – complicated. The relationships between chain microstructure, polymer structure (as such and as a function of processing conditions), and physico-mechanical properties are also not known to the level of detail that would be needed for rational material design, particularly for semi-crystalline systems. Last but not least, the search for new catalysts and co-catalysts/activators is far from exhausting its thrust, and continues to lead to novel and/or more controlled polyolefin architectures; recent results in the scientific and patent literature provide a clear indication of how large the margins for substantial innovation in the field still are. The research in the Polyolefins technology area faces all the above aspects with an integrated approach.

Research themes and highlights

Heterogeneous catalysis and single-centre catalyst immobilisation

Substantial progress was achieved in the implementation of new approaches for the immobilisation and activation of single-centre catalysts for olefin (mainly ethene) polymerisation, making use of magnesium chloride based supports. Using Ti, V, Cr and Ni catalysts, high activity systems were achieved with retention of single-centre behaviour, excellent particle morphology, and control over molecular weight distribution. In the latter respect, in particular, catalyst formulations suitable for the production of unimodal and bimodal polyethylenes were identified. Aside from the applied work, more fundamental studies were aimed at a better understanding of industrial $MgCl_2$-supported $TiCl_4$-based catalysts. Methods for the preparation of catalyst single crystals and their characterisation by means of Atomic Force Microscopy (AFM) and electron microscopy were successfully developed (more on this can be found in the case study). Moreover, High Resolution - Magic Angle Spinning (HR-MAS) NMR tools led to the first in situ observations of Lewis-base chemisorption and reaction at the active surfaces of these catalysts in hydrocarbon suspension under conditions not far from those of practical application. Last, but not least, the controlled immobilisation on silica of borate activators for single-centre (mainly metallocene) catalysts in combination with the use of molecular "traps" to reversibly tag the surface active species led to NMR solutions for the precise quantification of activator and transition metal species uptake.

Homogeneous catalysis

Novel ancillary ligands for transition metal-based ethene homo- and copolymerisations, including processes for the incorporation of polar monomers, have been synthesised and screened for activity, in some cases with highly promising results.
Very important progress was achieved in the field of olefin block copolymerisation. New Zr(IV) and Hf(IV) catalysts with bis(phenoxyamine) ligands for the "living" (controlled) polymerisation of ethene and propene, the latter with exceedingly high isotactic selectivity, were prepared and used successfully for the production of block copolymers of isotactic polypropylene with polyethylene, ethylene/propylene rubber and other isotactic poly(1-alkenes). The physical and mechanical characterisations of these novel materials are currently in progress. Attempts to develop new activators for single-centre catalysts have also been carried out.

In particular, replacements of methylalumoxane were discovered that, in contrast to the latter which needs to be used in large excess relative to the transition metal precatalyst, are able to activate metallocene precatalysts in stoichiometric amount. The possibility to file a patent for this is being considered.

Process engineering

Several studies on different reactors and technology unit operations were targeted to a quantitative description and understanding of the crucial aspects of the polymerisation processes. As an example, catalytic gas-phase olefin polymerisation was investigated by means of radioactive particle tracking and computational fluid dynamic studies. Another project focused on the comparison of slurry and gas phase polymerisation for the production of high-density polyethylene (HDPE). Special emphasis was given to innovative technologies. A typical case is that of gas phase olefin homo- and copolymerisations under “oscillating” process conditions, mimicking in small scale the behaviour of the new industrial “multi-zone” reactors and aiming to produce intimately dispersed reactor blends. Molecular kinetic aspects were also examined in this cluster. A tubular reactor was used to enable polymerisation reactors to operate up to very high pressure at very short reaction times, i.e. in the range of polymer molecular mass build-up. This may open the way to high-throughput measurements of active site concentrations and of kinetic constants of chain propagation and transfer. The application to catalyst systems prepared in the two catalysis clusters is already in progress.

Polymer structure, modelling and processing

Flow induced crystallisation (FIC) under processing conditions represented a major focus area for projects internal to TA and in collaboration with the DPI Corporate research programme, in all cases with a highly integrated experimental and theoretical approach. The investigations covered the initial states of nucleation and growth of different crystalline structures, the influence of processing conditions on the evolution of these structures and the relationship to end-product properties. Different experimental methods (WAXD, SAXS, SALS, FTIR, E-SEM, optical microscopy) were used to observe structure evolution at different length scales. Experimental set-ups were designed and built that allow for well-defined experiments, i.e. with known initial and boundary conditions for all variables (temperature history, pressure history, velocity history). This includes a) a novel PVT apparatus that allows the application of high pressures (100 MPa), high cooling rates as found in real processing and controlled shear histories; b) a special flow cell to be used on a multi-pass rheometer that can create complex flow histories; and c) a flow cell for prototype injection moulding. The use of the European synchrotron radiation beamline facility in Grenoble, crucial for the possibility to follow fast phase transformations in polymeric materials as a function of temperature and pressure changes, has been consolidated, and a special project was launched in collaboration with the DPI Corporate research programme in order to ensure constant competent follow-up of the measurements carried out by scientists of the TA.

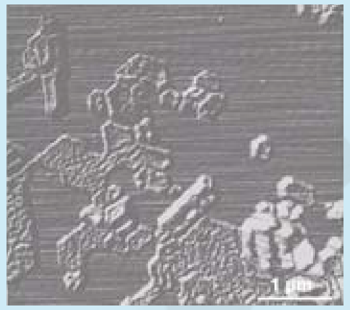
fact sheet

Facts and figures

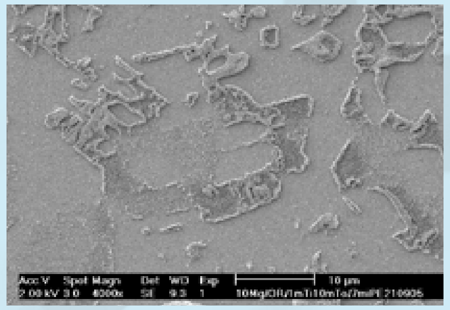
- **Partners Industry:** Akzo Nobel, Basell, Borealis, Dow, DSM, NPC Iran, Sabic and Shell.
- **Academia and research institutes:** the Universities of Technology of Delft, Twente, and Eindhoven, the universities of Amsterdam, Groningen, Nijmegen, and Utrecht, are our Dutch academic partners. The increasing international character of our activities is reflected by the participation of the University of Naples Federico II and by the ESPCE in Lyon.
- **Budget and Organisation:** Total Costs allocated in 2005 in our TA amounted to EUR 2.4 million (budget EUR 2.4 million). The number of research staff employed with DPI sponsorship was 37 (25 full time equivalent). In 2005 Prof.Dr Vincenzo Busico as scientific chairman (SC) was responsible for scientific development alongside the programme area coordinator (PAC) Dr Jan Stamhuis with more operational focus.
- **Networking:** 3 subcluster review meetings were organised with overview lectures by the subcluster coordinators and detailed presentations by research staff of their project results. The Polyolefins PC and the scientific support committee (SSC) held 3 meetings in 2005.
- **Publications:** 36 referenced publications on DPI Polyolefins TA sponsored work appeared in the scientific literature. In addition to the large number of contributions to scientific symposia in the form of posters or presentations, this reflects the significant contribution of this TA to science development in this area.
- **Inventions:** Registration of 2 reported inventions and the filing of 1 patent application indicated that our pre-competitive programmes offer also openings for technological and economical impact.

Advanced characterisation of Ziegler-Natta catalysts on flat surfaces

Ziegler-Natta catalysts occupy a dominant position in polyolefin production. To improve the understanding of state-of-the-art $MgCl_2$-supported catalysts, relating to polymerisation behaviour and the effect of catalyst type on polymer composition and properties, detailed insight into the nature of the active species is required. The aim is to develop a realistic model for a Ziegler-Natta system that allows a detailed study of surface chemistry and morphology, employing surface science techniques (XPS, Polyolefins SIMS) and microscopy (AFM, SEM). This has now been achieved by the spin coating of a $MgCl_2$ solution onto a flat Si wafer, followed by controlled crystal growth to give well-defined $MgCl_2$ crystallites in which the relative proportions of 120 and 90 degree edge angles indicate the preference for the formation of a particular crystallite face. A fundamental question in Ziegler-Natta catalysis is which crystallite face is most effective for coordination of the active site precursor, $TiCl_4$, and where the active species are located. Treatment of the $MgCl_2$ crystallites with $TiCl_4$, $AlEt_3$ and ethylene, followed by the application of Scanning Electron Microscopy and Atomic Force Microscopy, has clearly revealed polymer growth at the edges and in particular at the crystallite corners. This breakthrough now opens the way to detailed and fundamental characterisation of a range of industrially important Ziegler-Natta catalysts.



Magnesium chloride crystals on flat silica



After polymerisation polyethylene has formed at the edges of the magnesium chloride crystals

Output

Theses

K. Garkhail Sharma
Easily Processable ultra high Molecular Weight Polyethyleen with narrow molecular weight distributiebon.
TU Eindhoven.

M. Stol
Aryl Metal Complexes Stabilized by Intramolecular Coordination. Synthesis, Charaterization and Catalytis Activity.
University of Utrecht.

M. Smit
Heterogenization on Silica of Metalloncene Catalyst for Olefin Polymerization.
TU Eindhoven.

G.A. Bokkers
Multi-Level Modelling of the Hydrodynamics in gas phase polymerisation reactors.
Twente University.

S.H. Jain
Effect of polymeer adsorption on processibiliy and properties.
TU Eindhoven.

D.J. Beetsra
structure-property relationships in early transition metal based olefin poymerisation catalyses.
RU Groningen.

T.J.J Scairone
Electron deficient organiron(II) Complexes of amidinates and beta-diketiminates RU Groningen.

Scientific Publications

S. Rastogi, A.E. Terry
Morphological implications on interphase linking crystalline and amorphous regions in semi-crystalline polymers
Advances in Polymer Science 180, 161-194

S. Rastogi, L. Kurelec, D. Lippits, P. Lemstra
A novel route to fatigue resistant fully sintered UHMW-PE for knee-prosthesis
Biomacromolecules 6-2, 942 – 947

S. Rastogi, L. Kurelec
Polymer Crystallization under High Pressure
Encyclopedia of Materials: Science and Technology, 7261-7266

P.J. Lemstra, S. Rastogi
Processing Flexible Polymers to High Performance Fibers
Encyclopedia of Materials: Science and Technology, 7877-7883

Christian A. Nijhuis, Erica Jellema, Timo J.J. Sciarone, Auke Meetsma, Peter H.M. Budzelaar, Bart Hessen
First-Row Transition Metal Bis(amidinate) Complexes; Planar Four-Coordination of FeII Enforced by Sterically Demanding Aryl Substituents
European Journal of Inorganic Chemistry 11, 2089-2099

Timo J.J. Sciarone, Auke Meetsma, Bart Hessen
Neutral and cationic Fe(II) ß-diketiminate complexes
Inorganica Chimica Acta, 359-6, 1815-1825

M.H.E. van der Beek, G.W.M. Peters, H.E.H. Meijer
A dilatometer to measure the influence of cooling rate and melt shearing on specific volume
International Polymer Processing XX(2), 111-120

F. Picchioni, J. G. P. Goossens, M. van Duin
Solid-state modification of isotactic polypropylene (iPP) via grafting of styrene. II. Morphology and melt processing
J. Applied Polymer Science 97-2, 575-583

Madri Smit, Xuejing Zheng, Joachim Loos, John C. Chadwick, Cor E. Koning
Effects of methylaluminoxane immobilization on silica on the performance of zirconocene catalysts in propylene polymerization
J. Polymer Science A, Polymer Chemistry 43-13, 2734-2748

Michiel F. Bergstra, Günter Weickert
Ethylene Polymerization Kinetics with a Heterogeneous Metallocene Catalyst – Comparison of Gas and Slurry Phases
Macromol. Materials and Engineering 290, 610-620

W. Kaminsky, F. Mueller, O. Sperber
Comparison of olefin polymerization processes with metallocene catalysts
Macromol. Materials and Engineering 290-4, 347-352

Claudia Stern, Achim Robert Frick, Joachim Theodorus Maria Pater, Günter Weickert
Comparison of Gas and Liquid Propylene Polymerization Technique - Hydrogen Effect on Thermal, Rheological, and Morphological Properties of PP
Macromol. Materials and Engineering 90-4, 372-383

W. Kaminsky, C. Piel, K. Scharlach
Polymerization of Ethene and Longer Chained Olefins by Metallocene Catalysis
Macromol. Symp. 226-1, 25-34

F.G. Karssenberg, C. Piel, A. Hopf, V.B.F. Mathot, W. Kaminsky
Bernoullian, terminal, penultimate or third order Markov statistics?
Macromol. Theory Simul. 14, 295-299

M.H.E. van der Beek, G.W.M. Peters, H.E.H. Meijer
The influence of cooling rate on the specific volume of isotactic polypropylene at elevated pressures
Macromol. Theory Simul. 290-5, 443-455

Soazig G. M. Périn, John R. Severn, Cor E. Koning, John C. Chadwick
Unusual Effect of Diethyl Zinc and Triisobutylaluminium in Ethylene/1-Hexene Copolymerisation using an MgCl2-Supported Ziegler-Natta Catalyst
Macromol. Chemistry and Physics 207-1, 50-56

Claudia Stern, Achim Robert Frick, Joachim Theodorus Maria Pater, Günter Weickert
Comparison of Gas and Liquid Propylene Polymerization Technique - Hydrogen Effect on Thermal, Rheological, and Morphological Properties of PP
Macromol. Materials and Engineering 290-4, 372-383

Makarand S. Pimplapure, Xuejing Zheng, Joachim Loos, Günter Weickert
Low-Rate Propylene Slurry Polymerization: Morphology and Kinetics
Macromol. Rapid Commun. 26-14, 115-1158

Makarand S. Pimplapure, Günter Weickert
Catalytic Polymerization of Liquid Propylene: Effect of Low-Yield Hexene Prepolymerization on Kinetics and Morphology
Macromol. Rapid Commun. 26-16, 1294-1298

John R. Severn, Nileshkumar Kukalyekar, Sanjay Rastogi, John C. Chadwick
Immobilization and Activation of a Single-Site Chromium Catalyst for Ethylene Polymerization using MgCl2/AlRn(OEt)3 - n Supports
Macromol. Rapid Commun. 26-3, 150-154

Audrey Di Martino, Jean Pierre Broyer, Roger Spitz, Günter Weickert, Timothy F. McKenna
A Rapid Quenched-Flow Device for the Characterisation of the Nascent Polymerisation of Ethylene under Industrial Conditions
Macromol. Rapid Commun. 26-4, 215-220

Xuejing Zheng, Makarand S. Pimplapure, Günter Weickert, Joachim Loos
Influence of Copolymerization on Fragmentation Behavior Using Ziegler-Natta Catalysts
Macromol. Rapid Commun. 27-1, 15-20

Xuejing Zheng, Makarand S. Pimplapure, Günter Weickert, Joachim Loos
Cover Picture: Macromol. Rapid Commun. 1/2006
Macromol. Rapid Commun. 27-1, NA

A. Rastogi, A.E. Terry, V.B.F. Mathot, S. Rastogi
A study of thermodynamically favorable crystals in branched polymers; a disentangled and crystallizable interphase
Macromolecules 38, 4744-4754

C. Piel, F.G. Karssenberg, W. Kaminsky, V.B.F. Mathot
Single-Site and Dual-Site Metallocene Ethene/Propene Copolymerizations: Experimental and Theoretical Investigations
Macromolecules 38, 6789-6795

X. Zheng, M. Smit, J. C. Chadwick, J. Loos
Fragmentation behavior of silica-supported metallocene / MAO catalyst in the early stages of olefin polymerization
Macromolecules 38-11, 4673-4678

B. Heuer, W. Kaminsky
Alternating Ethene/Propene Copolymers by C1-Symmetric Metallocene/MAO Catalysts
Macromolecules 38-8, 3054-3059

Claudia Stern, Achim R. Frick, Günter Weickert, Georg H. Michler, Sven Henning
Processing, Morphology, and Mechanical Properties of Liquid Pool Polypropylene with Different Molecular Weights
Macromol. Materials and Engineering 290, 621-635

M. Stol, D.J.M. Snelders, J.J.M. de Pater, G.P.M. van Klink, H. Kooijman, A.L. Spek, G. van Koten
Synthesis and structural characterization of 2,6-bis(oxazolinyl)phenyl-lithium and trimethyltin complexes
Organometallics 24, 743–749

W. Kaminsky
Polyolefins
Plastics Engineering, Handbook of Polymer Synthesis, New York, 1-72

W. Kaminsky, B. Hinrichs
Polymeric dienes
Plastics Engineering, Handbook of Polymer Synthesis, New York, 333-380

Audrey Di Martino, Günter Weickert, Timothy F. McKenna
A quenched flow reactor fort the observation of polyolefin morphology under industrial conditions at short times
Wiley-VCH, Weinheim, DECHEMA Monographs 138, 173-179, ISBN 3527102329

R.R. Tupe, G. Weickert
Novel reactor concept for catalytic olefin polymerization
Wiley-VCH, Weinheim, DECHEMA Monographs 138, 311-316, ISBN 3527102329

Erik Eriksson, Yahya Banat, Guenter Weickert, Timothy F. McKenna
CFD simulation of gas phase olefin polymerization
Wiley-VCH, Weinheim, DECHEMA Monographs 138, ISBN 3527102329

G. Weickert
New reactor concepts for gas phase olefin polymerization
Wiley-VCH, Weinheim, DECHEMA Monographs 138, ISBN 3527102329

N. Sushko, P. van der Schoot
Geometry explains the large difference in the elastic properties of fcc and hcp crystals of hard spheres
Physical Review E 72, 067104

Filed patent applications

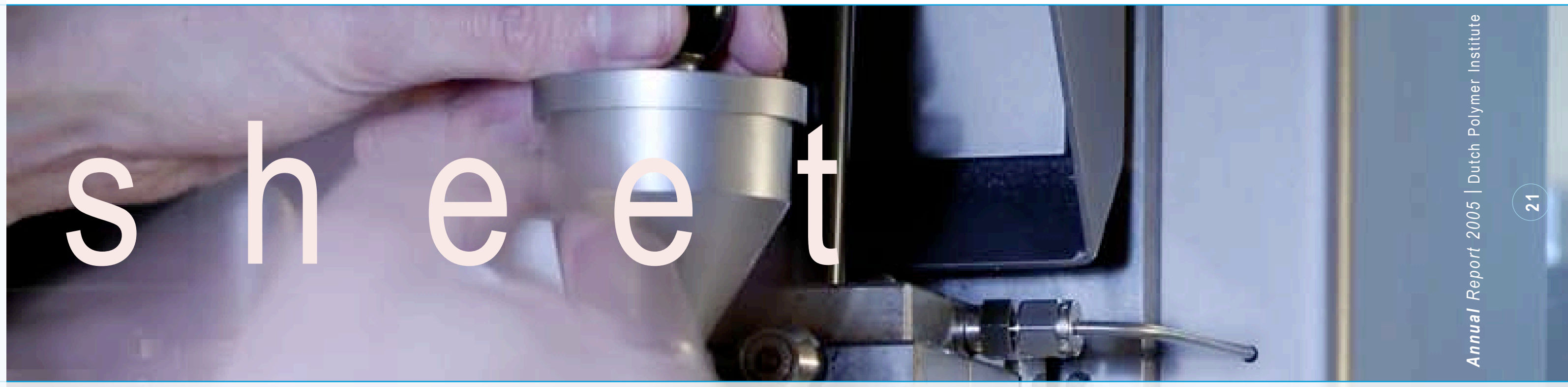
#133 S. Jain, J.G.P. Goossens, G.W.M. Peters
Novel nanocomposite

Reported inventions

#319 P.L. Shutov, B. Hessen
Brønsted acidic boralumoxane cocatalysts

#495 W. Huang, J.D. Chadwick
Synergetic effect of different catalysts

f a c t s h e e t



Engineering Plastics

Introduction

The Engineering Plastics Technology Area (TA) is able provide a solution to part- and assembly performance requirements through close co-operation between polymer supplier, converter and end-user. This requires a thorough understanding of polymerisation and polymer modification as well as polymer processing, properties and design.
The engineered solution is driven by the need to obtain the best system economy during its life cycle or, in the case of new opportunities, to create new applications as opposed to "classic" material choices and fabrication methods.
The rate at which engineering materials are diversified by new polymers is low and declining. Improvements to the chemical routes by which existing polymers are manufactured, by contrast, have an important role to play because their impact on both environmental and economical results is high. Other important issues for the industry are new chemical routes, monomers obtained from sustainable resources, new catalytic routes (including enzymatic catalysis) and the modification of polymers by post-reactor chemistry.
New opportunities can primarily be found in combining different polymers and/or polymers with non-polymer materials, especially nano-particles. The high surface area per unit volume between nano-particles and polymer(s) and the increased freedom in selecting the interaction parameters enables control over morphologies and properties that are not attainable with current material systems.

Research themes and highlights

Polymer chemistry and modification

The industry is continuously seeking step changes in the balance of flow (for low-cost processing and/or dimensional precision) and mechanical and functional properties. New concepts of molecular structure may provide a breakthrough in this respect. Other important industrial and societal issues are the need for lower cost polymerisation and the developing use of sustainable raw materials.

Melt and solid-state chemistry are the primary focus of the programme. The following projects are currently exploring new opportunities:

- Monodisperse amide blocks in polyester-amides
- A three-step route towards polyamides
- New diols in polyesters, CO_2 as (co)monomer for polycarbonates
- New catalysts for polyesters based on terephtalic acid
- Reactive compatibilising through reactive extrusion
- Sustainable monomers.

Properties control via chemistry

It has now been demonstrated that multiblock copolymers containing small amounts mono-disperse amide segments are capable of having exceptional combinations of properties in comparison with a large number of polymers (polyethers, polyesters, polyurethanes, polycarbonate).
For construction materials, such as polycarbonate, the high glass transition temperature can be exploited and properties improved by introducing crystalline domains. These crystalline domains bring improvements in the dimensional stability, the solvent resistance and even processability, a combination otherwise not attainable. In thermoplastic elastomers the elastic properties are improved, the modulus is almost constant over a large temperature range and processability is enhanced. The maximum use temperature can be in excess of 200°C if required. This represents a much-sought-after set of characteristics in thermoplastic elastomers. The research in this area, conducted at Twente University by the group under Professor Gaymans, now provides an almost complete toolbox of properties control through chemistry. This programme is now in its final stage and three concluding projects are looking into further controlling the structure (e.g. the effect of amide-end-blocks).

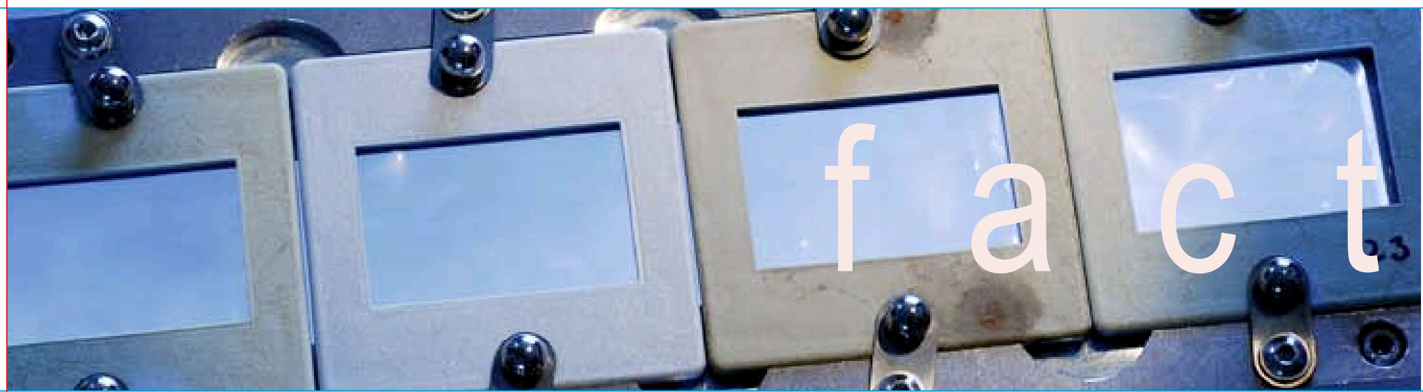
Chemistry for a lower environmental impact

The synthesis of polyamide 6 involves a large number of steps and the formation of large amounts of by-product. A three-step route, starting from butadiene, would therefore provide a very attractive alternative. The third step of the process, however, namely polymerisation through the hydrolytic coupling of nitrile and amine functionalities, as reported in the literature, did not lead to linear polymers of sufficiently high molecular weight. A new catalytic route was explored with which highly selective polymerisation towards PA6 with more than 99% nitrile conversion was successfully demonstrated. The possibility of designing a phosgene-free route to polycarbonate using CO_2 as one of the monomers has been studied.

Processing for properties

Increasingly, engineering plastics are finding their way into mechanical actuators (with gears), miniaturised parts with integrated functions and optical parts. Better understanding of the principles of wear, friction and shaping will support the creation of new opportunities. Non-covalent interactions in polymers can have important implications for particular processes such as the production of nano-composites or the processing of unstable or intractable polymers, both synthetic and originating from bio-chemistry.
The intention is to understanding the relationship between (molecular) structure of a polymer, the processing conditions it is subjected to in manufacturing parts and the resulting properties of those parts. Active projects in this field deal with:

- Wear and friction mechanisms of unfilled and filled materials
- The influence of water at elevated temperatures and pressures on polymers with hydrogen bonds.



fact sheet

The most promising chemical and catalytic routes lead to aliphatic polycarbonates, thus not directly to the replacement of the aromatic polycarbonate currently used as the high-volume engineering plastic. However, the toolbox for making polycarbonates from carbon dioxide has been expanded. The resulting polycarbonates have good potential for application in durable coatings. Further research into polycarbonate-based coatings has been taken up by the DPI Coatings Technology area.

Advanced reinforced thermoplastics and synthetic fibres

Composites, nano-composites and (nano)structured materials provide new leads for materials applications. This explicitly includes academic studies related to the manufacture and use of very strong fibres such as Twaron and Dyneema. Developing new nano-composites with well-dispersed carbon nano-tubes.

- Understanding and finding leads to improve the behaviour of aramid fibres in terms of adhesion to the matrix material.
- Understanding and finding leads to improve the tribological behaviour (wear and friction) of fibre-reinforced engineering plastics in a wide range of technical applications.

Stabilisation

Predicting the lifetime of a polymer in its application is becoming increasingly important in view of product liability, fit-for-use design and sustainability. Current methods of testing lifetime are time consuming and thus expensive. Finding the underlying mechanism and detecting degradation at an early stage with advanced analysis techniques offers new opportunities. The narrow portfolio reflects our idea to maintain a sharp focus in this otherwise vast theme. In the near future we intend to study the interaction between chemical and physical ageing and the effect on properties. Understanding the mechanism of chemical degradation in polymers and finding ways to predict long-term behaviour in practical use, focusing on the heat stability and UV stability of polyamide and polycarbonate.

Facts and figures

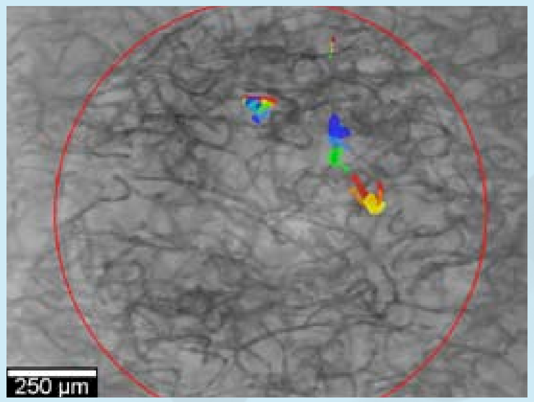
- **Partners Industry:** Bayer, Degussa, Dow, DSM, GE Plastics, Océ Technologies, Shell, Teijin and TNO Science and Industry.
  Academia and research institutes: France (Ecole Superieure Physique and Chimie Industrielle, Paris) and the UK (Queen Mary and Westfield College at the University of London, the University of Birmingham). In the Netherlands: university of Groningen and the Delft, Twente and Eindhoven universities of technology (the latter is affiliated with the University of Stellenbosch, South Africa). Research institutes were A&F and TNO Science and Industry.
- **Budget and Organisation:** Total costs allocated in 2005 in our TA amounted to EUR 1.8 million from a budget of EUR 2.0 million. The total number of scientific staff employed with DPI sponsorship was 38 (21 full-time equivalents). In 2005 Ir Richard van den Hof as scientific chairman (SC) was actively engaged in scientific development alongside the programme area coordinator (PAC) Dr Jan Stamhuis, whose focus was more operational.
- **Networking:** 2 cluster review meetings were organised at which research staff gave detailed presentations on the progress of their projects. An important NanoDispersion review meeting was hosted by DPI in October. Speakers whose expertise is internationally recognised were invited. The Engineering Plastics programme committee (PC) held[4] meetings in 2005.
- **Publications:** In addition to a significant number of contributions to scientific symposia in the form of posters or presentations, the publication of 34 referenced papers and 3 theses reflects the significant contribution of this TA to science development.
- **Inventions:** The registration of 4 reported inventions indicated that our pre-competitive programmes offer good scope for technological and economic applications.

Wear now made visible at ESPCI, Paris

An understanding of the micro-mechanisms behind friction and wear in plastic parts is essential in the field of durability. Plastic parts are used not only in sliding and rotating devices. Today, owing to their advantages – light weight, low noise and maintenance free – they are increasingly finding their way into small drive systems, gearboxes and actuators.

A joint research programme involving

ESPCI Paris and Birmingham University found interesting results on the wear behaviour of aramid-fibre-reinforced polyamides. With a powerful in situ visualisation technique developed at ESPCI, the formation and displacement of debris can be made visible during the course of wear, thus providing the basic observations from which mechanistic backgrounds can be derived. In addition to fibre abrasion and pull-out, localised changes in the matrix deformation modes were also identified close to the surface during repeated sliding. An important conclusion that has already been drawn is that a mechanism proposed earlier based on fatigue phenomena is not sufficient to explain the behaviour of filled systems. This implies that other effects such as compaction and the flow of wear particles within the contact interface play a role that will be important to the further development of these materials.



"In situ visualisation of wear damage processes within a contact between a sapphire lens and a polyamide composite reinforced with short aramid fibres. Pull-out and the displacement of individual fibres during the course of cyclical sliding motions are indicated by the colour overlay."

Output

Theses

D.P.N. Vlasveld, Fibre reinforced polymeer nanocomposities. TU Delft.

M.A.G. Jansen Modification of Poly (buitelende terephtalate) by incorporation of comonomers in the solid state. TU Eindhoven.

O. van den Berg, Fluorescent and dielectric Molecular Porbes for the Study of Phase transitions and Structural relaxtions in polymers. TU Delft.

Scientific publications

J.B. McLeary, F.M. Calitz, J.M. McKenzie, M.P. Tonge, R.D. Sanderson, B. Klumperman A 1H NMR investigation of reversible addition fragmentation chain transfer (RAFT) polymerization kinetics and mechanism; initialization with different initiating and leaving groups Macromolecules 38, 3151-3161

Rajan Venkatesh, Frank Vergouwen, Bert Klumperman Atom Transfer Radical Copolymerization of -Olefins with Methyl Acrylate: Determination of Activation Rate Parameters Macromol. Chemistry and Physics 206-5, 547-552

R. Venkatesh, F. Vergouwen, B. Klumperman Atom transfer radical copolymerization of a-olefins with methyl acrylate: determination of activation rate parameters Macromol. Chemistry and Physics 206, 547-552

N.K. Singha, A.L. German Atom transfer radical polymerization of styrene using a copper catalyst with a pseudohalogen anion J. Applied Polymer Science 98, 1418

Otto van den Berg, Michael Wübbenhorst, Stephen J. Picken, Wolter F. Jager Characteristic size of molecular dynamics in polymers probed by dielectric probes of variable length J. Non-Crystalline Solids 351, 33-36, 2694-2702

S. Hoffmann, B. Vanhaecht, J. Devroede, W. Bras, S. Rastogi, C.E. Koning Cocrystallization in piperazine-based polyamide copolymers: small- and wide angle X-ray diffraction studies at 30 ºC Macromolecules 38, 1797-1803

B.H. Tan, D.W. Grijpma, T. Nabuurs, J. Feijen Crosslinkable surfactants based on linoleic acid-functionalized block copolymers of ethylene oxide and e-caprolactone for the preparation of stable PMMA latices. Polymer 46-4, 1347-1357

Martijn van der Schuur, Reinoud J. Gaymans Influence of chemical crosslinks on the elastic behavior of segmented block copolymers Polymer 46-18, 6862-6868

W.C.J. Zuiderduin, D.S. Homminga, J. Huetink, R.J. Gaymans Influence of copolymerisation on fracture behaviour of aliphatic polyketones. Polymer 46-11, 1921-1934

W.C.J. Zuiderduin, J. Huetink, D.P.N. Vlasveld, R.J. Gaymans Influence of sample thickness on fracture behaviour of polyketone and a polyketone-rubber blend. Polymer 46-23, 10321-10330

Y.J. Mergler, R.J. van Kampen, W.J. Nauta, R.P. Schaake, B. Raas, J.G.H. van Griensven, C.J.M. Meesters Influence of yield strength and toughness on friction and wear of polycarbonate Wear 258, 915-923

Juan Li, Manoranjan Prusty, Han Goossens, Martin van Duin, Gert de Wit Infrared Monitoring of the Modification of Styrene Acrylonitrile Copolymers with Oxazoline and Its Interfacial Reaction with Acid-Containing Polymers Macromol. Symposia 230-1, 59-66

Wolter F. Jager, Otto van den Berg, Stephen J. Picken Novel Color-Shifting Mobility Sensitive Fluorescent Probes for Polymer Characterization Macromol. Symposia 230-1, 11-19

M.A.G. Jansen, J.G.P. Goossens, G. de Wit, C. Bailly, C. Schick, C.E. Koning, Poly(butylene terephthalate) Copolymers Obtained via Solid- State Polymerization and Melt Polymerization. A Study on the Microstructure via 13C NMR Sequence Distribution. Macromolecules 38-26, 10658-10666

L.E. Govaert, T.A.P. Engels, E.T.J. Klompen, G.W.M. Peters, H.E.H. Meijer Processing-induced properties in glassy polymers: development of yield stress in polycarbonate, International Polymer Processing XX(2), 170-177

E.T.J. Klompen, T.A.P. Engels, L.C.A. van Breemen, P.J.G. Schreurs, L.E. Govaert, H.E.H. Meijer Quantitative prediction of long-term failure of Polycarbonate Macromolecules 38-16, 7009-7017

M.A.G. Jansen, J.G.P. Goossens, G. de Wit, C. Bailly, C.E. Koning Reaction kinetics of the incorporation of a diol in poly(butylene terephthalate) via solid state polymerization Macromolecules 38, 2659-2664

J. Krijgsman, R.J. Gaymans Segmented copolymers of poly(phenylene ether) and polyester Polymer 46-16, 6122-6127

J. Krijgsman, G.J.E. Biemond, R.J. Gaymans Segmented copolymers of uniform tetra-amide units and poly(phenylene oxide). Part 4. Influence of the extender Polymer 46-19, 8250-8257

Y. Ma, U.S. Agarwal Solvent assisted post-polymerization of PET Polymer 46-15, 5447-5455

Nadia Grossiord, Joachim Loos, Cor E. Koning Strategies for dispersing carbon nanotubes in highly viscous polymers Materials Chemistry 15-24, 2349 (Cover page paper and Highlight Article)

J.M. van der Schuur, J.de Boer, R.J. Gaymans Structure-property relations of poly(propylene oxide) block copolymers with monodisperse and polydisperse crystallisable segments. Polymer 46-22, 9243-9256

J.M. van der Schuur, E. van der Heide, J. Feijen, R.J. Gaymans Structure–property relations of segmented block copolymers with liquid–liquid demixed morphologies Polymer 46-11, 3616-3627

J.M. van der Schuur, J. Feijen, R.J. Gaymans Synthesis and characterization of bisester-amide segments of uniform and random length. Polymer 46-13, 4584-4595

A.J.P. van Zyl, R.F.P. Bosch, J.B. McLeary, B.Klumperman Synthesis of liquid-filled polymeric nanocapsules through the use of living polymerization techniques Polymer 46-11, 3607-3615

Martijn van der Schuur, Jan Feijen, Reinoud J. Gaymans Synthesis of polyether-based block copolymers based on poly(propylene oxide) and terephthalates Polymer 46-2, 327-334

Z. Bashir, S. Rastogi The explanation of the increase in slope at the Tg in the plot of d-spacing versus temperature in polyacrylonitrile J. Macromolecular Science, Physics B 44-1, 55-78

Nadia Grossiord, Joachim Loos, Cor E. Koning The tool-box for dispersing carbon nanotubes into polymers to get conductive nanocomposites Analytical Chemistry 77-16, 5135-5139

Nadia Grossiord, Oren Regev, Joachim Loos, Jan Meuldijk, Cor E. Koning Time-dependent study of the exfoliation process of carbon nanotubes in aqueous dispersions by using UV-VIS spectroscopy Analytical Chemistry 77, 5135-5139

R.J. Gaymans, W.C.J. Zuiderduin Toughening with rigid particles. Polymeric materials science and engineering 93, 917-918

Wouter J. Van Meerendonk, Robbert Duchateau, Cor E. Koning, Gert-Jan M. Gruter Unexpected side reactions and chain transfer for zinc-catalyzed copolymerization of cyclohexene oxide and carbon oxide Macromolecules 38, 7306-7313

Joachim Loos, Alexander Alexeev, Nadia Grossiord, Cor E. Koning, Oren Regev Visualization of Single-Wall Carbon Nanotube (SWNT) Networks in Conductive Polystyrene Nanocomposites by Charge Contrast Imaging Ultramicroscopy 104-2, 160-167

C.S.J. Corstjens, G.W.H. Hoehne, S. Rastogi Inverse melting in syndiotactic polystyrene Macromolecules 38-5, 1814-1821

Richard P. Schaake, Jaap M.J. den Toonder, Willem-Pier Vellinga, Han E.H. Meijer One-Minute Wear-Rate Measurement Macromol. Rapid Commun. 26-3, 188-191

Reported inventions

w#313 R.J. Gaymans, D. Husken Copolymers with amide chain-ends

#416 N. Grossiord, J. Meuldijk, C.E. Koning Reinforced polymer

#312 R.J. Gaymans, W.C.J. Zuiderduin Polycarbonate with crystallisable units

#137 R.J. Gaymans, G.J.E. Biemond Segmented copolymers

#451 + #471 B.A.J. Noordover, R. Sablong, R. Duchateau, R.A.T.M. van Benthem, W. Ming, C.E. Koning Polyesters with improved properties

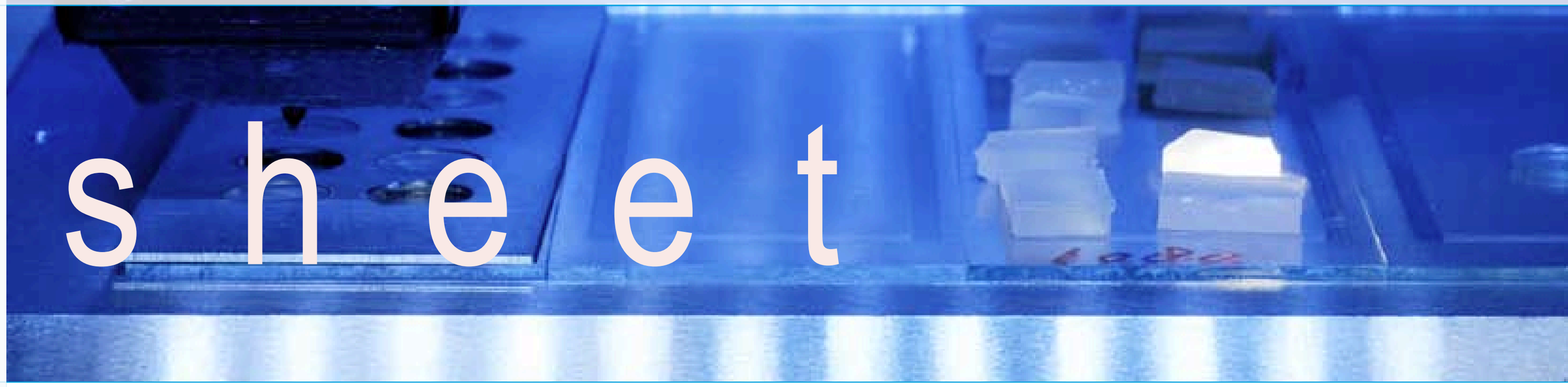
Rubber Technology

Introduction

The mission of the TA Rubber Technology is to establish a “chain-of-knowledge” in the field of Rubber Technology, aiming at research subjects, which position themselves at the forefront of the new developments in this field. And to act as an academic training ground for students and scientists for the rubber world at large.

The industrial participants in our Rubber Technology Area are active in synthetic rubber manufacture and applications. However, it is important to note that approximately 70% of all rubber materials is applied in the field of tyres, in which basically none of our present industrial sponsors are involved. Accordingly, our research themes (New Product Technologies, Elastomer Blends and Composites and New Network Technologies) are focused on more generic rubber material science and technology development.

fact sheet



Research

New technologies to break through existing vulcanisate property balances

Studies in this area compared the dynamic and rheological properties of thermoplastic vulcanisates (TPV) with block-copolymer type thermoplastic elastomers (TPEs) and conventional vulcanisates. With special network chemistry based on single molecule peroxide/coagent curing compounds the properties of peroxide cured TPVs could already substantially be improved. Further studies continued in 2005 concerned the application of acrylate based co-agents and the elucidation of the underlying mechanisms. A solid state NMR study on cross-link density was conducted in association with a project in the Corporate TA.

A thesis was completed on the morphology-rheology studies of block copolymer and TPV- type thermoplastic elastomers. This delivered clear insight into and a complete model of the composition-rheology-morphology relationships of these materials.

Investigations on the balance of tear, fatigue and tackiness of per-fluorinated rubbers were continued. A unique apparatus to measure the relatively low tack values of silicon rubbers has been developed and the characterisation of silicon tackiness in terms of cross-link density and network topology, i.e. loose ends and cross-link functionality, is fully underway. A mechanistic picture is gradually emerging.

A breakthrough shift in the balance of properties was found for mixed sulphur/peroxide cure of EPDM vulcanisatesas well as a novel effect of scorch retardation without loss in mechanical properties using flexible co-agents. Finally in this area we have investigated the UV-stability of light coloured rubbers, addressing a longstanding issue of stability improvement of elastomer compositions without carbon black in the context of recently developed insights into stabiliser technology. The effect of a range of variables has been studied, ranging from molecular characteristics of the elastomer (nature and amount of co-monomers in EPDM), peroxide curing agent and catalyst residues.

Elastomer blends and composites

Studies on blends with both saturated and unsaturated elastomers (EPDM/NR/BR) applying a new concept using EPDM as chemical carrier for conventional sulphenamide accelerators resulted in a marked improvement in vulcanisate properties and significant changes in blend morphologies. Whilst this is of great scientific interest, it also has interesting potential applications e.g. in tyre side wall formulations. Recently, a patent application

based on these results was filed.
Fibre-cord/matrix adhesion technologies are studied within the Advanced Fibres subcluster in the Engineering Plastics technology area. This project is an example of the increasing common ground and options for cross fertilisation and synergy between Engineering Polymers and Rubber Technology.

New network technologies

In this area the focus is on new physical cross-linking systems as well as low temperature/ultra high-speed chemical cross-linking.
Studies on new physical network systems concern elastomer networks based on maleic-anhydride grafted ethylene propylene rubbers (EPRs). Several organic and metallic compounds are being tested as thermo-reversible cross-links.
Synthetic routes to new TPE systems, e.g. copolymer systems with polar and non-polar blocks have been identified and, currently, the first molecules and network systems are being made, for instance, by living free radical RAFT copolymerisation.
A project on novel cross-linking chemistry based on functionalised azides was delayed by budget restrictions, but started at the beginning of 2006.

f a c t s h e e t

Facts and figures

- **Partners Industry:** Akzo Nobel Polymer Chemicals, DSM Research, Kraton Polymers, Océ Technologies and TNO Science and Industry.
  Academia and research institutes: the Universities of Technology of Eindhoven, and Twente and TNO Science and Industry.
- **Budget and organisation :** Total costs allocated in 2005 in our TA amounted to EUR 0.8 million (budget EUR 0.8 million). The total number of scientific staff employed with DPI sponsorship was 13 (8 full time equivalents).
  Part of the cost of a full professorship at the University of Twente was supported.
  A scientific chairman (SC) Prof. Dr Ir J.W.M. Noordermeer, was in position for the whole of 2005 for scientific development alongside a programme area coordinator (PAC) Dr Jan Stamhuis, with operational focus.
- **Networking:** The programme committee (PC) of the Rubber Technology Area met 3 times in 2005. Presence and sponsorship at the main International Rubber Conference in Europe (IRC 2005, Maastricht).
- **Publications:** 8 scientific papers, 10 contributions to international conference proceedings.
- **Inventions:** 3 patent applications filed and 1 new reported invention registered.

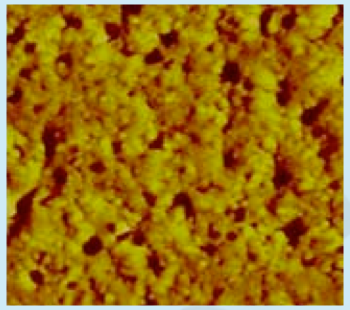
Case

Novel grafting concept for elastomer blends with EPDM

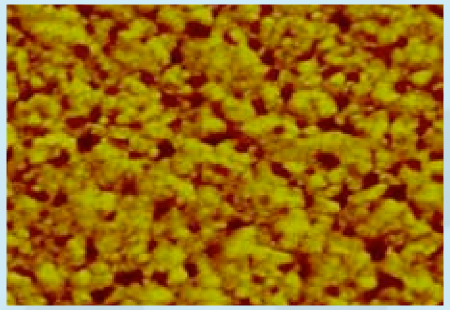
Low-unsaturation Ethylene-Propylene-Diene (EPDM) has the potential to improve the ozone resistance in elastomer blends that contain unsaturated rubbers such as natural rubber (NR) or polybutadiene (BR), e.g. for high performance dynamic applications in tyres. However, the chemical difference of the saturated EPDM and unsaturated rubbers causes uneven distribution of cross-linking chemicals and reinforcement throughout the blends, leading to loss of critical dynamic and mechanical properties.

In order to overcome these deficiencies, a new concept has been developed using EPDM as chemical carrier for conventional sulphenamide accelerators, by grafting the sulphenamides onto the EPDM-chain.
If subsequently blended with NR and BR, the curing speed of the EPDM is increased to the level of the other two rubbers, resulting in a balanced cure and a greatly improved degree of reinforcement of the EPDM phase.

This has significant potential for a breakthrough in EPDM Rubber application in such high performance blends, e.g. tyre sidewalls. A patent application describing this grafting concept has recently been filed.



1. Straight mix



2. Grafted mix formaat plaatjes even groot

In DPI project #532, "polymer MEMS", responsive polymeric materials are being developed that can be actuated by electrical, magnetic, or optical stimuli. The polymer micro-actuators are integrated in micro-fluidic devices to manipulate biological fluids for biomedical applications. The project is a cooperation between the TU/e departments of Mechanical Engineering, Chemical Engineering, and Physics, and has strong links with Philips Research.

Output

Theses

W.G.F Senger
Rheological properties of olefinic thermoplastis elastomeer blends.
TU Delft.

Scientific publications

H. Zhang, F.R. de Risi, J.W.M. Noordermeer
Effects of 1,2-polybutadiene as crosslinking agent in ethylene propylene diene monomer/polypropylene thermoplastic vulcanizate
China Synthetic Rubber Industry 28-3, 228

E.H.D. Donkers, R.X.E. Willemse, B. Klumperman
Chain end modification of living anionic polybutadiene with diphenylethylenes and styrenes
J. Polymer Science A, Polym. Chem. 43-12, 2536-2545

S. Datta, K. Naskar, J. Jelenic, J.W.M. Noordermeer
Dynamically vulcanized PP/EPDM blends by multifunctional peroxides: Characterization with various analytical techniques
J. Applied Polymer Science 98-3, 1393-1403

Ellen H. D. Donkers, Robin X. E. Willemse, Bert Klumperman
Chain-end modification of living anionic polybutadiene with diphenylethylenes and styrenes
J. Polymer Science A, Polymer Chemistry 43-12, 2536-2545

Pratip Sengupta, Jacques W. M. Noordermeer
Three-Dimensional Structure of Olefinic Thermoplastic Elastomer Blends Using Electron Tomography
Macromol. Rapid Commun. 26-7, 542-547

P. Sengupta, J.W.M. Noordermeer
A comparative study of different techniques for microstructural characterization of iol extended thermoplastic elastomer blends
Polymer 45, 12298-12305

E.A. Snijders, A. Boersma, B. van Baarle, J.W.M. Noordermeer
Effect of third monomer type and content on the UV stability of EPDM
Polymer Degradation and Stability 89, 200-207

K. Naskar, J.W.M. Noordermeer
Thermoplastic elastomers by dynamic vulcanization
Progress in Rubber, Plastics and Recycling Technology 21-1, 1-26

Filed patent applications

#356 J.W.M. Noordermeer, K.N. Naskar, R. Datta
Preparation of a vulcanized blend of rubbers

#357 J.W.M. Noordermeer
Cross-linking copolymers using a co-agent

#357 M.M. Alvarez Grima, A.G. Talma, R. Datta, J.W.M. Noordermeer
Free-radical-initiated vulcanization processes of rubbers

Reported inventions

#344 E.H.D. Donkers, L. Klumperman
Macromolecular RAFT agent

Functional Polymer Systems

Introduction

The TA FPS performs research on polymers and their prototype devices that are capable of an electrical, optical, magnetic, ionic or photo-switching function and that offer potential for industrial applications. The potential number of applications based on functional polymers increases rapidly since these materials are recognised as potentials in many other markets besides ICT and electronics. Initially the aim of functional polymers was to reduce costs and improve efficiencies in electronic (displays) and solar cell applications. More and more, medical, healthcare and disposable diagnostics require increasingly sophisticated materials and additional functionalities for which functional polymers might make a significant contribution.

The major industrial drivers for Functional Polymer Systems (FPS) are the increasing demand for information and communication systems, for energy generation from renewable resources and for medical, healthcare and disposable diagnostics, the latter a steeply growing future market driven by increasing longevity. In 2005 FPS successfully launched a new research programme, which will significantly grow beyond 2006, to address this application field.

The major academic drivers are the increasing power of modelling studies that demonstrate real fundamental understanding of the behaviour of materials under operational device conditions, the synthetic capabilities for preparing well-defined and functional control over new materials as well as morphology analysis and development of processing tools for nanostructuring of large areas.

The themes of field-effect transistors, polymers for information and communication technology, photovoltaics and responsive materials for microfluidics are all considered to be at the strategic forefront of the international science scene. The smaller themes of conductive blends and proton conductive membranes for fuel cells contribute significantly to the development of the forefront programmes but lack critical mass. Those themes will be merged with the forefront programmes or closed during 2006.
FPS continuously seeks leading academic experts to achieve focus, mass and an international leading position in a limited number of industrially relevant programmes. Therefore, FPS will launch a new competitive call for proposals in 2006 with a major focus on growth for responsive materials, sensors and actuators for biomedical applications and diagnostics whereas light-emitting diode activities will shift focus towards solid-state lighting applications.
Professor Dietrich Haarer (University of Bayreuth, Germany) was appointed as independent scientific chairman for the TA FPS. Professor Haarer will keep up with the scientific progress of all FPS projects and identify potential future research areas and developments to which TA FPS can make a significant contribution

Research themes and highlights

Light-emitting diodes and field-effect transistors

The aim of this theme is to gain thorough fundamental understanding of materials behaviour under operational device conditions and thus generate breakthroughs in device performance. The research on understanding charge transport and mobility resulted in a theoretical model that excellently describes the full dependence of charge carrier mobility on the charge carrier density. This model is now extensively used at Philips Research since it is applicable to a large variety of (polymer) materials. Project #518 continues the further development of this model for complex polymer-dye blends like light-emitting layers.
Studies on ambipolar FETs demonstrated that the variable-range-hopping theory, developed for disordered unipolar organic transistors, can also be applied for ambipolar transistors. An excellent concord between theory and experiment is observed over a wide range of biasing regimes and temperatures. Finally, new stable blue light-emitting polymers have been prepared and these show promising LED performance.
The theoretical model that provides, simultaneously, excellent descriptions of charge carrier transport in LEDs and FETs received high international recognition). It was mentioned as one of the research highlights in Nature Materials and one of the PhD students was awarded with the DPI Golden Thesis Award 2005 for her excellent contribution to the development of the mode.

Making use of high-throughput experimentation techniques for optimisation of photo-embossing processing conditions, a tenfold increased aspect ratio compared to lab experiments could be achieved.
Studies on ambipolar FETs demonstrated that the variable-range-hopping theory, developed for disordered unipolar organic transistors, can also be applied for ambipolar transistors. An excellent agreement between theory and experiment is observed over a wide range of biasing regimes and temperatures.

Conductive blends

This subprogramme studies conductive filler/polymer matrix composites aiming at very low filler amounts (< vol. 2%) without affecting the processing conditions and other functional properties of the antistatic film. The research focuses on the fundamental understanding of filler network formation to influence the percolation threshold as well as on parameters that determine the maximum conductivity level. These technological leads are vital for producing stable conductive polymer composites with good mechanical performance for copier machines and for producing antistatic foils with tuneable and durable conductivity.

Two major conclusions were drawn from this research in 2005:

- The maximum conductivity levels are determined by the intrinsic powder conductivity of the filler itself once the proper processing conditions have been selected.
- Optimisation and control of the processing conditions can yield very low percolation thresholds based on fundamental understanding of the fractal network formation.

This research is being pursued in 2006 with the focus on tuning the intrinsic conductivity of the filler particles and on the proper dispersal of single-wall carbon nanotubes in polymer matrices.

Polymers for information and communication technology

The objective of the subprogramme is the structuring of polymers on nano and micro scale via ‘top-down’ approaches combined with ‘bottom-up’ techniques on the basis of, for example, self-assembly. In this way new or strongly enhanced properties for optical, electrical and biomedical applications should be generated. Top-down approaches are typically designed to produce patterned, isotropic polymers; the intrinsic anisotropy is not exploited. Bottom-up approaches based on self-assembly usually produce anisotropic domains, which lack monolithic organisation on a mesoscopic or macroscopic scale.

A major achievement in 2005 is the development of a phase separation model that accurately describes the experimental conditions and reaction mixture composition for creating a multilayered structure with alternating liquid crystalline and isotropic polymeric structure (Bragg reflector) in one single processing step. Furthermore, the use of inhibitors in photo-embossing processing improves significantly the aspect ratio (tenfold compared to previous results). High-throughput experimentation techniques made a significant contribution obtaining the optimal processing conditions for achieving this large aspect ratio. Additionally, holographic polymer dispersed liquid crystal films were developed showing good polarisation selective diffraction that is wavelength (colour) independent. Licensing this invention to a US-based start-up company, active in projection displays, is currently being investigated. Initial results for generating submicron patterns using self-organisation of smectic and/or chiral nematic liquid crystals look promising. This approach should eventually lead to cheap nanolithography or making of nanoporous materials for applications such as food packaging, separation technology or biomedical applications.

Photovoltaics

The aim of this theme is to explore new materials and develop fundamental understanding of all (photo)physical processes occurring in the next generation photovoltaic (PV) technology, namely polymer PV. Polymer PV holds strong potential for cost-effective PV for sustainable energy production covering a large area. After having explored hybrid inorganic/organic and all-organic bulk heterojunction systems, considerable effort is now being put into the optimisation of polymer-fullerene solar cells. These appear to be the most promising polymer PV concept in terms of high efficiency and stability. Now research is focusing on the preparation of new low band-gap materials to improve the overlap of the polymer absorption with the solar spectrum. Furthermore, the morphology of the films and the effectiveness of the photo-induced processes were continuously studied. Based on former experiences a theoretical model has been developed that accurately describes device operation as a function of light intensity, active layer thickness and band-gaps of donor and acceptor species. This model has generated new future research leads for achieving the ultimate efficiency in a polymer solar cell. A theoretical model was developed providing excellent fundamental understanding of polymer solar cell operation as a function of light intensity, active layer thickness and band-gaps of donor and acceptor species. The model proves a polymer solar cell can potentially achieve 11% external efficiency.

Fuel cells and batteries

The aim of this theme is to develop new proton conducting solid electrolyte materials with high temperature operational stability in prototype fuel cells. Principles of self-organisation and/or alignment via liquid crystallinity are used to improve mechanical stability and achieve the two-dimensional conduction of protons.
One of the prepared sulfonated polyaramides showed good and stable performance as material on a support membrane in a prototype fuel cell operated at 65°C for more than 500 hours. Cross-linking of the material should result in improved performance at higher temperatures and mechanical stability at high humidity.
Sulfonated polyaramides demonstrated comparable prototype fuel-cell performance to Nafion®, which is currently the market standard for proton conductive fuel-cell membranes (see case study).

Responsive materials, sensors and actuators

The aim of this theme is to develop new materials and processes that result in a response upon an external electrical, magnetic, optical and/or chemical trigger. Proof of principle should be demonstrated in prototype devices. First light-driven actuator materials were developed, which functioned in water for micro-fluidic purposes. Furthermore, good progress was made for plastic memory using dispersed zinc-oxide particles in a polystyrene matrix whereby materials were initially explored for a push-pull muscle fibre. The involvement of high-level scientific experts ensured that this programme made significant progress in 2005 and already contributed at an international level, particularly in microfluidics.

The new theme of responsive materials, sensors and actuators made significant scientific progress and contributed to raising the international level of microfluidics.

Light-driven actuator materials were developed with response times of 0.2 seconds, film bending of over 180° and internal work/volume ratio of approximately 50 kJ/m3. Furthermore, the actuators were shown to function in water.

p r e f a c e

Facts and figures

- **Partners Industry:** AKZO Nobel, Avery Dennison, Bayer MaterialScience, Ciba Specialty Chemicals, Degussa, DSM, ECN, Merck, Océ Technologie, Philips, Shell and TNO Science and Industry.
  Academia and research institutes: the Universities of Technology of Delft and Eindhoven; Universities of Amsterdam, Wageningen, Groningen and Cologne; ECN, TNO Science and Industry and Max Planck Institute für Polymerforschung Mainz.
- **Budget:** The total costs over 2005 were EUR 2.9 million (budget EUR 3.1 million). The total number of FTEs allocated at the end of 2005 was 32. The 59 researchers involved comprised 29 PhD students, 13 post-doctorate graduates, 7 TNO and ECN senior researchers, 2 research fellows, 4 technical staff and 4 senior lecturers.
- **Networking:** The FPS programme committee, consisting of the Programme Area Coordinator (PAC) Dr John van Haare, the industrial partner representatives and 4 academic subprogramme experts, met 3 times in 2005 to discuss research programme issues, scientific reporting and inventions/Intellectual Property issues. Subprogramme thematic meetings, involving industrial experts and DPI researchers, were organised on LED-FET, conductive blends, polymers for information and communication technology, photovoltaics, fuel cells & batteries, responsive materials, sensors and actuators.
- **Publications:** FPS researchers frequently disseminated research results by attending scientific conferences, submitting 44 scientific papers to academic journals.
- **Inventions:** although the FPS scientific programme dramatically refocused during 2005, 3 FPS patents were priority filed and 1 description of invention was submitted for which a patent application will be written.

Output
Theses

T. van Woudenbergh,
Charge injection into
organic semiconductors.
RU Groningen.

C. Tanase,
Unified charge transport in
disordered organic field-ffect
transistors and light-emitting
diodes.
RU Groningen.

S. Viale,
Liquid Crystalline Behavior
of Water-Soluble Sulfonated
Polyaramids.
TU Delft.

T. Offermans,
Charge carrier dynamics in
polymeer solar cells:
an opto-electronic study.
TU Eindhoven.

Scientific publications

L.J.A. Koster, E.D. Smits,
V.D. Mihailetchi,
P.W.M. Blom
Device model for
the operation of bulk
heterojunction solar cells
Physical Review B 72,
085205

Lambert van Eijck, Adam
S. Best, John Stride, Gordon
J. Kearley Softening of
the potential-energy surface
in polymer electrolytes on
the addition of nanoparticles
Chemical Physics 317, 2-3,
282-288

S. Viale, A.S. Best,
E. Mendes, S.J. Picken
Formation of aqueous
molecular nematic
liquid crystal phase in
poly(p-sulfophenylene
sulfoterephthalamide)
Chemical Commun.
12, 1528

D. Cangialosia,
M. Wübbenhorst, H. Schut,
A. van Veen, S.J. Picken
Amorphous-amorphous
transition in glassy polymers
subjected to cold rolling
studied by means of
positron annihilation lifetime
spectroscopy
J. Chemical Physics 122,
64702

F.C. Grozema, A.S. Best,
L. van Eijck, J. Stride,
G.J. Kearley, S.W. de
Leeuw, S.J. Picken
Dynamics and lithium
binding energies of
polyelectrolytes based on
functionalized poly(para-
phenylene terephthalamide)
J. Physical Chemistry B 109,
7705

S. Viale, N. Li, A.H.M.
Schotman, A.S. Best,
S.J. Picken
Synthesis and formation
of supramolecular
nematic liquid crystal
in poly(p-phenylene-
sulfoterephthalamide)-H2O
Macromolecules 38, 3647

S. Viale, E. Mendes,
S.J. Picken
A direct observation by
XRD of reorientation in
a supramolecular liquid
crystal polymer induced by
magnetic field.
Molecular Crystals and
Liquid Crystals 437, 1287

C. Tanase, J. Wildeman,
P.W.M. Blom
Luminescent poly
(p-phenylenevinylene)
hole-transport layers with
adjustable solubility
Advanced Functional
Materials 15, 2011

A.J.J.M. van Breemen,
P.T. Herwig, C.H.T. Chlon,
J. Sweelssen, H.F.M.
Schoo, D.M. de Leeuw,
M.E. Mena Benito,
C. Tanase, J. Wildeman,
P.W.M. Blom
High-performance solution
processable poly
(p-phenylene vinylene)s
for air-stable organic
field-effect transistors
Advanced Functional
Materials 15, 872

P.W.M. Blom, C. Tanase,
D.M. de Leeuw,
R. Coehoorn
Thickness scaling of the
space-charge limited
current in poly(p-phenylene
vinylene)
Applied Physics Letters 86,
092105

C. Tanase, J. Wildeman,
P.W.M. Blom, M.E. Mena
Benito, D.M. de Leeuw,
A.J.J.M. van Breemen, P.T.
Herwig, C.H.T. Chlon, J.
Sweelssen, H.F.M. Schoo
Optimization of the charge
transport in PPV-derivatives
by processing and chemical
modification
Applied Physics 97,
123703

T. van Woudenbergh,
J. Wildeman, P.W.M. Blom
Charge injection across a
polymeric heterojunction
Physical Review B 71,
205216

R. Coehoorn, W.F. Pasveer,
P.A. Bobbert,
M.A.J. Michels
Charge-carrier
concentration dependence
of the mobility in organic
materials with Gaussian
disorder
Physical Review B 72,
155206

W.F. Pasveer, P.A. Bobbert,
M.A.J. Michels
Scaling of current
distributions in variable-
range hopping transport on
two- and three-dimensional
lattices
Physical Review B 72,
174204

W.F. Pasveer, J. Cottaar,
C. Tanase, R. Coehoorn,
P.A. Bobbert, P.W.M.
Blom, D.M. de Leeuw,
M.A.J. Michels
Unified description of
charge-carrier mobilities in
disordered semiconducting
polymers
Physical Review Lett. 94,
206601

W.F. Pasveer, J. Cottaar,
P.A. Bobbert, M.A.J.
Michels
Temperature, charge carrier
density, and electric field
dependence of mobilities
in disordered conjugated
polymers: simulation results
Synth. Metals 152, 157

C. Sánchez, M.J. Escuti,
C. van Heesch, C.W.M.
Bastiaansen, D.J. Broer,
J. Loos, R. Nussbaumer
TiO2 Nanoparticle-
Photopolymer Composites
for Volume Holographic
Recording (paper + front
cover)
Advanced Functional
Materials 15, 1623

C. Sánchez, B.-J. de Gans,
D. Kozodaev, A. Alexeev,
M.J. Escuti, C. van Heesch,
T. Bel, U.S. Schubert,
C.W.M. Bastiaansen,
D.J. Broer
Photoembossing of periodic
relief structures using
polymerization - induced
diffusion: a combinatorial
study
Advanced Materials 17,
2567

C. Sanchez, M.J. Escuti,
C. van Heesch, C.W.M.
Bastiaansen, D.J. Broer
An efficient illumination
system for liquid crystal
displays incorporating an
anisotropic hologram.
Applied Physics Letters 87,
094101

T.J. Savenije, J.E. Kroeze,
X. Yang, J. Loos
The Effect of Thermal
Treatment on the
Morphology and Charge
Carrier Dynamics in a
Polythiophene-Fullerene
Bulk Heterojunction.
Advanced Functional
Materials 15, 1260

W.J.E. Beek, L.H. Slooff,
M.M. Wienk, J.M. Kroon,
R.A.J. Janssen
Hybrid solar cells using a
zinc oxide precursor and a
conjugated polymer.
Advanced Functional
Materials 15, 1703

P.A.C. Quist, T.J. Savenije,
M.M. Koetse, S.C.
Veenstra, J.M. Kroon,
L.D.A. Siebbeles
The effect of annealing on
the charge-carrier dynamics
in a polymer/polymer
bulk heterojunction for
photovoltaic applications.
Advanced Functional
Materials 15, 469

L.H. Slooff, J.M. Kroon,
J. Loos, M.M. Koetse,
J. Sweelssen
Influence of the Relative
Humidity on the
Performance of Polymer/
TiO2 Photovoltaic Cells
Advanced Functional
Materials 15, 689

J. Loos
The art of SPM: Scanning
Probe Microscopy in
Materials Science
Advanced Materials 17,
1821

L.J.A. Koster,
V.D. Mihailetchi,
R. Ramaker, P.W.M. Blom
Light intensity dependence
of open-circuit voltage of
polymer:fullerene solar
cells.
Applied Physics Letters 86,
123509

L.J.A. Koster,
V. D. Mihailetchi, H. Xie,
P.W.M.Blom
Origin of the light
intensity dependence of
the short-circuit current
density of polymer:
fullerene solar cells
Applied Physics Letters 87,
203502

T. Offermans, S.C.J.
Meskers, R.A.J. Janssen
Monte-Carlo simulations of
geminate electron–hole pair
dissociation in a molecular
heterojunction: a two-step
dissociation mechanism
Chemical Physics 308,
125-133

P. Ganesan, X. Yang,
J. Loos, T.J. Savenije,
R.D. Abellon, H. Zuilhof,
E.J.R. Sudhölter
Tetrahedral n-type
materials: Efficient
quenching of the excitation
of p-type polymers in
amorphous films.
J. Am. Chem. Soc. 127,
14530

J. Loos, X. Yang,
M. Koetse, J. Sweelssen,
H. Schoo, S. Veenstra,
W. Grogger, G. Kothleitner,
F. Hofer
Morphology determination
of functional poly[2-
methoxy-5-(3,7-
dimethyloctyloxy)-1,4-
phenylenevinylene]/
poly[oxa-1,4-phenylene-
1,2-(1-cyanovinylene)-
2-methoxy-5-(3,7-
dimethyloctyloxy)-
1,4-phenylene-1,2-(2-
cyanovinylene)-1,4-
phenylene] blends as used
for all-polymer solar cells.
J. Applied Polymer
Science 97, 1001

W.J.E. Beek, M.M. Wienk,
R.A.J. Janssen
Hybrid polymer solar cells
based on zinc-oxide
J. Materials Chemistry 15,
2985

W.J.E. Beek, M.M. Wienk,
M. Kemerink, X.N. Yang,
R.A.J. Janssen
Hybrid zinc-oxide -
conjugated polymer bulk
heterojunction solar cells.
J. Physical Chemistry B
109, 9505

E. Holder, V. Marin,
A. Alexeev, U.S. Schubert
Greenish-yellow, yellow
and orange light-emitting
iridium(III) polypyridyl
complexes with poly(alpha-
caprolactone)-bipyridine
macroligands
J. Polymer Science A,
Polym. Chem. 43, 2765

E. Holder, V. Marin, D.A.
Kozodaev, M.A.R. Meier,
B.G.G. Lohmeijer, U.S.
Schubert
Iridium (III) complexes
with PEO and PS
polymer macroligands
and light-emitting
properties: synthesis and
characterization
Macromol. Chemistry and
Physics 206, 989

V. Marin, E. Holder,
M.M. Wienk, E. Tekin,
D. Kozodaev,
U.S. Schubert
Inkjet printing of electron
donor/acceptor blends:
toward bulk heterojunction
solar cells.
Macromol. Rapid Commun.
26, 319

V. Marin, E. Holder,
U. Schubert
Ruthenium(II) complexes
and polymers with
potential applications in
mesostructured thin film
solar cell devices
Macromol. Rapid Commun.
26, 319

X.N. Yang, A. Alexeev.
M.A.J. Michels, J. Loos
Effect of spatial
confinement on the
morphology evolution of
thin poly(p-phenylene
vinylene)/methanofullerene
composite films.
Macromolecules 38, 4289

E. Holder, V. Marin, M.A.R.
Meier, D. Kozodaev,
U.S. Schubert
A Novel Light-Emitting
Mixed-Ligand Iridium(III)
Complex with a Polymeric
Terpyridine-PEG
Macroligand: Synthesis and
Characterization
Materials Research Soc.
Symp. Proc. 846, 295

X.N. Yang, J. Loos,
S.C. Veenstra, W.J.H.
Verhees, M.M. Wienk,
J.M. Kroon, M.A.J. Michels,
R.A.J. Janssen
Nanoscale morphology of
high-performance polymer
solar cells.
Nano Letters 5, 579

T. Offermans, P. van Hal,
M. Koetse, S.C.J. Meskers,
R.A.J. Janssen
Exciplex dynamics in a
blend of pi-conjugated
polymers with electron
donating and accepting
properties (MDMO-PPV
and PCNEPV)
Physical Review B 72,
45213

P.A.C. Quist, L.H. Slooff,
H. Donker, J.M. Kroon,
T.J. Savenije,
L.D.A. Siebbeles
Formation and decay of
charge carriers in hybrid
MDMO-PPV:ZnO bulk
heterojunction produced
from a ZnO precursor.
Superlattices and
Microstructures 38, 308

K.D. Harris, P. Scheibe,
R. Cuypers, C.L. van
Oosten, J. Lub, C.W.M.
Bastiaansen
Thermo-mechanical
responses of liquid crystal
networks with a splayed
molecular organization.
Advanced Functional
Materials 15, 1155

K.D. Harris, R. Cuypers,
P. Scheibe, C.L.
van Oosten, C.W.M.
Bastiaansen, J. Lub,
D.J. Broer
Large amplitude light-
induced motion in high
elastic modulus polymer
actuators.
J. Materials Chemistry
47, 5043

A.L. Elias, K.D. Harris,
C.W.M. Bastiaansen,
D.J. Broer, M.J. Brett
Large area microfabrication
of three dimensional helical
polymer structures.
J. Micromechanics and
Microengineering 15, 49

K.D. Harris, C.W.M.
Bastiaansen, J. Lub,
D.J. Broer
Self-assembled polymer
films for controlled
agent-driven motion.
Nano Letters 5, 1857

Filed patent applications

#293 Z. Chen,
J.C.M. Brokken
Electrically conductive
polymer composition

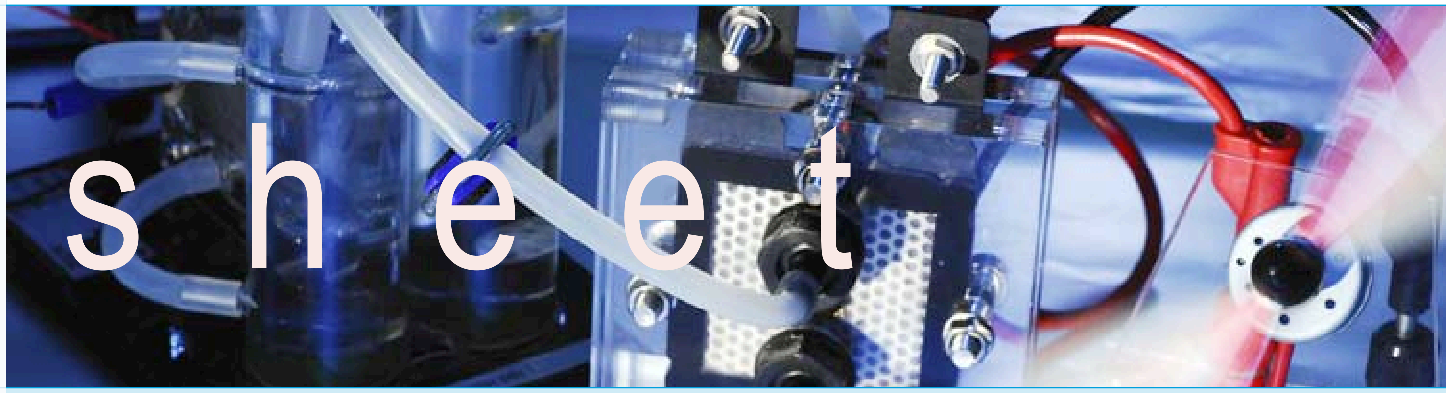
#298 C.W.M. Bastiaansen,
D.J. Broer, C. Sanchez
Polymeric relief structures

#304 C.W.M. Bastiaansen,
D.J. Broer, C. Sanchez,
M. Escuti
Polarization gratings in
mesogenic films

Reported inventions

#530 + #546 K. Hermans,
J. Perelaer, C.W.M.
Bastiaansen, D.J. Broer
Photo embossing

f a c t



Case

Designing high performance polymer electrolyte membranes for fuel cells

Our ever-increasing energy demands are pushing natural resources to the limit, prompting the need for alternative energy sources to be considered. The utilisation of hydrogen in a fuel cell provides a clean and efficient form of electricity that can be used to power almost anything, from laptops and mobile phones to cars and houses. The performance of the fuel cell is largely dependent on the properties of the membrane electrode assembly, which consists of a polymeric membrane and carbon based electrodes. The role of the polymer membranes is threefold: it should separate the two electrodes and act as an electronic insulator, ensure that there is no mixing of the gases (hydrogen and oxygen), but also allow for efficient transport of protons between the two electrodes. The ideal polymer electrolyte membrane should also exhibit good mechanical, chemical and thermal stability to ensure that the fuel cell can function for up to 5000 hours. Furthermore, the molecular structure of the polymer membrane should also promote proton transport as this is of key importance for the cell reaction process. With many of the new materials that are being developed as fuel cell membranes, there is very little control over the polymer morphology. Consequently, the proton transport is expected to follow a random path, which may lead to a reduction in fuel cell efficiency. Ideally, a linear path between the two electrodes should provide the most efficient means of proton transport. Therefore, the most effective polymer membrane should consist of a morphology that incorporates a linear path within the structure. With this in mind, the emphasis of the research being conducted at DPI was to study a series of sulfonated rigid-rod polymers that display liquid crystalline behaviour in solution. Results have shown that the alignment that is seen in solution is also present the corresponding polymer films. It also seems that the molecular architecture is influencing the film properties, particularly the proton transport. Preliminary fuel cell tests have also indicated that these materials compete well with the standard fuel cell membranes. Encouraged by these results, our future research directions are to fully understand the relationship between the film structure and the properties in order to optimise the fuel cell performance.

Coatings Technology

Introduction

Coatings Technology creates fundamental understanding and explores innovative ideas for waterborne and powder coatings to increase the application field and contribute to a sustainable and durable environment. Furthermore, while creating economic value for coatings, it is the objective of Coatings Technology to develop new coating systems with additional functionality at the surface.

Stringent government regulations have turned the industry's focus towards sustainable, durable and environmentally friendly coatings such as waterborne and powder coatings. In moving away from organic solvents the coatings industry is currently faced with a lack of fundamental understanding about the behaviour of these new systems in coating formulations and application methods. DPI Coatings Technology (CT) generates fundamental understanding of the new coating systems and explores innovative new ideas for environmentally friendly and sustainable coatings.

Moreover, as well as covering the underlying substrates, coatings are now increasingly being required to offer additional functionality. This has motivated CT to invest heavily in the development of functional coatings based on modern polymer-science and nano-science tools. During 2005 this theme grew significantly and generated the focus and critical mass necessary to make a relevant contribution at the level of international science.

The first competitive call for proposals generated four new projects in 2005. Based on the success of the first call, which drew proposals of significantly increased scientific quality and greatly increased the scientific quality of the CT research programme, a second competitive call for proposals was launched at the end of 2005. Of the 15 proposals submitted, five new projects will start during the course of 2006.

As a result of the calls for proposals the Forschunginstitut für Pigmente und Lacke (FPL), Stuttgart, and the University of Stellenbosch (SA) became new academic partners in 2005.

The acknowledged expertise of FPL will be a valuable contribution to the CT research programme. Professor Claus Eisenbach (Director Forschunginstitut für Pigmente und Lacke, Stuttgart) was appointed as Scientific Chairman for the TA CT. Professor Eisenbach will keep up with the scientific progress of all CT projects and identify potential future research areas and developments to which CT FPS can make a significant contribution.

Research themes and highlights

Raw materials, formulations and powder coatings

The aim of this theme is the development of sustainable and environmentally friendly coatings to meet stringent government regulations (e.g. REACh). The shift away from solvent-borne coatings to waterborne or even non-solvent coating systems leaves the coatings industry facing many fundamental questions to be resolved.

Fundamental understanding of colloidal stability and interface interaction of waterborne coatings Fundamental understanding was obtained for the adhesion of different particles present in colloidal suspension at interfaces. Different non-ionic polyethyleneoxide (PEO) – surfactant mixtures were studied demonstrating an adhesion competition at the substrate depending on PEO molecular weight and pH. To gain more fundamental insight into the stabilisation of pigments in complex paint systems, the colloidal stability of model compounds was studied under real coating application conditions. The study focused on stability in relation to exchange of surfactants between different types of pigments and stability after the solvent evaporation stage (phase inversion process).

Recently a new project started with the objective of understanding the influence of associative thickeners on macroscopic coating properties like rheology and stability. Associative thickeners consist of a hydrophilic backbone (water soluble) end-capped with hydrophobic blocks (interaction with binder and/or pigment particles). Associative thickeners have the advantage that they improve the rheological properties in waterborne paints, but can cause dramatic instability during the drying of the paint due to phase separation.Finally, excellent research results were obtained in an approach to encapsulate hydrophilic clay platelets in an emulsion polymerisation. After exfoliation, the clay platelets could be encapsulated in an emulsion polymerisation process only when the rim is properly functionalised. When dispersed in a latex material these encapsulated clay platelets should demonstrate increasing mechanical coating properties.

New bio-based building blocks for coating and toner resins

This project aims at the preparation of new bio-based monomeric building blocks from renewable resources for application in toner and powder-coating resins without compromising the end product properties. Series of polyesters were prepared based on dianhydrosugars. One of the materials showed superior impact and solvent resistance of the coating film. In addition, the prepared materials demonstrate outstanding toner properties, which are being further developed at Océ Technologies. The current focus of the project shifted to the synthesis of renewable cross-linkers for the production of coatings based exclusively on renewable resources.

Powder coatings

In order to extend the application window for powder coatings (wood, MDF, plastics), the objective is to find innovative solutions to meet the stringent demands of the cure window with respect to rheology and reactivity. For curing below 140°C the reaction rate should significantly increase while pre-reaction should be avoided during melt extrusion (80-100°C). Additionally, the Tg of the resin should be at least 50°C to obtain non-sticky free-flowing powder under storage conditions. The spray-drying process of an emulsion of epoxidised linseed oil (ELO) for encapsulation in a polyvinylpyrolidone (PVP) was studied extensively. Optimisation of the spray-drying conditions unfortunately did not yield 100% encapsulated ELO in thin shell PVP particles. Now researchers focus on the preparation of nano-micron sized ELO encapsulated particles using (micro)emulsion polymerisation.

Another approach is the use of ionomers to improve flow properties, storage stability and control reactivity. The metal neutralisation of ionomeric polyester resin changes the viscosity-temperature profile. In the case of zinc ionomers, the onset of the curing temperature is lowered compared to the parent polyester whereas nothing changes using potassium. However, the curing rate decreased towards the end of the reaction for both metal ionomers. Ionomers exhibit higher viscosities compared to their parent materials, which affects the final coating appearance. The effect of flow additives is now under investigation.

Functional coatings

The aim of this subprogramme is to develop new coatings with additional functionality at the surface without compromising the protective property for the underlying substrate. Modern polymer and nano-science tools provide new opportunities to significantly enhance the coating performance and application range by engineering their surface structure and ultimate properties. Applying these tools gives coatings a higher economic added value.

In order to obtain an equal distribution in depth of anti-replenishing fluorine species, polyurethanes were end-functionalised with fluorine atoms only in the dangling chains (see CT case). Contact angle measurements showed surface saturation even with low fluorine content. Non-destructive magnetic resonance imaging proved to be a powerful analysis technique ultimately showing the equal depth-profiling of fluorine in a coating film.

In addition, by controlling the length of the dangling chain and tuning the monomer/initiator ratio properly, one can adjust the crystallinity, miscibility of fluorinated/non-fluorinated species and T_g of the product.

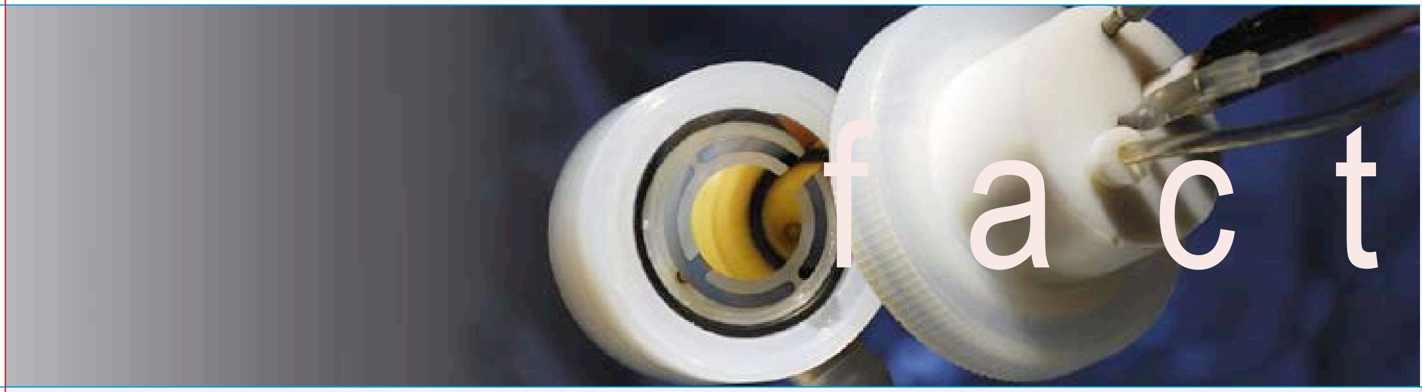
Another project aims to produce reversible cross-linking using an appropriate light wavelength. The coating formulation contains coumarin dimer moieties. The resulting coating will be cross-linked using thiolene chemistry whereas the coumarin dimers can be (de-)cross-linked using appropriate UV light. Using this strategy one can control the flow of the coating film independent of the throughcure of the whole system. Furthermore, self-healing of the coating film can be achieved by applying UV light only. The project achieved the synthesis of a RAFT agent with a fluorescent label attached to it. Polymerisation with acrylates and the RAFT agent were performed successfully. Following this successful approach, a coumarin RAFT agent was prepared and the dimerisation of coumarin as a model compound using UV light was studied.

The successful competitive call for proposals in 2004 enabled three new projects in functional coatings to begin. The aims of these projects are self-healing of coatings upon scratching, superhydrophobic (self-cleaning) waterborne coatings and anti-fouling properties based on self-assembled polymers. These new projects create significant critical mass and focus for the functional coatings field.

Durability lifetime and testing of coatings

The resistance of industrial and decorative coatings to weathering as a result of outdoor exposure (UV radiation, heat/cold, moisture) is an extremely important topic in coating related industrial R&D. Direct cause-and-effect correlation data have never been obtained but are essential for a better understanding of coating durability. It is the object of this study to make a start with such cause-and-effect studies on well-defined coating systems in a parallel project.

Model polyesters were prepared and artificially aged in different atmospheres in especially designed aging cells. Analytical tools were developed to describe the photochemical oxidation, both on surface and in deeper layers. First degradation studies in the presence of metal oxides were performed. Analysis of the data obtained with the JKR method on PDMS cross-linked networks demonstrated similar results for the work of adhesion and elastic modulus as obtained using nano-indentation. Moreover, the amount of dangling chains and cross-link density does not influence the work of adhesion of cross-linked silicon rubbers.



f a c t s h e e t

Facts and figures

- **Partners Industry:** AKZO Nobel, Degussa, Dow, DSM, Océ, SEP, Shell and TNO Science and Industry. Bayer MaterialScience joined the technology area from 1 January 2006.
  Academia and research institutes: the Eindhoven University of Technology, the universities of Wageningen and Stellenbosch (SA); TNO Science and Industry, Agro Technology and Food Innovations (A&F) and the Forschunginstitut für Pigmente und Lacke.
- **Budget:** The total costs over 2005 were EUR 1.5 million (budget EUR 1.5 million). The total number of FTEs allocated at the end of 2005 was 16. The 28 researchers involved comprised 17 PhD students, 4 post-doctorate graduates, and 7 TNO and A&F senior researchers.
- **Networking:** The CT programme committee, consisting of the programme area coordinator (PAC) Dr John van Haare and the industrial partner representatives, met 4 times in 2005 to discuss research programme issues, scientific reporting and inventions/intellectual property issues.
  A general "DPI Coatings Day" was organised during which all researchers presented their latest research results, and project members and industrial partners had discussions about the programme and future plans. Clustered project review meetings were implemented to intensify the communication between industrial and scientific partners as well as to cross-fertilise between scientific partners.
  Project kick-off meetings were organised for newly awarded projects to discuss the project proposal in detail and obtain mutual agreement between industrial and academic partners on the research plan for the first 12 months. Clear deliverables and milestones were defined so that future project meetings could tangibly measure progress.
- **Publications:** CT researchers frequently disseminated research results by attending scientific conferences and submitting 12 papers to academic journals.
- **Inventions:** 4 new inventions were reported, 2 of which were chosen by the industrial partners for further patent application and 1 is still under consideration. One patent application was filed.

Output

Theses

V.V. Khatavkar,
Capillary and low inertia spreading of a microdroplet on a solid surface.
TU Eindhoven.

V.G.R Lima,
Tailor-made poly(meth)acrylate-based networks.
TU Eindhoven.

D. Wouters,
Bottom-up and top-down assembly of functional nano-structures: Scanning Probe Microscopy as an imaging and patterning tool.
TU Eindhoven.

Scientific publications

V. Lima, X. Jiang, J. Brokken-Zijp, P. Schoenmakers, B. Klumperman, R. van der Linde
Synthesis and characterization of telechelic polymethacrylates via RAFT polymerization
Journal of Polymer Science A, Polym. Chem. 42, 959

S.Y. Trofimov, E.L.F. Nies, M.A.J. Michels
Constant-pressure simulations with dissipative particle dynamics
J. Chemical Physics 123, 144102

X. Jiang, A. van der Horst, V. Lima, P.J. Schoenmakers
Comprehensive two-dimensional liquid chromatography for the characterization of functional acrylate polymers.
J. Chromatography A, 1076 (1-2), 51-61

D.J. Voorn, W. Ming, A.M. van Herk, P.H.H. Bomans, P.M. Frederik, P. Gasemijt, D. Johanssmann
Controlled heterocoagulation of platelets and spheres
Langmuir 21, 6950

J. Klein Wolterink, G.T. Barkema, M.A. Cohen
Diffusion and exchange of adsorbed polymers studied by Monte carlo simulations.
Stuart Macromolecules 38, 2009

N.K. Singha, B. de Ruiter, U.S. Schubert
Atom Transfer Radical Polymerization of 3-ethyl-3-(acryloyloxy)methyloxetane
Macromolecules 38, 3596

D.J. Voorn, W. Ming, A.M. van Herk
Control of Charge Densities for Cationic Latex Particles.
Macromolecules 38, 3653

S. Schmatloch, H. Hofmeier, U.S. Schubert
Metallo-Supramolecular Polymers: Synthesis, Material Properties and Potential Future Applications
Macromolecules Containing Metal and Metal-like Elements,
Wiley-Interscience Inc., New York, 5, 69

R.D. van de Grampel, W. Ming, W.J.H. van Gennip, F. van der Velden, J. Laven, J.W. Niemantsverdriet, R. van der Linde
Thermally cured low surface-tension epoxy films
Polymer 46, 10531

M. Al-Hussein, W.H. de Jeu, B.G.G. Lohmeijer, U.S. Schubert
Phase Behaviour of the Melt of Polystyrene-Poly (ethylene oxide) Metallo-Supramolecular Diblock Copolymer with Bulking Counterious.
Macromolecules 38 (7), 2832-2836

Filed patent applications

#423 T. Dikic, W. Ming, R.A.T.M. van Benthem, G. de WIth
Low adherence coating

Reported inventions

#451 + #471 B.A.J. Noordover, R. Sablong, R. Duchateau, R.A.T.M. van Benthem, W. Ming, C.E. Koning
Polyesters with improved properties

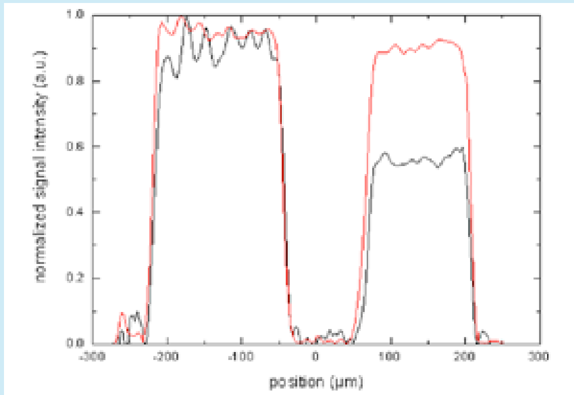
#423 T. Dikic, W. Ming, R.A.T.M. van Benthem, B. de With
Low adherence coating

#424 D.J. Voorn, W. Ming, A.M. van Herk
Armored latex particles

#424 D.J. Voorn, W. Ming, A.M. van Herk
Encapsulation of clay platelets

Self-replenishing coatings

Low adherence coatings have already been developed via surface segregation of fluorinated species during film formation. However, the segregation of fluorinated species is strong, resulting in a thin fluorine rich layer that may not sustain low surface tension upon mechanical abrasion. The aim of the DPI project #423 is to synthesise model coatings that will sustain low surface tension after removal of the surface layers. Our approach is to distribute the fluorinated species relatively homogeneously through the coating. Incorporating perfluoroalkyl-end-capped long, potentially mobile dangling chains in the coating network will allow their reorientation from sub-layers towards the newly created air/film interface in the event of surface damage. This reorientation means that the low-adherence character will be self-replenished. For the synthesis of model compounds, the controlled ring opening polymerisation of ε-caprolactone has been used. For preparation of fluorinated dangling chains perfluorooctylethanol was used as initiator, whereas trimethylol-propane was used for the resin. The use of the same spacer for the fluorinated species and the resin enhances their miscibility. These species were used for the preparation of the low surface tension polyurethane coatings. Preliminary results from magnetic resonance imaging (MRI) measurements indicate that the fluorinated species were distributed quite uniformly along the film depth. Figure 1 shows the MRI depth profile of hydrogen and fluorine for two films containing different fluorine concentration (1% and 2% wt), with a glass plate sandwiched in between.



Fluorine depth profile of fluorinated polyurethane coatings obtained by MRI.

High-Throughput Experimentation

Introduction

Combinatorial materials research opens the way to the construction of libraries of polymers, blends and materials with a systematic variation of composition with the concomitant changes in properties this induces. This will help to develop a more detailed understanding of structure-property relationships. In the long term, a kind of “materials informatics” could be developed, allowing the knowledge-based design and preparation of tailor-made materials and devices with predetermined properties.
The DPI technology area wants to establish a leading centre for “Combinatorial Materials Research and High-Throughput Experimentation” on polymers and polymer-based materials. The main focus will be geared towards creating and applying full workflows, covering the design of experiments, automated and parallel synthesis (including formulation and compounding), the fast characterisation of molar mass, and polydispersity index, type and degree of functionalisation as well as growth kinetics, the reliable preparation of gradient thin film libraries (from solutions, melts and suspensions), the fast and efficient investigation of the important properties of materials (such as T_g, T_m, hardness, morphology, mechanics, cross-linking density, fluorescence, etc.), formulation, up-scaling, combinatorial compounding, processing and complete data-handling, data-mining and modelling.

It is the unique combination of leading industries (ranging from polymer suppliers, equipment manufacturers, analytical services to software developers) and academic partners that provides an excellent basis for successful output. It also guarantees speed in the pre-competitive evaluation of the new (platform) technologies and rapid transfer into commercial R&D programmes of the industrial partners. At the same time, considerable efforts will be made to educate students and post-doctorate graduates in the new field.

Research themes and highlights

Synthesis, catalysis & formulation

This research programme focuses on the broadening of the materials basis for a variety of application fields, making use of controlled polymerisation techniques and applying automated parallel synthesis. The development and application of fast automated and semi-automated techniques for the characterisation of molecular weights, polymerisation kinetics, viscosity, etc. is also part of the activities. Application fields include the design of novel coatings materials based on different acrylate monomers, the rapid synthesis of oxazoline based multi block copolymers as a scientifically challenging field with potential applications and the synthesis of styrene based block copolymers as elastomers for high-temperature applications. A further field of application is the development of novel star-shaped polymers for drug delivery and catalytic applications that use automated parallel synthesis and high-throughput screening (in collaboration with the corporate research programme).
The ultimate goal of the programme is the development of structure property relationships of materials for several application fields on the basis of defined (design of experiment) compound libraries and application of data capture and modelling tools (see subcluster Materials Informatics & Modelling) in collaboration with other DPI programmes.

Thin-film libraries & screening

The programme focuses mainly on detailed understanding and application of thin-film preparation technologies (mainly inkjet printing) and the parallel automated investigation of materials properties (mainly of thin film), applying novel AFM and nano-indentation technologies. Fields of research are the understanding of the processability of polymer inks (coatings and light-emitting materials) and the homogeneous drop and film formation on different substrates (including polymeric). Application fields include the processing of light-emitting materials, surface patterning and the preparation of conductive tracks on polymeric substrates. Application fields in the area of AFM cover the investigation in collaboration with the Technology Area Functional Polymer Systems of photo-embossed relief structures, the characterisation of core-shell architectures with the aim of developing structure performance relationships for the encapsulation and release of active compounds. AFM method development aims at the development of tools for adhesion and I/V curve measurement. Furthermore, correlations of macroscopic hardness measurements of EPDM rubbers with nano-indentation measurements have been developed. Further research deals with optical reader techniques (UV/Vis, fluorescence, FT-IR and Raman) and techniques related to surface property.

Combinatorial compounding

The programme on combinatorial compounding is executed at the Deutsches Kunststoff Institut (DKI) in Darmstadt. The central objective of the programme is the development of a process, closely related to technical production processes, that facilitate a one to twofold acceleration of production and the characterisation and optimisation of plastic formulations. The process will be supported by in-line and on-line screening techniques (IR, UV/Vis, rheometry, ultrasonic spectroscopy, etc.) and a data acquisition, analysis and visualisation system.
The established process will be used for materials development related to typical industry problems. The main focus in 2005 was on finalising the instrumental set-up and developing the experimental strategies (design of experiment). Currently, the main focus lies on the set-up of - in-line characterisation tools and the determination of the phase behaviour of block copolymers.

Materials informatics & modelling

This programme concerns data handling, database construction and the build-up of integrated knowledge capture systems for combinatorial materials and polymer research as well as experimental design, hard and soft modelling tools and tools for deriving quantitative structure property relationships, supporting mainly the programmes on Synthesis, Catalysis and Formulation, Thin-Film Library Preparation & Screening and Combinatorial Compounding. The main aspects were the model development for MALDI matrices to facilitate a faster screening of molecular weights, the experimental design for optimising formulations for photo embossing in collaboration with the Functional Polymer Systems technology area and the statistical experiment design for POM extrusion in collaboration with the Combinatorial Compounding programme.

Detailed characterisation techniques

The programme focuses on the development of detailed characterisation methodologies (mainly microscopic and chromatographic techniques) for specific applications in addition to thin-film preparation & screening. One aspect is the combination of different measurement techniques (high-resolution TEM and AFM in combination with SAXS/WAXS measurements) that aim to characterise multiphase (amorphous/crystalline) or multicomponent materials (rubber reinforced polymers or nanocomposites) on macro, micro and nano scales. A further focus of interest is the analysis of branched polymers by means of two-dimensional liquid chromatography and the development of tools and models for the nano-scale characterisation of interfaces using AFM technology.

Facts and figures

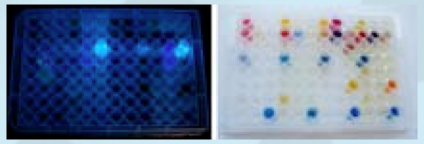
- **Partners Industry:** Accelrys, Analytik Jena, AstraZeneka, Avantium, Basell, Bayer, Chemspeed Technologies, Degussa, DOW Benelux, Forschungsgesellschaft Kunststoffe, Hysitron, Microdrop Technologies, NTI-Europe, Ticona and Waters.
- **Academia and research institutes:** Eindhoven University of Technology, the Deutsches Kunststoff Institut, the University of Amsterdam and the University of Twente.
- **Budget and organisation:** The total costs of the technology area High-Throughput Experimentation in 2005 amounted to EUR 2.2 million. About EUR 0.4 million (EUR 1.2 million in 2004) was spent on equipment. The remaining budget was allocated for 40 researchers (23 full time equivalents). In 2005 Prof. Ulrich Schubert acted as scientific chairman (SC) alongside the programme area coordinator (PAC) Dr Stefan Schmatloch.
- **Networking:** The programme committee met 3 times. The research programme of the TA was discussed with the industrial members at 3 project review meetings. An international DPI HTE workshop on "Inkjet Printing of Polymers" was organised in June 2005, attracting approximately 120 participants from industry and academia. Keynote speakers from Philips, Xenia, IBM, Microdrop Technologies and Orgatronics reported on technologies and industrial applications while academic speakers from the DPI community and from other centres (Arizona State University, UMIST and University of Bielefeld) made presentations related to ongoing research in the field.
- **Publications:** The research programme of the TA generated 31 scientific publications (and 7 technical publications) in 2005, including contributions in high-ranking scientific journals. 10 further scientific papers were published in collaboration with other DPI programmes.
- **Inventions:** The collaboration with other Technologies Areas resulted in 5 reported inventions and 2 filed patents.

s h e e t

Unimolecular reversed micelles

Unimolecular micelles are an interesting class of materials due to their manifold application possibilities, ranging from drug delivery applications and the stabilization of nanoparticles to sensors and catalysts. In 2004 novel reversed unimolecular micelles based on star-shaped block copolymers were discovered and fully characterized within the DPI Corporate researchproject in cooperation with the cluster HTE #360 applying robotic synthesizer techniques. Utilizing high-throughput screening technology it was shown that these materials behave as nanometer sized unimolecular objects that can encapsulate and phase transfer a large variety of different guest molecules. Moreover, large solubilising effects of the guest molecules were observed, making this class of materials an interesting candidate for drug delivery applications. More recently, we were able to apply the concept of guest encapsulation for the design and parallel evaluation of a novel sensoric system with high sensitivity towards transition metal ions by encapsulating a fluorescent guest molecule in the core of a supramolecular star-shaped polymer. The subsequent binding of transition metal ions to the receptors of this polymer led to a quenching of the fluorescence of the guest molecule resulting in a linear response of the sensoric system in the micromolar range of analyte. Moreover, we could show (in cooperation with Prof. J.-F. Gohy, Louvain-la-Neuve, Belgium) that these star-block copolymers are able to stabilize metal nanoparticles. These nanoparticles were already evaluated for their ability to act as catalysts for C-C coupling reactions by high-throughput screening techniques revealing high efficiencies for, e.g. Heck cross-coupling reactions of small, defined and stabilized palladium-nanoparticles.

Encapsulation and phase transfer of a guest molecule by reversed unimolecular micelles.



Guest screening in microtiter plates showing a on-off fluorescence (left) or colour changes (right) upon guest encapsulation revealing changes in the guests microenvironment that are indicative for encapsulation events.

Output

Scientific publications

C.A. Guerrero Sanchez, U.S. Schubert
Automated Parallel Anionic Polymerizations: Enhancing the possibilities of a widely used Technique in Polymers
Journal of Polymer Science A, Polym. Chem. 43-18, 4151-4160

C. Guerrero-Sanchez, F. Wiesbrock, U.S. Schubert
Polymer Synthesis in Ionic Liquids: Free Radical Polymerization in Water-Soluble Systems
ACS Symp. Book, Ionic Liquids in Polymer Systems, 913, 37-49

R. Hoogenboom, M.A.R. Meier, U.S. Schubert
The Introduction of High-Throughput Experimentation Methods For Suzuki-Miyaura Coupling Reactions in University Education
Chemical Engineering Edu. 82, 1693-1696

C.A. Guerrero Sanchez, U.S. Schubert
Experimental Techniques in (Parallel) Anionic Polymerizations
Chemistry Today 23-6, 34-38

R. Hoogenboom, M.W.M. Fijten, H.M.L. Thijs, B.M. van Lankvelt, U.S. Schubert
Microwave-assisted Synthesis and Properties of a Series of Poly(2 alkyl-2-oxazoline)s
Des. Monomers Polym. 8(6), 659-671

Michael A.R. Meier, Ulrich S. Schubert
Combinatorial Evaluation of the Host-Guest Chemistry of Star-Shaped Block Copolymers
J. Combinatorial Chemistry 7, 356-359

B.J. Gans, de, S. Wijnans, D. Wouters, U.S. Schubert
Sector spin coating for fast preparation of polymer libraries
J. Combinatorial Chemistry 7, 952-957

R. Hoogenboom, R.M. Paulus, M.W.M. Fijten, U.S. Schubert
Understanding concentration effects in the living cationic ring-opening polymerization of 2-ethyl-2-oxazoline in N,N dimethylacetamide
J. Polymer Science A, Polym. Chem. 43-7, 1487-1497

R. Hoogenboom, F. Wiesbrock, Mark A. M. Leenen, Michael A. R. Meier, Ulrich S. Schubert
Accelerating the Living Polymerization of 2-Nonyl-2-oxazoline by Implementing a Microwave Synthesizer into a High-Throughput Experimentation Workflow
J. Combinatorial Chemistry 1, 10-3.

Martin W.M. Fijten, Renzo M. Paulus, Ulrich S. Schubert
Systematic parallel investigation of RAFT polymerizations for eight different (meth)acrylates: A basis for the designed synthesis of block and random copolymers
J. Polymer Science A, Polymer Chemistry 43-17, 3831-3839

B.J. de Gans, L. Xue, U.S. Agarwal, U.S. Schubert
Inkjet printing of linear and star polymers
Macromol. Rapid Commun. 26-4, 310-314

Richard Hoogenboom, Mark A.M. Leenen, Frank Wiesbrock, Ulrich S. Schubert
Microwave Accelerated Polymerization of 2-Phenyl-2-oxazoline: Microwave or Temperature Effects?
Macromol. Rapid Commun. 26-22, 1773-1778

Emine Tekin, Ulrich S. Schubert
Inkjet Printing of Functional Polymers and Materials: 2nd International Workshop in Eindhoven
Macromol. Rapid Commun. 26-22, 1814-1816

Ulrich S. Schubert
Ink-Jet Printing of Functional Polymers and Materials: A (Future) Key Technology in Polymer Science
Macromol. Rapid Commun. 26-4, 237

Berend-Jan de Gans, Lijing Xue, Uday S. Agarwal, Ulrich S. Schubert
Ink-Jet Printing of Linear and Star Polymers
Macromol. Rapid Commun. 26-4, 310-314

B.-J. de Gans, U.S. Schubert
Ink-Jet Printing of Functional Polymers and Materials: First International Workshop in Eindhoven
Macromol. Rapid Commun. 26-4, 331-332

C.A. Guerrero Sanchez, D. Wouters, C.A. Fustin, J.F. Gohy, B.G.G. Lohmeijer, U.S. Schubert
Structure-Property Study of Diblock Copolymer Micelles: Core and Corona Radius with Varying Composition and Degree of Polymerization
Macromolecules 38, 10185-10191

C.A. Guerrero Sanchez, B.G.G. Lohmeijer, M.A.R. Meier, U.S. Schubert
Synthesis of Terpyridine-Terminated Polymers by Anionic Polymerization, Macromolecules 38, 10388-10396

H. Zhang, M.A.R. Meier, U.S. Schubert
Combinatorial and high-throughput approaches in polymer science
Meas. Sci. Technol. 16-1, 203-211

Ulrich S. Schubert
Materials Informatics: From Data to Knowledge Towards Integrated eScience Approaches
QSAR & Combinatorial Science 24-1, 5

Nico Adams, Ulrich S. Schubert
From Science to Innovation and From Data to Knowledge: eScience in the Dutch Polymer Institute's High-Throughput Experimentation Cluster
QSAR & Combinatorial Science 24-1, 58-65

Renzo M. Paulus, Martin W.M. Fijten, Mariska J. de la Mar, Richard Hoogenboom, Ulrich S. Schubert
Reversible Addition-Fragmentation Chain Transfer Polymerization on different Synthesizer Platforms
QSAR & Combinatorial Science 24-7, 863-867

Nico Adams, Ulrich S. Schubert
New Frontiers in Combinatorial and High-Throughput Materials and Polymer Research: 3rd DPI Workshop on Automated Synthesis and High-Throughput Experimentation in Polymer and Materials Research at the Eindhoven University of Technology
QSAR & Combinatorial Science, 24-1, 155-158

R. Hoogenboom, U.S. Schubert
High-Throughput Synthesis Equipment Applied to Polymer Science
Rev. Sci. Instrum. 76, 1-7

D. Wouters, R. Willems, S. Hoeppener, C.FJ. Flipse, U.S. Schubert
Oxidation Conditions for Octadecyl Trichlorosilane Monolayers on Silicon: A Detailed Atomic Force Microscopy Study of the Effects of Pulse Height and Duration on the Oxidation of the Monolayer and the Underlying Si Substrate
Advanced Functional Materials 15, 938

Filed patent applications

#360 M.A.R. Meier, U.S. Schubert, J.-F. Gohy
Unimolecular micelles

#546 B.J. de Gans, J. Perelaer, U.S. Schubert
Metal surface structures

Reported inventions

#530 + #546 K. Hermans, J. Perelaer, C.W.M. Bastiaansen, D.J. Broer
Photo embossing

#360 M.A.R. Meier, U.S. Schubert, J.-F. Gohy
Unimolecular micelles

#399 D. Wouters, S. Höppener, D.A. Kozodaev, U.S. Schubert
ITO coated AFM tips

#546 B.J. de Gans, J. Perelaer, U.S. Schubert
Polymer etching

#546 B.J. de Gans, J. Perelaer, U.S. Schubert
Metal surface structures

V. Sciannamea, C.A. Guerrero Sanchez, U.S. Schubert, J..M. Catala, R. Jerome, C. Detrembleur
Ability of Nitrones of various structures to control the radical polymerization of styrene mediated by in situ formed nitroxides
Polymer 46, 9632-9641

M. Filali, M.A.R. Meier, U.S. Schubert, J.-F. Gohy,
Star-Block Copolymers as Templates for the Preparation of Stable Gold Nanoparticles
Langmuir 21, 7995-8000.

Corporate Research

Introduction

The mission of the corporate research area is to perform enabling and strategic research in fields of relevance for all DPI research programmes. In 2005, the restructuring into three main areas - enabling science, emerging technologies and strategic projects - was further substantiated. The enabling science programme should be science-driven and operate at the forefront of scientific knowledge and capabilities. Emerging technologies is intended to foster research on science-driven research in its embryonic phase if it holds the promise of a new technology area (TA) in the future. In order to strengthen such initiatives, companies are entitled to directly contribute financially to the corporate research programme. As the third main area, the corporate research area focuses on strategic projects that cannot be easily accommodated within the TAs, but that have the potential of short-term implementation among the industrial partners.

Here the driver is not necessarily the new science, but rather breakthrough technological opportunities and capabilities – sometimes of a high-risk/high-impact nature.
Based on the elaborated research programme and the commitment of the companies Degussa, DOW, DSM, Friesland Foods and Agrotechnology and Food Innovations (A&F) the decision was taken by the Supervisory Board to start the technology area Bio-Inspired Polymers in 2006.

Research themes and highlights

Enabling Science

Structure vs. performance

A large set of coherent projects is focusing on the modelling on different length scales, fluid dynamics (rheology) and solid-state properties (bulk materials and surface properties). The work is being performed in the groups of Prof. H.E.H. Meijer and Prof. M.A.J. Michels (TU/e), Prof. D.N. Theodorou (National Technical University of Athens) and Prof. T.C.B. McLeish (University of Leeds). The central themes are the simulation and prediction of deformation: damage and failure on one hand and structure development during flow and the investigation of the relationship between structure properties on the other. The strategy focuses on combining experimental work (both characterisation and validation) with numerical work.

f a c t s h e e t

Polymer characterisation

The programme deals with two main themes, namely surfaces and interfaces (applying mainly microscopic techniques) and molecular characterisation, with a focus on the development of fast SEC techniques, the investigation of cross-linked architectures and networks, and the analysis of accurate polymer distribution. Research on evaluating the possibilities of ultra-performance liquid chromatography was implemented into the research programme in 2005. A first project was started in the area of characterisation of polymers for bio-medical applications, namely the development of methodologies for the detailed characterisation of chemically modified polysaccharides.

Emerging Technologies

Polymers for Bio-medical Applications

A part of the research programme concerns the development of new materials for intervertebral disc prothesis. This is being performed in cooperation with the University of Maastricht. Further research projects deal with the development of bioactive scaffolds for tissue engineering of cardiovascular substitutes.
To overcome challenges in the organised in-vitro growth of collagen and elastin, the development of novel hybrid scaffolds is the target of one of the research projects.
Joint research interests within the groups of Prof. J. Feijen (University of Twente), Prof. E.W. Meijer (TU/e) and Prof. F.P.T. Baaijens / Prof. H.E.H. Meijer (TU/e) deal with the development of novel scaffolds, bioactive materials for tissue engineering and heart-valve engineering.

Bio-inspired polymers

The research programme includes projects on enzymatic catalysis, focusing on the preparation of block copolymers and polymerisations in supercritical CO_2 as well as the investigation of self-assembling of protein building blocks. The latter programme was strengthened by an additional project on self-organisation on keratin-derived oligomers and a modelling project, investigating the influence of hydrogen bonding in crystalline polymers, was also granted.

Strategic Projects

Mesoscopic chemistry & physics and breakthrough technologies

The phasing out of the programme mesoscopic chemistry & physics resulted in several reported inventions and two filed patent applications. The content of the research is widespread and currently only a project on colloidal LC reinforced composites, aiming at materials that exhibit toughness of fibre-filled composites with the ease of processing of unfilled materials, is still running. The remaining projects in the breakthrough programme focus on the evaluation of microwave synthesis and improved strategies for knowledge capture and data handling.

Plastic electronics

Activities in 2005 focused on the installation of the plastic electronics line (Orgatron). A first project was started to develop custom-made substrates, optimise processing conditions for distinct materials and ultimately produce first devices. A detailed research programme focusing on understanding the mechanisms of processing conditions for large-area lighting applications as well as research on novel device architectures and novel materials with enhanced processing conditions and performance have been worked out and are being started up.

Corporate Research

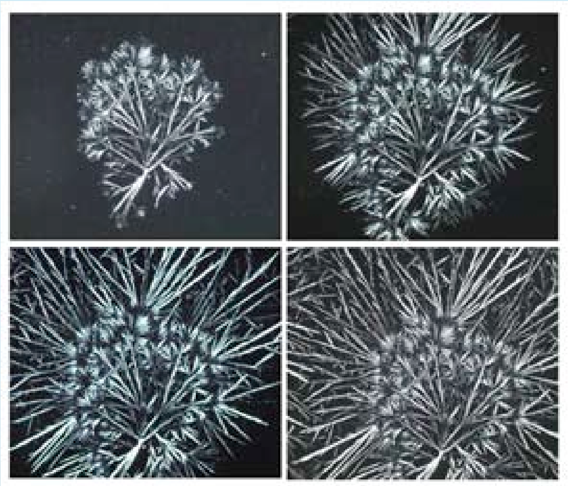
Facts and figures

- **Partners Academia and research institutes:** the Universities of Technology of Amsterdam, ESRF in Grenoble and the University of Twente, the University of Leeds, and the National Technical University of Athens, the University of Maastricht, the University of Wageningen and the University of Nottingham, the Queen Mary University of London, the Delft University of Technology, the University of Stellenbosch and the Eindhoven University of Technology.
  Industry: Bio-Inspired: Agrotechnology and Food Innovations (A&F) and DOW; Plastic Electronics TNO Science and Industry and OTB Engineering.
- **Budget:** The corporate research budget in 2005 was EUR 1.9 million. The actual costs were EUR 2.5 million (budget EUR 2.5 million). An extra investment is made for the Plastic Electronics research line ad EUR 1.6 million. The number of staff employed with DPI sponsorship ws 46 (27 full time equivalents). In 2005 Prof. Thijs Michels acted as scientific chairman (SC) alongside the programme area coordinator (PAC) Dr Stefan Schmatloch.
- **Networking:** The programme committee meets on a regular basis. A review meeting on the research programme Polymer Characterisation was organised. The areas of characterisation of crosslinking, in-depth characterisation, characterisation of polymers for biomedical applications and X-ray scattering and diffraction techniques were identified as main areas of interest and implemented in the running programme. The Plastic Electronics Conference formed the platform for various presentations of the DPI community, promoting particularly work from the research programme Functional Polymer Systems and High-Throughput Experimentation (inkjet). The installation of the Plastic Electronics Line (Orgatron) was promoted in a joint opening event by TNO, OTB and DPI. The research programmes for the emerging technology area of bio-inspired polymers and the strategic research area of plastic electronics were finalised in several bilateral meetings with interested industries and academic experts.
- **Publications:** The performed research resulted in 25 scientific publications and two filed patent applications.
- **Inventions:** Two patent applications were filed.

Case

Self-assembly of oligopeptides from eco-friendly water solution of keratin

Keratins are self-organised proteins that are abundantly available in wool, feathers, human hair, etc. making them a potential cheap feedstock for amino-acids. Here we explore the hydrolysis of keratin in water under specific pressure-temperature conditions where the hydrolysis yields oligo-peptides. Under appropriate conditions, the oligo-peptides self assemble, which results in a hierarchical architecture. Optical microscopy enables the self-assembling process of the oligo-peptides to be followed in time. The observations are that birefringent needle-like crystals tend to nucleate heterogeneously. When given sufficient time, these needles, initially tens of microns in length, act as further nuclei, developing a structure of several hundreds of microns. Micro-focus X-ray diffraction studies supported by in-situ microscopy reveal that these needles have a crystal structure similar to the native protein, though better organised along the ab-plane. Spectroscopic studies on these structures reveal crystalline bands that disappear above 150°C coinciding with an endothermic peak in DSC. Series of such characterisation studies confirm that the self-assembled birefringent entities are indeed oligo-peptides, of several tens of sequences of amino-acids. The oligo-peptides can be used to make important building blocks for the synthesis of a range of novel polymers. The proposed eco-friendly route provides an effective means for managing waste products.



Output

Theses

M.H.E. van der Beek,
Specific volume of polymeters. Influense of thermomechanical history.
TU Eindhoven.

Scientific publications

E. Holder, B.M.W. Langeveld, U.S. Schubert
New Trends in the Use of Transition Metal-Ligand Complexes for Applications in Electroluminescent Devices Advanced Materials 17-9, 1109-1121

A.Olah, H. Hillborg, G. Julius Vancso
Hydrophobic recovery of UV/ozone treated poly(dimethylsiloxane): adhesion studies by contact mechanics and mechanism of surface modification
Applied Surface Science 239, 410–423

Michael A.R. Meier, Ulrich S. Schubert
Fluorescent sensing of transition metal ions based on the encapsulation of dithranol in a polymeric core shell architecture
Chemical Commun. 4610–4612

D.N. Theodorou
Hierarchical modelling of amorphous polymers
Computer Physics Communications 169, 82-88

P.D. Anderson
Polymer Melt Mixing: Distributive Mixing
Encyclopedia of Materials: Science and Technology, 7411-7420

M.A.M. Leenen, F.D. Wiesbrock, R. Hoogenboom, U.S. Schubert
Microwave-assisted Nitroxide-mediated Polymerization of Alkyl Acrylates
e-Polymers 71, 1-9

M.A.R. Meier, U.S. Schubert
Synthesis and Characterization of 4 and 6 arm star-shaped poly(-caprolactone)s
e-Polymers, 085

Alexey V. Lyulin, Bart Vorselaars, Mikhail A. Mazo, Nikolay K. Balabaev, M.A.J. Michels
Strain softening and hardening of amorphous polymers: atomistic simulation of bulk mechanics and local dynamics
Europhysics Letters 71, 618-624

D.N. Theodorou
Multiscale Modeling of Polymers
Handbook of Materials Modeling. I: Methods and Models; S. Yip, Ed.
Springer, 2757-2761

Michael A.R. Meier, Sebastianus N.H. Aerts, Bastiaan B.P. Staal, Mircea Rasa, Ulrich S. Schubert
PEO-b-PCL Block Copolymers: Synthesis, Detailed Characterization, and Selected Micellar Drug Encapsulation Behavior
Macromol. Rapid Commun. 26-24, 1918-1924

Ramona A. Orza, Pieter C.M.M. Magusin, Victor M. Litvinov, Martin van Duin, M.A.J. Michels
Network Density and Diene Conversion in Peroxide-Cured Gumstock EPDM Rubbers. A Solid-State NMR Study
Macromol. Symposia 230-1, 144-148

G. Tsolou, V.G. Mavrantzas, D.N. Theodorou
Detailed atomistic molecular dynamics simulation of cis-1,4 polybutadiene
Macromolecules 38, 1478-1492

Matthijs de Geus, Joris Peeters, Martin Wolffs, Thomas Hermans, Anja R.A. Palmans, Cor E. Koning, Andreas Heise
Investigation of factors influencing the chemoenzymatic synthesis of block copolymers
Macromolecules 38, 4220-4225

F.D. Wiesbrock, R. Hoogenboom, M.A.M. Leenen, S.F.G.M. van Nispen, M. van der Loop, C.H. Abeln, A.M.J. van den Berg, U.S. Schubert
A Microwave-assisted synthesis of a 42-membered library of diblock copoly(2-oxazoline)s and chain-extended homo poly-(2-oxazoline)s and its thermal characterization
Macromolecules 38, 7957-7966

T. Mulder, A.V. Lyulin, P. van der Schoot, M.A.J. Michels
Architecture and conformation of uncharged and charged hyperbranched polymers: computer simulation and meanfield theory
Macromolecules 38, 996-1006

F.D. Wiesbrock, R. Hoogenboom, M.A.M. Leenen, M.A.R. Meier, U.S. Schubert
Investigation of the living cationic ring-opening polymerization of 2-Methyl-,2-Ethyl-,2-Nonyl- and 2-Phenyl-2-Oxazoline in a Singel-Mode Microwave Reactor
Macromolecules 38-12, 5025-5034

E.T.J. Klompen, T.A.P. Engels, L.E. Govaert, H.E.H. Meijer
Modelling of the post-yield response of glassy polymers: influence of thermomechanical history
Macromolecules 38-16, 6997-7008

S. Rastogi, D. Lippits, G.W.M. Peters, R. Graf, Y. Yao, H. Spiess
Heterogeneity in polymermelts from melting of polymer crystals
Nature Materials 4, 635

W.R. Hwang, P.D. Anderson, M.A. Hulsen
Chaotic advection in a cavity flow with rigid particles
Physics of Fluids 17, 043602

Han E.H. Meijer, Leon E. Govaert
Mechanical performance of polymer systems: The relation between structure and properties
Progress in Polymer Science 30 8-9, 915-938

M.A.R. Meier, U.S. Schubert
Integration of MALDI-TOFMS as high-throughput screening tool into the workflow of combinatorial polymer research
Rev. Sci. Instrum. 76, 062211/1-062211/5

Attila Oláh, G. Julius Vancso
Characterization of adhesion at solid surfaces: Development of an adhesion-testing device
European Polymer Journal 4-12, 2803-2823

H. Kosonen, S. Valkama, A. Nykänen, M. Toivanen, G. ten Brinke, J. Ruokolainen, O. Ikkala
Functional Porous Structures Based on the Pyrolysis of Cured Templates of Block Copolymer and Phenolic Resin
Advanced Materials, 18-2, 201 - 205

T. Ruotsalainen, J. Turku, P. Heikkilä, J. Ruokolainen, A. Nykänen, T. Laitinen, M. Torkkeli, R. Serimaa, G. ten Brinke, A. Harlin, O. Ikkala
Towards Internal Structuring of Electrospun Fibers by Hierarchical Self-Assembly of Polymeric Comb-Shaped Supramolecules
Advanced Materials 17-8, 1048-1052

G.W.M. Peters, A.N. Zdravkov, H.E.H. Meijer
Transient Interfacial Tension and Dilatational Rheology of Diffuse Polymer-Polymer interfaces.
J. Chemical Physics 122-10, 104901

Filed patent applications

#503 S. Frahn, L. Klumperman
Amphiphilic alternating hetero-arm brushes

#414 A.A. Martens, F.A. de Wolf, G. Eggink, M.A. Cohen Stuart
A&F,
Self-assembling monodisperse polymers

Reported inventions

#450 S. Fischer, R. van Ee
Rapid manufacturing of a composite article

#160 M.H.E. van der Beek, G.W.M. Peters, J.M.G. Kunen
TNO, Dilatometer

Some impressions of the DPI Annual Meeting organised in December 2005, hosted by Degussa in Marl (Germany). Christina Tanase (University of Groningen) won the DPI Golden Thesis Award.