Working on the future of the polymers innovation programme

Pride
Ten years ago, a Leading Technology Institute in the field op polymers was launched – the Dutch Polymer Institute (DPI). This effort has resulted in an organisation that we may be proud of. Now, a total of 36 companies and 30 knowledge institutes are jointly managing and executing an ambitious and challenging research programme in the field of polymers – a programme worth approximately 16 million euros in which more than 250 scientists are engaged. The Dutch Polymer Institute has succeeded in building a reputation for itself over the past decade. Organisations outside the Netherlands are sometimes envious of the way our institute is working, and in a European context DPI is mentioned as an example of how a “Knowledge and Innovation Community (KIC)” should be set up. Together with our partners we have put the Netherlands on the map in the field of polymers. Some large companies that are DPI partners (Dow, Teijin, DSM) have recently decided to concentrate their R&D in the Netherlands or to expand their R&D activities in this country, one of the reasons being the value-added of the DPI partnership. That is something we can be proud of as well, for it means we are achieving the objectives that the Dutch Ministry of Economic Affairs formulated at the time of our foundation: building focus and mass in the Key Area of polymers in the Netherlands, generating more business, making the Netherlands an attractive country for top-level knowledge workers, and improving our competitive position. No less important is the aim of retaining long-term research in the Netherlands, which will enable our country to continue to play a leading role in the field of technology.

People
After completing their project, DPI researchers usually find a job with one of the associated partners. Our partners mention this as one of the most obvious advantages of their involvement in DPI. Long-term research requires long-term investment. We are now beginning to reap the rewards. Through the close contacts with industrial partners they learn to see the added value of an industrial approach to R&D at an early stage of their careers. As a result, it is easier for them to make the transition to a business environment after completing their project.

Polymers for a sustainable society
Meanwhile, we are busy setting up a programme for the next ten years, around the theme of “polymers for a sustainable society”. Partner companies and knowledge institutes have been involved in determining the content of this programme. With the Triple P (People, Planet, Profit) concept in mind, we will be focusing our efforts on quality of life, sustainability and economic growth in the years to come. Our underlying objective will be to continue to deliver excellence and impact as we have been doing for several years now.

Excellence
We have defined four key themes:

1. Design of durable high-volume, high-performance materials,
2. New polymers for sustainability,
3. High-value-adding coatings and barrier films,
4. Materials for high-tech and bio-functional applications. Via calls for research proposals we have invited universities to jointly give shape to these themes. In close collaboration with the scientific chairmen, our partner companies will decide on the ultimate selection of projects.

The Scientific Reference Board, - consisting of four independent internationally renowned experts, in their turn assess the scientific merit of the total DPI programme.

Impact
Our output is becoming increasingly important to industry, judging from the growth in the number of patents and the growing interest in the transfer of patents. DPI rewards its researchers for their contributions. During the annual meeting in 2006, which was hosted by Dow in Terneuzen (Netherlands), 42 researchers were presented with a DPI patent award. In addition, in 2006 the first Pieter Jan Lemstra Invention Award was presented, in honour of Professor Piet Lemstra of Eindhoven University of Technology, co-founder of DPI and its first scientific director. The recipients of the Award were top researchers Dick Broer and Kees Bastiaansen,

who were jointly responsible for research activities in the Functional Polymer Systems technology area that have meanwhile generated 13 patent applications. The Pieter Jan Lemstra Invention Award will be presented every two years to researchers who have demonstrated outstanding performance with an impact on industry.

DPI Value Centre

Together with the Dutch Ministry of Economic Affairs we are working on the creation of a separate Value Centre. We should do more in the field of valorisation, in particular valorisation that will benefit Dutch SMEs. With DPI's current set-up we are unable to meet this demand, but we are convinced we will be able to do more for Dutch SMEs without compromising the current success formula. We think there are opportunities that we are currently leaving unused but that might be of interest to other parties, like SMEs.

Anniversary

Our annual meeting on 21 and 22 November 2007, which will be hosted by DSM, will have an extra festive touch because this year is our tenth anniversary. The end of 2007 will also mark the start of the implementation of our new business plan. Since the core themes of this plan have been defined by our partners, we trust we will be able to continue our relationship with you for many more years.

Dr Jacques Joosten
Managing Director

Jacques Joosten, Dutch Polymer Institute

Annual Report 2006

Summary of financial data 2006

Income (x EUR million)

Contributions from industrial partners	4.61	28 %
Contributions from knowledge institutes	3.72	22 %
Contributions from Ministry of Economic Affairs	8.21	50 %
Total income	**16.5**	**100 %**

Expenditure (x EUR million)

By nature

Personnel costs	13.18	80 %
Depreciation	1.72	10 %
Other costs	1.63	10 %
Total expenditure	**16.5**	**100 %**

By Programme Area

Polyolefins	2.31	14 %
Engineering Plastics	1.77	11 %
Rubber Technology	0.65	4 %
Functional Polymer Systems	2.98	18 %
Coating Technology	1.77	11 %
High-Throughput Experimentation	2.73	17 %
Plastic Electronics	0.18	1 %
Bio-Inspired	0.20	1 %
Corporate Programme	1.73	10 %
Organisation and support	2.21	13 %
Total expenditure	**16.5**	**100 %**

data

2006 Key Performance Indicators

Number of industrial partners
End 2005: 34
End 2006: 35

Number of partner knowledge institutes (universities etc.)
End 2005: 24
End 2006: 30

Industrial contribution (cash and in-kind) as % of total expenditure
End 2005: 27%
End 2006: 28% EUR 3,950,434 cash +
EUR 656,893 in kind

Contribution Ministry of Economic Affairs
End 2006: 50%

Number of patents filed by DPI
In 2005: 12
In 2006: 7

Number of patents licensed or transferred to industrial partners
In 2005: 1
In 2006: 0

Number of patents to be transferred:	21
Interest shown by industrial partners:	11
Interest shown by third parties:	6

Track record DPI researchers 2006

Left in total	65
Employed by partner knowledge institute	12
Employed by non-partner knowledge institute	4
Employed by partner industrial company	27
Employed by industrial non-partner company	7
Returned to native or foreign country	8
Unknown	6

European governmental (EU) funding (% of total funding)
In 2005: 0%
In 2006: 0%

Participation of foreign knowledge institutes (% of total expenditure)
In 2005: 7.4%
In 2006: 11.4%

Research output	**2005**	**2006**
Scientific publications:	219	175
PhD theses:	15	19

Overhead costs as % of total expenditure
In 2005: 10%
In 2006: 13%

Expenditure for knowledge transfer
In 2005: EUR 400,000
In 2006: EUR 291,000

Partners

Industry

- Accelrys
- Agrotechnology & Food Innovations
- Akzo Nobel
- Analytik Jena GmbH •
- Astra Zeneca
- Avantium Technologies
- Avery Dennison
- Basell
- BASF •
- Bayer MaterialScience
- Borealis
- Braskem •
- Chemspeed Technologies
- Ciba Specialty Chemicals Inc.
- Degussa
- Dow Benelux
- DSM
- ECN
- Forschungs Gesellschaft Kunststoffe
- Friesland Foods
- GE Plastics
- Hysitron
- Merck
- Microdrop Technologies
- Nano Technology Instruments - Europe
- Philips
- Océ Technologies
- OTB Engineering
- National Petrochemical Company Iran
- Sabic
- Shell
- SKF
- Stichting EmulsiePolymerisatie •
- Symyx •
- Teijin Twaron
- Ticona
- TNO Science and Industry
- Waters Technologies Corporation

Knowledge Institutes

- Delft University of Technology
- Eindhoven University of Technology
- University of Twente
- Radboud University Nijmegen
- University of Amsterdam
- Energieonderzoek Centrum Nederland ECN
- Leiden University
- University of Groningen
- University of Utrecht
- Maastricht University
- Wageningen University and Research Centre
- Agrotechnology & Food Innovations
- NWO/Dubble
- TNO
- Polymer Technology Group Eindhoven
- University of Birmingham •
- University of Nottingham
- University of Leeds
- Queen Mary & Westfield College, University of London
- Loughborough University
- Friedrich Schiller Universität Jena •
- Forschungsinstitut für Pigmente und Lacke (FPL)
- Universität zu Köln
- Leibniz-Institut für Polymerforschung Dresden
- Max-Planck Institut für Polymerforschung
- Deutsches Kunststoff Institut (DKI)
- Università degli studi di Napoli Federico II
- Stellenbosch University
- National Technical University of Athens
- ESPCI/CNRS
- ESCPE-Lyon

Ministry

- Dutch Ministry of Economic Affairs

• left in 2006
• new per 2007

Organisation

Supervisory Board

Prof. M. Dröscher, Degussa GmbH
Prof.Dr Ir C.J. van Duijn,
Eindhoven University of Technology
Prof. Ir K.C.A.M. Luyben,
Delft University of Technology
Prof. T.C.B. McLeish, University of Leeds
Prof. Dr J. Put, DSM Research
Dr H.M. van Wechem, Shell International,
Chairman
Dr P.E. Wierenga, Philips Research

Council

Dr Ir M. Steijns, Dow Benelux, Chairman

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

Dr Ir J.G.H. Joosten, Managing Director,
Scientific Director a.i. •
Prof. Dr M.A.J. Michels, Scientific Director •

Programme Area Coordination

Dr J.A.E.H. van Haare, Functional Polymer Systems,
Coating Technology, Large-Area Thin-Films
Electronics •
Ir. R.P.A. van den Hof, Bio-Inspired,
Corporate Research •
Dr. S. Schmatloch, High-Throughput
Experimentation, Plastic Electronics
Corporate Research •
Prof. Dr. U.S. Schubert, High-Throughput
Experimentation •
Dr J.E. Stamhuis, Polyolefins, Engineering Plastics,
Rubber Technology

Scientific Programme Chairmen

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

Organisation Staff

A.F.J. van Asperdt, Financial Administrator
Ir. Drs. A. Brouwer, Operational Manager •
Drs M.C.A. van Egmond, Office Manager •
I.N.H.M. Hamers, Secretary
S. Koenders, Programme Secretary
P.J.J. Kuppens, AA, Controller
Ir J.G.M. Nieuwkamp, Patent Attorney •
J.J.D. Tesser, Communications Manager
Ir S.K. de Vries, Trainee Patent Attorney

• left in 2006
• per 2006

IP regulations/transfer of patent applications

On 27 January 2006, the Council of Participants approved the new rules and regulations with respect to Industrial and Intellectual Property (the "IP regulations"). One of the reasons for changing the regulations was the growing patent portfolio, which led to increasing patent costs at the expense of the research budget. But most importantly, the intention was to optimise the conditions for valorisation by transferring the patent applications to those parties that would further develop the technology and bring new applications to the market.

DPI has been building up its patent portfolio since 1999. As soon as a patent application in our portfolio reaches the appropriate phase it is offered for transfer to the entitled partners. All partner companies that have a ticket in a certain Technology Area at the date of first filing have the right to participate in the transfer of patent applications resulting from that Technology Area. Partner companies have indeed expressed an interest in taking over about 50% of the patent applications offered in 2006. In cases where neither the partner companies nor the partner knowledge institutes are interested (which may be for various reasons), DPI can try and find third parties to take over the technology to further develop it into new products and processes. In about 25% of the cases, the possibility of a transfer is now being discussed with third parties that have shown an interest in DPI technology.

Currently DPI is in the first stage of the process; the negotiations with partner companies and third parties are still in progress.

Statistics

The statistics below show the growth of DPI's patent portfolio from 2000 to 2006. Although the absolute figures for 2006 are slightly lower than those for previous years, the portfolio keeps growing at a steady pace, along with the growth of the research programme.

Certificates of Invention

In 2006, at our annual general meeting in Terneuzen (Netherlands), we granted a total of 61 Certificates of Invention to 42 inventors for 17 patent applications filed in the period 2005-2006.

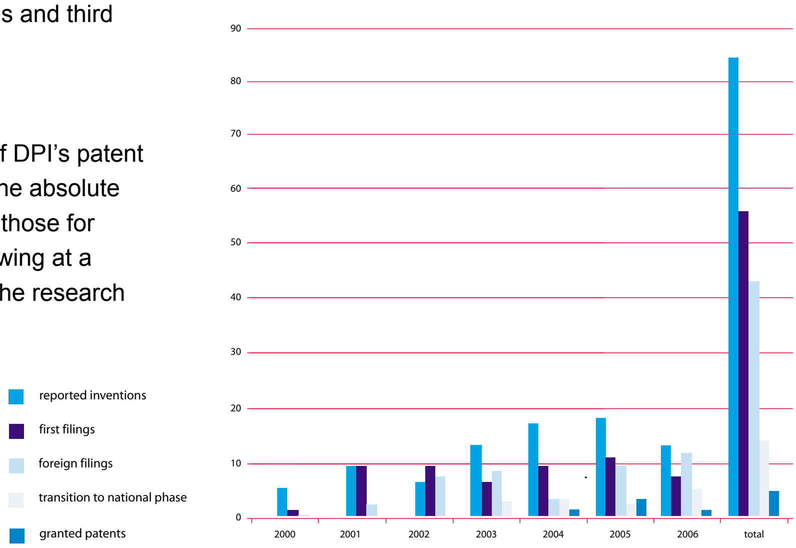
We grant Certificates of Invention to honour researchers who have made an invention that proved to be of interest to our partners. By means of these awards we hope to stimulate our researchers to help 'bridge the innovation gap' by performing research that is focused on our industrial partners' agenda. The Certificates of Invention carry a cash prize of €500.

Pieter Jan Lemstra Invention Award

In 2006 DPI presented Dr Kees Bastiaansen and Professor Dick Broer with the first Pieter Jan Lemstra Invention Award for their contribution to the development of polymer technology in the Netherlands. This prize was inaugurated to honour DPI's founder and very first director, Professor Piet Lemstra. The Institute commends the researchers' close collaboration with companies, which has enabled their scientific knowledge to be quickly converted into industrial applications. Furthermore, their top-quality research has attracted new companies to DPI.

fact

Bastiaansen and Broer jointly head the 'Polymers in Information and Communication Technology' subgroup of the Polymer Technology faculty at the Eindhoven University of Technology in the Netherlands (TU/e). Within DPI this group has been working on the development of a clever approach to the structuring of large-area polymer films for applications in informatics, communications technology and medical technology.



DPI Value Centre

In 2006 the first preparations were made to set up the DPI Value Centre, a new organisation that is closely linked to DPI but is legally separate from it.

While DPI focuses on pre-competitive research and (besides knowledge institutes) has attracted mainly larger companies as partners, the DPI Value Centre aims to boost the growth of start-ups and SMEs and to support larger companies beyond their research stage. Although SMEs in the Dutch polymer sector are highly innovative, they are insufficiently “connected” to knowledge generation. SMEs and larger companies also face difficulty in organising the stages following pre-competitive research, especially when other partners are involved. Many companies often lack the size, resources and market focus needed to innovate successfully. Furthermore, there are relatively few start-ups in the polymer value system due to regulations, investment barriers and a complex piloting phase hampering start-up and spin-out activities.

The DPI Value Centre aims to tackle these problems by

- supporting new and existing companies by coaching them, developing their business and facilitating their feasibility studies and development projects;
- pooling the interests of polymer producing or processing companies and translating these into new research or development projects, for instance on the field of sustainability;
- setting up and managing consortia of companies or knowledge institutes to jointly conduct research or development following a partner’s pre-competitive research;
- setting up cross-border partnerships within the Euroregion (mainly with German and Belgian partners);
- stimulating the build-up and transfer of knowledge between companies and knowledge institutes at various levels, for example by promoting traineeships or through exchange programs.

Shila de Vries, Arie Brouwer, Jacques Joosten, Dutch Polymer Institute

At the end of 2006 the funding for the first stage of the DPI Value Centre was provided by Brainport, an organisation that aims to stimulate economic activity in the Eindhoven region.

In the beginning of 2007 a Value Centre Taskforce will be formed with participants from stakeholders such as Brainport, Polymer Technology Group, NRK, DPI, TNO, Syntens, Technopartner, United Brains and Creative Conversion Factory.

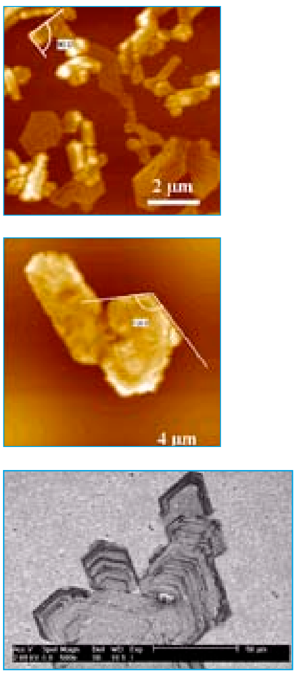
In the second half of 2007 the DPI Value Centre will be officially launched, with a small core organisation initiating the first pilot projects.
As of early 2008 the Value Centre should be fully operational and expand the range of initiatives and the number of participating partners, SMEs, start-ups and knowledge institutes.

Polyolefins

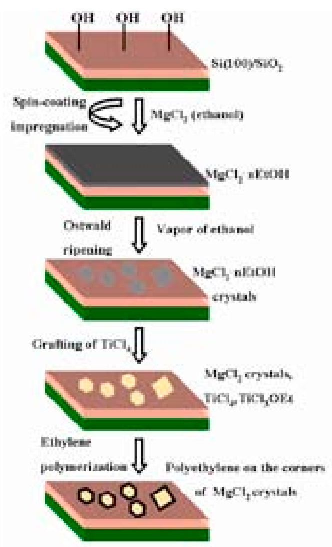
Guarding the full chain of knowledge

Polyolefins represent roughly half of the world's commodity and commodity-plus polymers, which in turn account for close to 90% by weight of global polymer production. In terms of chemical composition, polyolefins appear deceptively limited: polyethylene, polypropylene, and little else. Yet literally hundreds of polyolefin-based materials with dramatically different properties and applications can be found on the market. The offer spans from ultra-rigid thermosets (more resistant than steel, with the premium of a much lower specific weight) to high-performance elastomers. Behind this unique versatility are the very high level of molecular control in polymerisation, making it possible to fine-tune chain length and ability to crystallise over extremely wide ranges, and a rich toolbox for supramolecular material design, with an incredible variety of blending and processing options. In turn, this results from a close cooperation between catalyst chemists, process engineers and material scientists, in a true and highly integrated chain-of-knowledge approach.

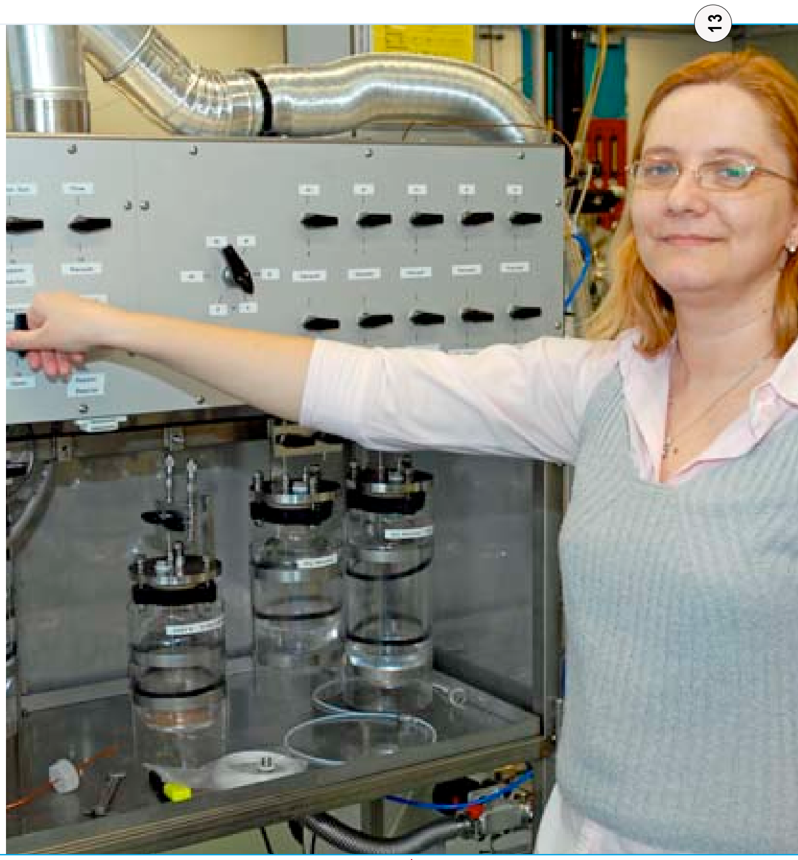
Vincenzo Busico, scientific chairman of DPI's Polyolefins Technology Area and professor at the Federico II University of Naples in Italy, is never tired of explaining this unique character of polyolefins. These polymers obviously have his undivided attention, judging by his enthusiasm in talking about them. "Polyolefins sell very well on the market but much less so in science. Because of their extremely efficient and atom-economical production processes they are perceived as a mature field, and academic research is drifting away towards more trendy subjects. But the fact that a product sells well does not mean that the science behind it is mature. In reality, the chance of new breakthroughs in polyolefins is still very high, and the disclosures of novel catalysts, processes and materials show no signs of slowing down. Polyolefin producers are well aware of these opportunities, and industrial investments in research



Polyethylene growing on the edges of MgCl2



Flat model approach



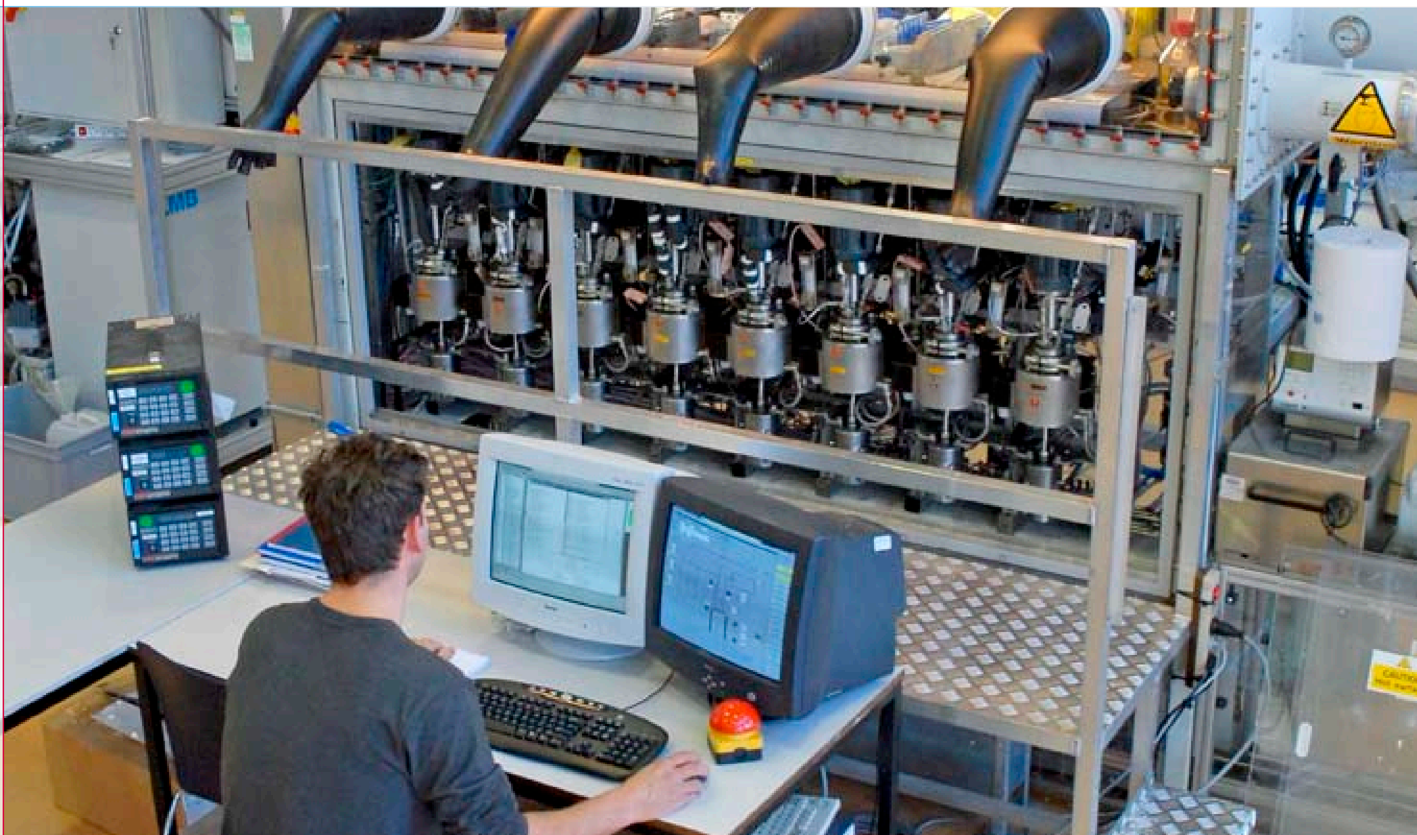
Adelaida Andoni, Eindhoven University of Technology are not declining. As a result, a gap is widening between academia and industry, the latter being often unable to identify high quality academic partnerships for extramural projects, and to recruit young research staff with a specific training. In this context DPI plays a unique and vital role by promoting and supporting a very significant pre-competitive research programme in polyolefins, bridging the gap between industry and academia with a chain-of-knowledge approach."

Philosophy

Dr Jan Stamhuis, programme area coordinator for Polyolefins, underlines this last remark by adding that more companies are joining the Technology Area. This triggers Busico to take his argument a bit further: "The involvement of industrial partners is growing not only in number, but also in scientific significance. It is of special importance that the American company Symyx, a leading producer of High Throughput Experimentation technology and equipment, recently became a DPI partner for Polyolefins. It should be noted that, apart from pharmaceuticals, polyolefins represent the area of chemistry with the most intensive use of HTE methods. Rather than following a combinatorial approach, polyolefin researchers implement parallel tools enabling them to run a very high number of well-designed and well-controlled experiments simultaneously. In an industrial environment this is being aimed primarily at catalyst and material discovery."

Stamhuis mentions an example of what can be achieved. "Under normal circumstances, a polyolefin chain is produced at one and only one catalytic species. It has now been discovered by scientists of Dow Chemical, by means of HTE campaigns, that with certain combinations of catalysts and co-catalysts it is possible to have individual polyolefin chains grow on different catalytic species, thus attaining what has been named a chain shuttling regime. This opened the door to the catalytic production of novel olefin block-copolymers with special properties - new thermoplastic elastomers with a wide usage temperature window that, contrary to vulcanized rubber, can be reprocessed and recycled." Busico adds enthusiastically: "This is only the tip of the iceberg. The beauty of it all is that we are not talking simply of a new catalyst or polymer, but rather of a novel concept of olefin polymerisation, in which chain growth occurs sequentially at different, and not necessarily new, catalytic species with full control of where and for how long they grow. This is something people have long been dreaming about. The possibilities to create

fact



Eindhoven, University of Technology

unprecedented polyolefin material architectures are virtually endless."

In pre-competitive research, on the other hand, HTE tools can be used for fast and efficient catalyst and material screening. Olefin polymerisations are sophisticated and complicated catalytic reactions. The catalyst systems involved are usually combinations of precursors, activators, promoters, scavengers and/or modifiers. Searching for the optimum composition (in terms of activity and selectivity) as a function of the main reaction variables (like temperature, pressure, solvent, etc.) is no sinecure. To do this properly, one has to screen ten to twenty parameters individually and in combination with all others. Not many catalyst systems have been unravelled completely - certainly not in academia but probably not in industry either, at least not exhaustively, according to Busico. "And now, by doing hundreds or even thousands of relatively well-controlled polymerisation experiments per day per lab we can, for the first time, really obtain exhaustive information. The expectation is that this will make it possible to improve fundamental understanding,

sheet

Busico:
"Being good does not mean being mature."

and ultimately lead to rational catalyst and material design."

Opportunities

The prospects for polyolefins are good. The market is growing and will continue to grow even faster for the next 10-20 years, not only because new markets are being addressed, but also due to the fact that polyolefins (in particular polypropylene) are replacing other materials such as glass, metal and other more expensive or less environmentally friendly polymers. On the one hand, the large-scale production of commodity polyolefins is progressively being moved from Europe and the US to the Persian Gulf area, where feedstock is available at a lower price, while on the other hand there seems to be a growing interest in new specialty polyolefins that are needed in smaller quantities and can be sold with higher margins. Busico sees this as an emerging opportunity for smaller high-tech companies, and in the long run even for combinations of knowledge institutes backed by an investor.

DPI is taking advantage of these good prospects by launching calls for innovative research proposals. The expectation is that the competition between a number of carefully selected world-class knowledge institutes will lead to an improved quality of the project portfolio. To ensure that the full chain of knowledge is addressed, multidisciplinary proposals coming from pools of well-assorted applicants from various knowledge institutes are favoured. "This is to prevent professors cultivating their 'prima donna syndrome' by claiming that they have everything in house," says Busico with a self-mocking smile.

This does not mean that the portfolio of research projects is not already well-balanced and of high quality. The report from DPI's Scientific Reference Board was very positive. The most interesting results have been obtained in the field of heterogeneous catalysts, according to Busico. "For the past thirty years or so, we have been working with heterogeneous catalysts that in some respects are still black boxes. What we knew we derived indirectly from the polymers produced – a backward deduction process which is the chemical equivalent of a detective's investigation based on a fingerprint. But now, with the tremendous progress in high-resolution electron and atomic force microscopy and in solid-state nuclear magnetic resonance, we are close to 'seeing' the reaction sites on the catalytic surfaces; several DPI projects are addressing this area at a very high level. In spite of breakthroughs in homogeneous catalysts, research into heterogeneous catalysts is extremely important because industry will continue to use these systems for a number of technical and economic reasons. Elusive and difficult to control, they still have important margins for improvement, and we expect much more from them."

Concern

Apart from success there is also reason for concern and this has to do with the reduced level of public funding in polyolefin research. Busico is very frank about this. "Of course it is good to fund areas such as nanotechnology and biotechnology that are important for the future of Europe, but we should not let other areas starve. Take chemical engineering for example. Chemical reactors, in particular high-pressure ones, are expensive to operate. Many laboratories in academia have been forced to close down these facilities because they cannot afford the costs any longer. Yet these tools represent an indispensable element of the polyolefin chain of knowledge, which is DPI's real strong point. For this reason, we have included in our call for proposals a number of European knowledge institutes which still operate high-pressure reactors suited for olefin polymerisation, and we are confident that by funding high quality projects in the area the integrity of the chain-of-knowledge will be safeguarded."

To round off, Busico mentions another concern he has. "If a discipline disappears from academia, companies have difficulty finding good people with specific skills to work for them. This can be fatal to the competitiveness of European polyolefin industry. DPI must keep polyolefins alive in academia, but can also contribute to solving the problem by seriously thinking about offering training to young employees of polyolefin companies. The natural environment of DPI, where academia and companies come together, is the ideal place to realise this – much more than other, less qualified institutes that smell money and pretend to have the necessary expertise."

Stamhuis:
"Polyolefins is still a fast growing technology area in DPI."

fact

Fluidization studies to go beyond trial and error

Polyolefins are the most widely produced plastics, but the production process is not yet completely understood and therefore not optimized. There is still a lot of fundamental research going on to get a grip on it. Polyethylene is made in gas-solid fluidized beds: ethylene reacts with catalytic particles and forms granules that grow while floating on the gas. The system behaves like a fluid and, as in fluids, there are gas bubbles. The behaviour of the bubbles influences the growth of the particles. The result is that not all granules have the same diameter. How these bubble diameters depend on the process conditions is not very well known.

Models

This is the field of research that Willem Godlieb is working on at the University of Twente (Netherlands) by developing a model of the process and by doing experiments. Almost two years ago he started his project and he has achieved some fine results with his models. The experimental part is a bit behind schedule, due to the fact that supply times for parts of his reactor are longer than expected. When the set-up is ready it will be a high-pressure reactor with a diameter of 30 cm. Godlieb can measure the diameters of bubbles throughout the reactor by determining their electrical capacity.

Godlieb:
"Industrial partners in DPI will benefit if we understand more of the process."

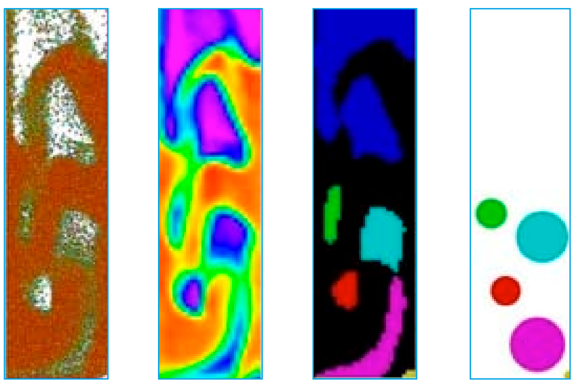
Willem Godlieb, University of Twente

His approach is new. Up to now most experiments were done in reactors with diameters of only a few centimetres under atmospheric conditions, which is quite different from industrial conditions, where reactors have a diameter of several metres and pressures are around 25 bar.

Godlieb: “The reactor geometry obviously has a large influence on the size of the bubbles and on the number of particles present in them. Bubbles have advantages and disadvantages. On the one hand they provide for the mixing of particles and they prevent particles from growing faster in one spot than in another. On the other hand they consist of gas that is not used in the reaction. This gas needs to be recovered and recycled, which involves costs that had better be avoided. With my models I have investigated how the pressure influences the bubbles. The first results are encouraging. The model can indeed be used with high pressures, which is not self-evident. And the diameters of the bubbles get smaller when the pressure is higher and thus provide better cooling.” His results have been well received at conferences and he has written several papers already.

High-pressure reactor

The models were developed and validated in other experiments. They can be used for fluids with high densities, for instance, so Godlieb is confident that once he can do his experiments, these will confirm the quantitative results of the models for high pressures. He hopes to be able to start with the experiments soon. Godlieb: “Our industrial partners are very interested in the modelling results, which are useful and will give them insight into the process, but they are also asking me about the equipment. They will benefit if we understand more of the process.

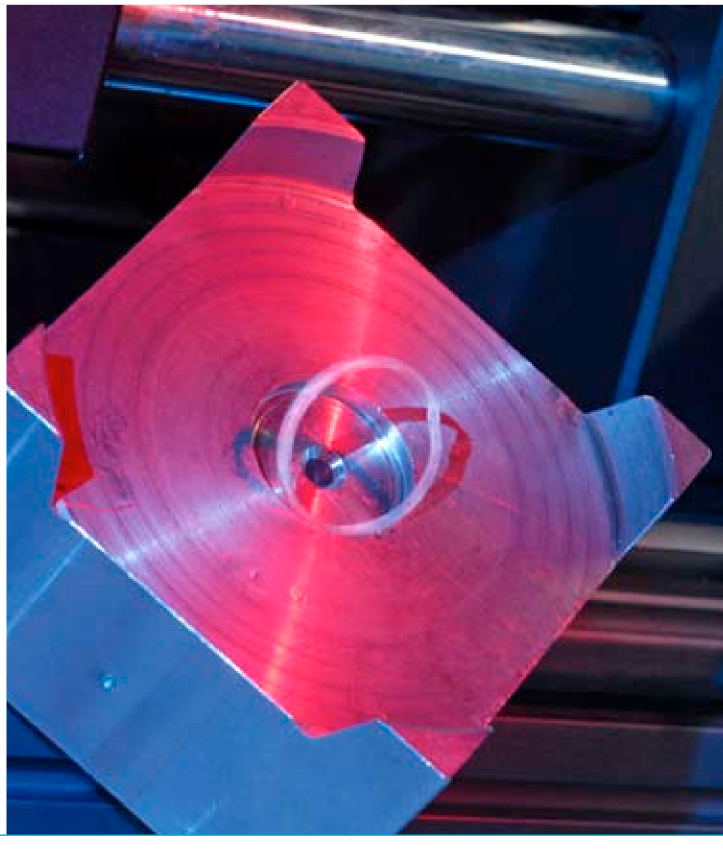


particle porosity results equivalent

Currently the only way to assess the influence of changes in parameters is to look at the resulting product. That is very much a trial and error approach.”

For Godlieb it was an obvious choice to study chemical engineering. At school he liked mathematics, chemistry and physics. At the university he acquired the necessary knowledge of informatics. “It is all coming nicely together in the work that I am doing now,” he says. “I was initially hesitant to start this PhD project, though. I realized I would be working on my own for four years, which is quite long. But on the other hand, you know when you have found a subject that is the right one for you.” And that seems to be the case. When his project is finished he would like to continue working in this field, not at a university but in industry, in plastics or other applications where fluidized beds are used.

fact



Facts and figures

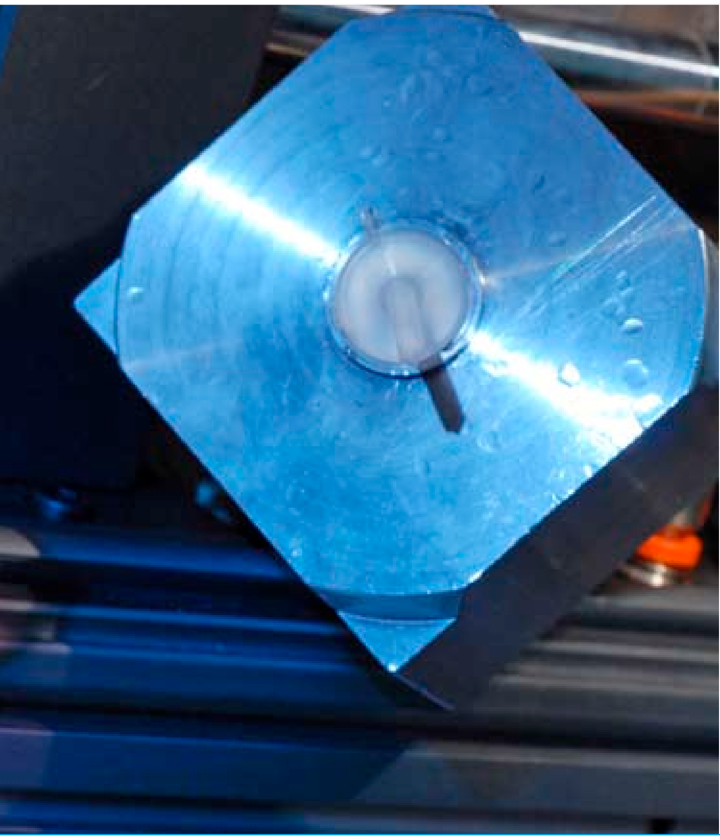
Subprogrammes

- **Catalysis**
  Investigation, screening and development of novel homogeneous catalyst systems

- **(Heterogeneous) Catalysis and single-centre catalyst immobilisation**
  Study and implementation of new approaches for the immobilisation and activation of heterogeneous and single-site catalysts for olefin (co)polymerisation.

- **Polymer process and reactor engineering.**
  Studies on various reactor and technology unit operations to produce a quantitative description and acquire a thorough understanding of the crucial aspects of polymerisation processes.

- **Polymer structure, modelling, processing and exploratory research**
  Understanding, modelling and predicting the relationships between polymer structure, processing and properties in polyolefin polymer systems.



Industry partners

Basell, Borealis, Dow, DSM, NPC Iran, Sabic and Shell. New members since 1 January 2007 Symyx and Braskem.

Research partners

Delft University of Technology, Eindhoven University of Technology, University of Groningen, University of Twente, University of Utrecht, University of Amsterdam (all in the Netherlands), Federico II University of Naples (Italy), ESPCE Lyon (France)

Budget/realised

Total costs € 2.3 million (same as budget), € 106,000 spent on equipment.

Organisation

Number of FTEs 22, Scientific Chairman Prof. Vincenzo Busico, Programme Area Coordinator Dr Jan Stamhuis

Networking

Number of PC meetings: 3; special workshops: three PO Cluster Review meetings with overview presentations by the Subcluster Coordinators and detailed presentations of their project results. Also, specially invited lectures were held on topics of specific interest to the Polyolefins technology area. These topics were presented by authoritative research staff from both within and outside DPI. These PO Cluster Review meetings are highly valued and attract typically more than 50 participants from academia and industry.
Publications: 20 referenced publications, 2 theses were finalized and publicly defended.
Reported Inventions: 1.

Output
Theses

M. Qasem Al-haj Ali
Modeling and control of molecular weight distribution in a liquid-phase polypropylene reactor.

R.R. Tupe
Tubular Reactor for Liquid-phase Propylene Polymerization

Scientific publicatios
A.K. Yaluma, P.J.T. Tait, J.C. Chadwick
Active center determinations on MgCl2-supported fourth- and fifth-generation Ziegler-Natta catalysts for propylene polymerization
Journal of Polymer Science Part A: Polymer Chemistry
44-5, 635-1647

J. Loos, M. Tian
Annealing behavior of solution grown polyethylene single kristal
Polymer
47, 5574-5581

M.H.E. van der Beek, G.W.M. Peters, R. Meijer
Classifying the combined influence of shear rate, temperature, and pressure on crystalline morphology and specific volume of isotactic (Poly)Propylene
Macromolecules
39, 9278-9284

Q.H. Zhang, D. Lippits, S. Rastogi
Dispersion and rheological aspects of SWNTs in intractable polymers
Macromolecules
39, 658-666

M. Smit, X. Zheng, R. Brüll, J. Loos, J.C. Chadwick, C.E. Koning
Effect of 1-hexene comonomer on polyethylene particle growth and copolymer chemical composition distributiebon
J. Plym.Scie. Part A: Polym. Chem.
44, 2883-2890

M. Smit, X. Zheng, J. Loos, J.C. Chadwick, C.E. Koning
Effects of propylene prepolymerization on ethylene/1-hexene and ethylene/1-octene copolymerization with an immobilized metallocene catalyst
Journal of Polymer Science Part A: Polymer Chemistry
44, 6652-6657

S. Rastogi, N. van Ruth, A.E.Terry, J.E. Vega
Fragility in Polymer Melts: A Study on Poly-4-methyl Penetene-1 Polymer
47, 5555-5565

R. Huang, N. Kukalyekar, C.E. Koning, J.C. Chadwick
Immobilization and activation of 2,6-bis(imino)pyridyl Fe, Cr and V precatalysts using a MgCl2/AlRn(OEt)3-n support: Effects on polyethylene molecular weight and molecular weight distributiebon
J. Mol. Catal.
260, 135-143

X. Zheng, M.S. Pimplapure, G. Weickert, J. Loos
Influence of Copolymerization on Fragmentation Behavior Using Ziegler-Natta Catalysts
Macromol. Rapid Commun.
27, 15-20

X. Zheng, M.S. Pimplapure, G. Weickert, J. Loos
Influence of porosity on the fragmentation of Ziegler-Natta catalyst in the early stages of propylene polymerization
E-polymers
028

Y.V. Kissin, J.C. Chadwick, I. Mingozzi, G.Morini
Isoselectivity Distribution of Isospecific Centers in Supported Titanium-Based Ziegler-Natta Catalysts
Macromolecular Chemistry and Physics
207, 1344-1350

Q. Zhang, S. Rastogi, D. Chen, D. Lippits, P.J. Lemstra
Low percolation threshold in single-walled carbon nanotube/high density polyethylene composites prepared by melt processing technique
Carbon
44, 778-785

D.R. Lippits, S. Rastogi, G.W.H. Hoehne
Melting Kinetics in Polymers
Physical Review Letters
96, 218303

M. Smit, J. R. Severn, X. Zheng, J. Loos, J. C. Chadwick
Metallocene-catalyzed olefin polymerization using magnesium chloride-supported borate activators
Journal of Applied Polymer Science
99, 986-993

G.A. Bokkers, J.A. Laverman, M. van Sint Annaland and J.A.M. Kuipers
Modelling of large-scale dense gas-solid bubbling fluidised beds using a novel Discrete Bubble Model
Chemical Engineering Science
61, 5590-5602

J.C. Chadwick, J.R. Severn
Single-site catalyst immobilization using magnesium chloride supports
Kinet. Catal.
47, 186-191

D.R. Lippits, S. Rastogi, S. Talebi, C. Bailly
The formation of entanglements in an initially disentangled polymer melts
Macromolecules
39, 8882 – 8885

M.H.E. van der Beek, G.W.M. Peters, H.E.H. Meijer
The influence of shear flow on the specific volume and the crystalline morphology of isotactic polypropylene
Macromolecules
39, 1805-1814

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

J.C. Chadwick
Ziegler-Natta Catalysis
Encyclopedia of Chemical Processing
3247-3259

Filed patent applications
#495 R. Huang, J.C. Chadwick
Process for the preparation of a polyethylene

Reported inventions
#321 N. Kukalyekar, J.C. Chadwick, S. Rastogi
Polyethylene containing nanoparticles

#319 + #332 P.L. Shutov, E. Novarino, M. Zuideveld, B. Hessen
Stabilized activated olefin polymerization catalyst

#495 + #106 A.V. Chuchuryukin, G.P.M. van Klink, G. van Koten, R. Huang, J.C. Chadwick
Catalyst system for preparation of UHMWPE

Stamhuis:
"In our future Value Centre we will try to facilitate the application of our results."

Jan Stamhuis, Dutch Polymer Institute

Shift in focus from individual properties to overall functional performance

Polymers are used in engineering applications not just because of their appearance, their workability or their ability to keep things together. They play a vital role in the complex mechanical behaviour of a system. A tyre that keeps a car on the road and a cogwheel that transfers motion are just a few examples. That is why the focus of industrial interest has shifted from individual polymer properties to overall functional performance, which depends on a range of properties. This shift in focus explains why the former technology areas of Engineering Polymers and Rubber Technology have been combined into a new technology area: Performance Polymers.

"The reason for this merger of technology areas is twofold," explains Dr Jan Stamhuis, programme area coordinator. "DPI is increasingly being approached by companies that are interested in a specific application rather than in a polymer as such. They want to realise a function, not a priori use a specific

Van den Hof:
"The elastic properties of such block-copolymers are very constant over a broad range of temperatures."

Noordermeer:
"The project to vulcanise synthetic rubber resulted in two patents that attracted the interest of the industry."

Richard van den Hof, Dutch Polymer Institute

Jacques Noordermeer, Dutch Polymer Institute polymer such as an elastomer or an engineering plastic. As a consequence, interest in Rubber Technology has dwindled. Companies want to become a member of DPI, but not exclusively of Rubber Technology."

Jacques Noordermeer, professor at Twente University (Netherlands) and former scientific chairman of Rubber Technology, adds that another reason for this dwindling interest might well be the fact that traditional rubber supporters, as he calls them, the few tyre companies left after a shake-out in that industry, are not (yet) involved in DPI. Noordermeer: "The tyre companies don't seem to be convinced that pre-competitive research generates mutual benefits."

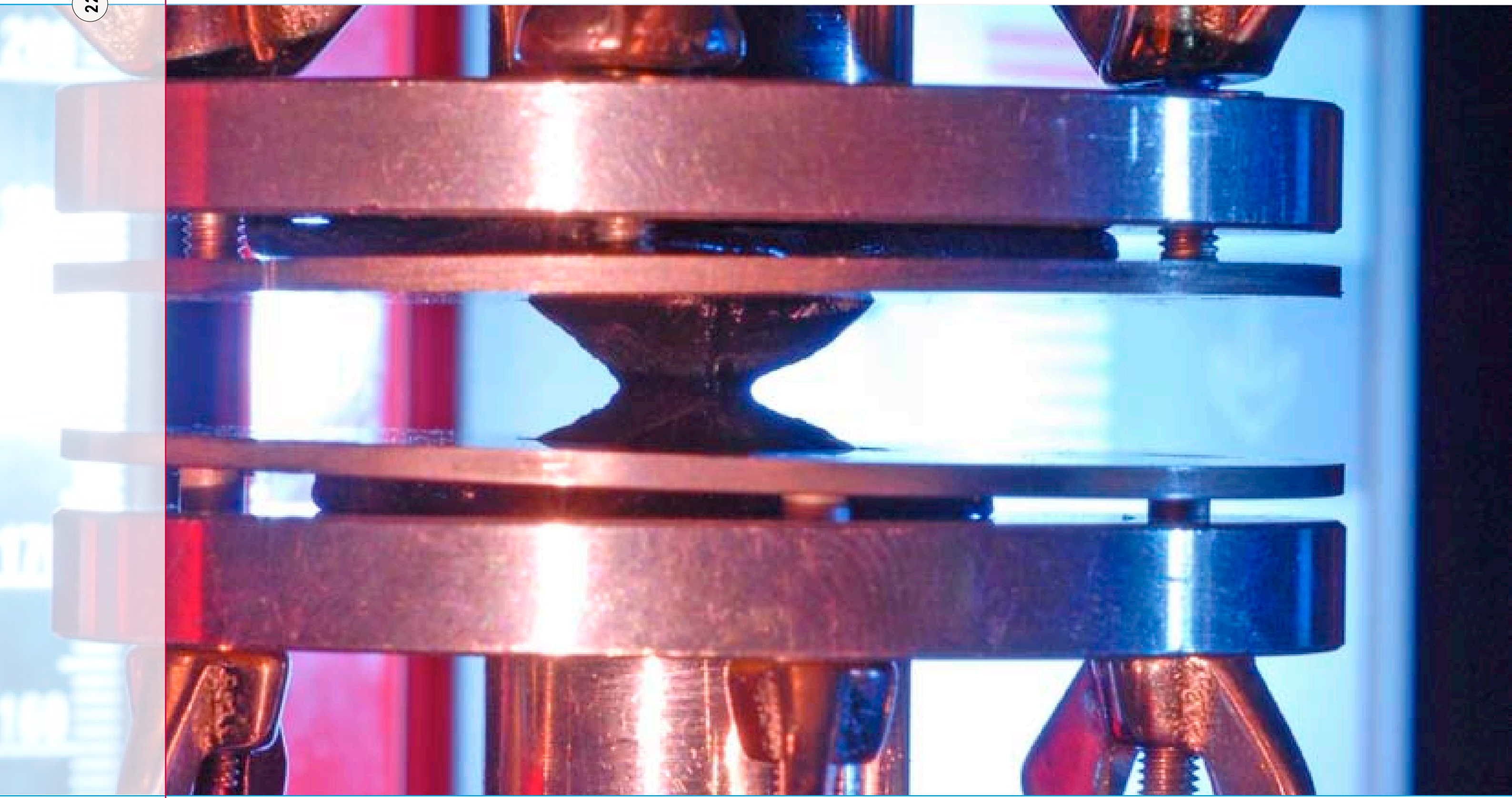
Synergy

"Yet we keep trying to get them interested," adds Richard van den Hof, scientific chairman of the former Engineering Polymers technology area. "The elastic properties of rubber and engineering polymers in general play a role in a wide variety of applications. The challenges are similar in such applications and are related to properties such as adhesion, stiffness and elasticity. We think there is quite some synergy there. This justifies joining forces in pre-competitive research and, at the same time, supporting the interest of a variety of companies. Moreover, our programme is getting new impulses through companies that are active in new application areas, for example SKF in seals and friction or Teijin-Twaron in new fibres for a broad application range."

The following example may help to illustrate the kind of synergy that DPI can generate. Natural rubber, still one of the best rubber types, is vulcanised with sulphur to improve for instance its strength and resilience. To remedy a few of the disadvantages of natural rubber - the sensitivity to temperature and ozone that makes natural rubber brittle - EPDM, a copolymer of ethylene (E) and propylene (P) with small quantities of unsaturated monomer (D), was developed some fifty years ago. However, this material could not easily be vulcanised with sulphur. In a DPI project additives were developed that enable this vulcanisation, leading to a synthetic rubber that is insensitive to UV light and ozone and has the outstanding elastic properties of natural rubber. "The project has attracted the attention of both the industrial and the scientific world and has resulted in two patents," says Noordermeer, stressing its importance.

fact

Besides using additives to improve workability, it is also possible to modify the properties of the polymer itself, as the next example shows. In a DPI project at the University of Twente, researchers built special



crystalline parts into polymers. These parts fit very well to each other and thus give a stable structure. With such materials, interesting and industrially relevant properties come into play. Van den Hof explains: "The elastic properties of such materials are very constant over a broad range of temperatures, until the melting point, which is very sharply defined. If other parts of such molecules show rubber-like behaviour, you can think of synthetic rubbers that you transform via a melt-extrusion process into granulate, which can be re-melted by a customer to make products with complex shapes. You cannot do that with conventional rubber, which can only be processed once." Another promising application, a free-standing membrane, is possible when the non-crystalline parts of the molecule allow water or gas to pass.

Sustainability

Most performance polymers are still based on monomers made from petroleum as basic building blocks. It might be considered to use other sources of monomers, for example bio-based monomers from renewable sources such as plants, in order to avoid a net CO_2 increase in the atmosphere. In cooperation with the University of Wageningen and the Technical University of Eindhoven (both in the Netherlands) this is being investigated in several technology areas, amongst others in Performance Polymers and in Coatings Technology. The researchers are trying to answer questions like 'Which biological source gives the best raw material?' and 'Which bio-based monomers polymerise best?'. Note that 'best' in this context does not just refer to the best technical properties; the considerations leading to a choice of material should, of course, also include economic viability and a full life cycle analysis.

Another aspect of sustainability is the wear resistance of parts made of polymers. It is a field that still requires lengthy experimental procedures. A true understanding of wear resistance phenomena could contribute significantly to the improvement of product design. This would minimise material and energy utilisation and optimise lifetime. "The industry is not primarily interested in improving wear resistance behaviour; they first of all want to be able to predict what will happen over time, so that they can decide when a part should be replaced in order to prevent the failure of a whole system," Stamhuis explains. "And of course, they want to know within one day what will happen in ten years," adds Van den Hof. "This is important not only for cogwheels in machines but also for artificial joints in human bodies. Given the ageing of the population this will increasingly become an issue."

Developing an understanding of what wear really is and of how it can be prevented by modifying polymers is typically a generic, pre-competitive activity in which DPI can play an important role. Scientists that can contribute to that kind of understanding have a background that differs from that of most DPI researchers. They will be found in research groups engaged in tribology, the science of friction and lubrication. "If we interest them in DPI, they will bring new people with new contacts and broaden DPI's horizon even further," says Van den Hof.

Critical mass of knowledge chain

DPI is in fact the only place where people involved in different aspects of polymers - synthesis, processing, (mechanical) properties, and durability - meet each other and exchange their views. This has already resulted in valuable cooperation between different university groups. These networks are increasingly being extended to include European university groups. DPI plays an important role in maintaining critical mass in all aspects of polymer research, in particular because chemical companies are increasingly diminishing their own fundamental or corporate research facilities.

Future challenges

Jan Stamhuis explains some of the challenges for the future: "Many of the results of DPI projects will be used for further development by our industrial partners. In addition, in our future Value Centre we will try to facilitate the application of our results even more. We can do that in smaller consortia of companies, where it will be easier to manage the less generic results. Or we can interest a company in patents that do not directly fit in with the strategies of the companies that have been involved until then, and thus use research results that would otherwise only be gathering dust in some drawer." But even before any project is undertaken, measures can be taken to ensure that the results of DPI's work will find application in industrial practice. The Performance Polymers technology area has whole-heartedly adopted a recommendation that the Scientific Reference Board made in 2005: to guarantee the scientific quality of projects, reviews of external experts are now part of the decision-making procedure for project granting.

Is cure better than prevention?

From time immemorial, mankind has made its structures and materials stronger than they actually needed to be, so that if damage occurred it was less likely to be catastrophic. But wouldn't it be equally useful if a damaged material could heal itself, without human intervention? Steven Mookhoek, PhD student at the Delft University of Technology (Netherlands), does not have the answer yet, but he has three more years to find it. His project started in 2006.

Capsules

Mookhoek: "By self-healing materials we don't mean materials with additives like the ones used in some paints and coatings. These additives can, through a reaction with sunlight, prevent sunlight-induced fading or breaking of paint and coatings. The additive depletes and the intended function disappears. We want to add something to a material that reacts only when needed, when damage has occurred, to prevent failure. This is usually done by adding a fluid in small capsules to the material. When the material cracks, the fluid is released and reacts with the material, fills the crack and prevents the crack from propagating." These capsules can be spheres or long hollow tubes. Over the last five years several research groups all over the world have been active in this field.

fact

Mookhoek is investigating the use of elongated capsules in thermoset polymers and thermoplastic materials. Elongated capsules have the same advantage as long hollow tubes – a large interface with the material, so that the chance of a crack affecting a capsule and releasing the fluid is higher. But the big disadvantage of long hollow tubes – the fact that it is extremely difficult to fill them with fluids, because of capillary action – is less pronounced in elongated capsules. In addition, elongated capsules can achieve the same self-healing effect as tubes but require less liquid to do so. It is always a trade-off between the original properties of the material – whose strength is affected by adding fluid in capsules – and the ability of the material to heal itself. An extra advantage is that these elongated capsules are relatively easy to make. And Mookhoek thinks that they might even be used as a kind of reinforcement, similar to fibre-rein-

Steven Mookhoek, Delft University of Technology forced of particle-reinforced polymers. He presented his initial experimental results at the first international conference on self-healing materials that was recently held in the Netherlands.

Distribution

Mookhoek studied chemical engineering at the University of Twente (Netherlands) and then moved to Delft for this project, a collaboration with TNO. “During the first few years of my study I did not think much about doing research after my graduation, but a practical project in a company made me change my mind. What attracts me in this project is that it is not based on previous research. It will take a lot of time and energy, but I will have the chance to realise my own ideas and plans. New environments and new people to learn from are very valuable to me, so I try to work in as many environments and with as many different people as possible.”

Mookhoek has just returned from a three-month trip to the United States, where he worked at the University of Illinois at Urbana-Champaign with researchers that are more experienced in this field. He learned a lot of practical things there. And next year he will go to Australia on a travel grant that he won at the first self-healing materials conference. He explains what he will be doing there. “The Commonwealth Scientific and Research Organization in Australia is capable of measuring particle distributions throughout a material in three dimensions. There I would like to measure the effect that the different distributions of elongated capsules and their orientation have on the material’s properties and its self-healing capacity.” Apart from this experimental work Mookhoek also wants to do some modelling to explain why certain geometrical distributions give the best results. But that will be for later; after all, he has three more years to go.

sheet

Self-healing meterials, Delft University of Technology

Facts and figures Engineering Plastics

Subprogrammes

- **Polymer Chemistry and Modification**
  Studies related to important industrial and societal issues, such as ways to increase the utilisation of sustainable materials and ways to reduce the cost and energy use of polymerisation. New concepts of molecular structure to achieve step changes in the balance of flow, mechanical and functional properties.
- **Processing for Properties**
  Understanding the relationship between the molecular structure of polymers, their processing characteristics and properties. Focus on the processing effects of intermolecular interactions, e.g hydrogen bonding. Studies to elucidate friction and wear mechanisms.
- **Advanced reinforced thermoplastics and synthetic fibres**
  Studies on interface effects in fibre-reinforced composite systems, effects of nano-reinforcement on polymer material properties on macroscopic and microscopic scale.
- **Stabilisation**
  Investigations into the chemical and physical ageing mechanisms with the ultimate objective of predicting lifetime and fit-for-use design over the life cycle.

Industry partners

Basell, Bayer, Degussa, Dow, DSM, GE Plastics, Océ Technologies, Shell, SKF, Teijin, TNO and since 1 January 2007 BASF.

Research partners

Delft University of Technology, Eindhoven University of Technology, University of Groningen, University of Twente (all in the Netherlands), ESPCI Paris (France), Queen Mary University of London, University of Birmingham (all in the UK).

Budget/realised

Total costs €1.8 million (budget € 2.1 million);
€ 90,000 spent on equipment.

Organisation

Number of FTEs 18, Scientific Chairman Richard van den Hof, Programme Area Coordinator Dr Jan Stamhuis

Networking

Number of PC meetings 4, jointly with the PC RT; special workshops: two EP Cluster Review meetings, one with a focus on Processing and Physical Properties and the other with Chemistry as theme.

Publications

18 referenced publications, 5 theses were finalized and defended in public.
Reported Inventions: 3, Filed Patent Applications: 4

Facts and figures Rubber Technology

New Product technologies

Studies to explore new functionalities to perform special functions for elastomers. Investigations into new concepts to break through existing vulcanisation property balances.

Subclusters

- **Elastomer Blends and Composites**
  Studies of blends of saturated and unsaturated elastomers, phase behaviour of blends with functionalised elastomer systems.

- **New network chemistry**
  Investigation of new crosslink chemistry for low-temperature and high-speed network formation and modification.

fact

Industry partners

DSM, SKF, Océ Technologies

Research partners

Delft University of Technology, Eindhoven University of Technology, University of Twente (all in the Netherlands)

Budget/realised

Total costs € 0.6 million (budget € 0.9 million);
€ 72,000 spent on equipment.

Organisation

7 FTE, Scientific Chairman Prof. Jacques Noordermeer, Programme Area Coordinator Dr Jan Stamhuis

Networking

Four PC meetings, jointly with EP PC, two Cluster Review meetings, one jointly with EP (December). Projects reviewed also included relevant Corporate TA projects.

Publications

9 referenced publications, 2 theses.
Reported Inventions: 3

Output

Theses

E.H.D. Donkers
Block copolymers with polar and non-polar blocks. Combination of living anionic polymerization and RAFT-mediated polymerization

M. Jager
Effects of stiffness and polydispersity on the phase behaviour of block copolymers

A.J.M van Dijk
6-Aminocapronithile as an alternative monomer for the nylon-6 synthesis

R. Schaake
Beyond scratching the surface. Intrinsic tribological performance of polymers

C. Ozdilek
Colloidal liquid crystalline reinforced nanocomposites

M. Prusty
De-black boxing of reactive blending. An experimental and computational approach

M.S. Pimplapure
Morphology control in propylene polymerization

Scientific publicatios

M.M. Alvarez Grima, J.G. Eriksson, A.G. Talma, R.N. Datta, J.W.M. Noordermeer
A Synergistic Concept of Co-agents for Sorch Delay and Property Improvement in Peroxide vulcanization
proceedings Kautschuk Herbstkolloquim. Hannover

K. Naskar, J. W. M. Noordermeer
Influence of premade and in situ compatibilizers in polypropylene/ ethylene-propylene-diene terpolymer thermoplastic elastomeric olefins and thermoplastic vulkanisatie
Journal of Applied Polymer Science
100-5, 3877-3888

K. Naskar, J.W.M. Noordermeer
Influence of various peroxides in PP/EPDM thermoplastic vulcanizates at varied blend ratios
Journal of Elastomers and Plastics
38, 163

W.B. Wennekes, R.N. Datta, J.W.M. Noordermeer
Investigation on the adhesion between Resorcinol/ Formaldehyde/ Latex treated reinforcing cords and rubber
Proceedings Polymer Fibres Conference 2006. Manchester

W.B. Wennekes, R.N. Datta, J.W.M. Noordermeer
Investigation on the adhesion between treated reinforcing cords and rubber
Proceedings DKT-Meeting. Neurenberg, Duitsland.

M. Mikrut, J.W.M.Noordermeer, G. Verbeek
Low Surface Energy Rubber Materials: influence of network structure of silicone rubber on tack
Elastomery
10, 12-18

M. Mikrut, J.W.M.Noordermeer, G. Verbeek
Low Surface Energy Rubber Materials: influence of network structure of silicone rubber on tack
Proceedings International Rubber Conference 2006. Lyon

M.M. Alvarez Grima, A.G. Talma, R.N. Datta, J.W.M. Noordermeer
New concept of co-agents for scorch delay and property improvement in peroxide vulcanization
Rubber Chemistry and Technology
79, 694-711

B.J. Keestra, P.D. Anderson, H.E.H. Meijer
2K Injection molding of phase separating blends
International Polymer Processing
2, 168-174

O. van den Berg, W.F. Jager, D. Cangialosi, J. van Turnhout, P.J.T. Verheijen, M. Wubbenhorst, S.J. Picken
A Wavelength-Shifting Fluorescent Probe for Investigating Physical Aging
Macromolecules
39, 224-231

Dr. N.K. Singha
Atom Transfer Radical Polymerization of Styrene using a Pseudohalogen anion
J. Applied Polymer Science

X. Zheng, M.S. Pimplapure, G. Weickert, J. Loos
Cover Picture: Macromol. Rapid Commun.
Macromolecular Rapid Communications
1

D. Cangialosi, M. Wubbenhorst, J. Groenewold, E. Mendes, S.J. Picken
Diffusion Mechanism for Physical Aging of Polycarbonate far below the Glass Transition Temperature Studied by means of Dielectric Spectroscopy

Journal of non-crystalline solids
351, 2605-2610

W. Godlieb, N.G. Deen, J.A.M. Kuipers
Discrete particle simulations of high pressure fluidization
Conference Proceedings CHISA 17th International Congress Of Chemical And Process Engineering

R. Duchateau, W.J. van Meerendonk, L.Yajjou, B.B.P. Staal, C.E. Koning, G.J.M. Gruter
Ester-functionalized polycarbonates obtained by copolymerization of ester-substituted oxiranes and carbon dioxide: A MALDI-ToF-MS analysis study
Macromolecules
39, 7900-7908

W. Suwanwatana, H.E.N. Bersee, A. Beukers, D.P.N. Vlasveld, S.J. Picken
Fiber Impregnation of continuous fiber reinforced thermoplastics nanocomposites
Proceedings SAMPE Europe International Conference Paris
467-472

E. Vinken, A.E. Terry, S. Hoffmann, B/ Vanhaecht, C.E. Koning, S. Rastogi
Influence of Hydrogen Bonding on the Conformational Changes, the Brill Transition, and Lamellae Thickening in (Co)polyamides
Macromolecules
39, 2546-2552

C.S.J. Corstjens, S. Rastogi
Molecular Blending by Polymerization of Intercalated Solvent: -benzyl-L-glutamate)/ Benzylmethacrylate as a Model System
Biomacromolecules
7, 1542-1550

X. Zheng, J. Loos
Morphology Evolution in the Early Stages of Olefin Polymerization
Macromol. Symp.
236, 249-258

K. van Rijswijk, H.E.N. Bersee, W.F. Jager, S.J. Picken
Optimisation of anionic polyamide-6 for vacuum infusion of thermoplastic composites: choice of activator and initiator
Composites A, Applied Science and Manufacturing

M.A.G. Jansen, J.G.P. Goossens, G. de Wit, C. Bailly, C.E. Koning
Poly(butylene terephthalate) Copolymers Obtained via Solid-State Polymerization and Melt Polymerization; A study on the microstructure via 13C-NMR sequence distributiebon
Analytica Chimica Acta

I.Cotiuga, F. Picchioni, U.S. Agarwal, B.B.P. Staal, J.A.J.M. Vekemans, P.J. Lemstra
Precise Block-Copolymers by Efficient Coupling of End-Functionalized Polymers Using Phosgene
Macromolecular Rapid Communications
27, 242-246

E. Vinken, A.E., Terry, C.E. Koning, S. Rastogi
The Influence of Hydrogen Bonding on the conformational Changes, the Brill Transition, and Lamellae Thickening in (Co)polyamides
Macromolecules
39, 2546-2552

M.A.G. Jansen, J.G.P. Goossens, G. de Wit, C. Bailly, C.E. Koning
The microstructure of poly(butylene terephthalate) copolymers via 13C NMR sequence distribution analysis: solid-state copolymerization versus melt copolymerization
Analytica Chimica Acta
557, 19-30

N. Grossiord, J. Loos, O. Regev, C.E. Koning.
Toolbox for Dispersing Carbon Nanotubes into Polymers To Get Conductive Nanocomposites
Chem. Mater.
18, 1089-1099

I.M. Cotiuga, F. Picchioni, U.S. Agarwal, D. Wouters, J. Loos, P.J. Lemstra
Block-Copolymer-Assisted Solubilization of Carbon Nanotubes and Exfoliation Monitoring Through Viscosity
Macromolecular Rapid Communications
27, 1073-1078

S. Jain, J.G.P. Goossens, M. van Duin
Synthesis, Characterization and Properties of (Vinyl Triethoxy Silane-grafted PP)/Silica Nanocomposites
Macromolecular Symposia
233, 225-234

Filed patent applications

#416 N. Grossiord, J. Meuldijk, C.E. Koning, J. Loos
Carbon Nanotube reinforced polymer

#137 R.J. Gaymans, G.J.E. Biemond
Process for the preparation of segmented copolymers

#451 + #471 B.A.J. Noordover, R. Sablong, R. Duchateau, R.A.T.M. van Benthem, W. Ming, C.E. Koning
Process for the production of a polyester

#313 R.J. Gaymans, D. Husken, S. Rijerkerk
Block copolymer elastomers

Reported inventions

#537 R.M.A. L'Abee, J.G.P. Goossens, M. van Duin
Thermoplastic vulcanizates by reaction-induced phase separation

#313 R.J. Gaymans, D. Husken, S. Rijerkerk
Block copolymer elastomers

#582 S.D. Mookhoek, S. van der Zwaag, H.R. Fischer
Self-healing materials

#490 R.J. Gaymans, D. De
Polyurethane segmented block copolymers

Adaptable in more than one sense

The technology area Functional Polymer Systems of DPI has strong internationally recognized leaders from the academic world on board who certainly have an influence in the scientific world. The influence of DPI on the industry and the decisions taken there is less pronounced. Prof. Dietrich Haarer, scientific chairman, and Dr John van Haare, programme area coordinator, discuss the reasons.

“The major change in the industrial scene in Europe as far as functional polymers are concerned is of course the move from display-oriented applications to other fields like sensors and actuators that will be used in biological and healthcare applications,” says Prof. dr Dietrich Haarer. Philips Research is the prime example of that. Combinations of sensors in arrays made in technologies similar to display technologies will change the scene in healthcare. It is good timing that just now the DPI has to reconsider its research programme because of renewed funding.

Micro-pumps

To show that DPI has been able to keep up with or even ahead of these changes Dr John van Haare explains a new research project in this field. “We have been able to get a programme with sufficient critical mass going in a very short time. This project was granted in 2004, the researchers were recruited in 2005 and now we already see the first results. Polymer chemists, physicists and mechanical engineers of three different groups of the University of technology in Eindhoven worked together in this project. They realized flaps of polymer material, with dimensions of 400 × 100 × 10 microns, that can move in a reproducible way when a stimulus is applied. These stimuli can be of either a chemical, electric, magnetic or photonic nature.”

The principle has been demonstrated recently. The researchers achieved this by aligning liquid crystal molecules and incorporating magnetic particles in a polymer matrix. The flaps show a significant movement, sufficient for using them as micro-pumps in micro-fluidic applications such as lab-on-a-chip systems. The next challenge is the further miniaturization of the flaps to implement them in micro-channels. Fluids are transported in the micro-channels when two or more flaps move in the same direction, or mixed when flaps move out of phase. “The big advantage is that you can operate them from a position outside the channel, for example by applying a magnetic field, without influencing the fluid that has to be moved. In that way you have a nice connection to the macroscopic world,” Haarer adds. The micro-pumps can also be used in printers. A broad spectrum of companies is interested in this development. It shows that DPI can build up critical mass soon in a new field of research, once the industry changes its focus.

Pragmatic approach

“You can ask why DPI can be so successful in such a short time,” Haarer asks. He answers his own question immediately. “The reason is that researchers are working in these kinds of projects in industry, in Philips in this case, and have a part time position in a university. In Germany or other countries you will not find this construction. It is a unique, very helpful, pragmatic approach. I myself am an exception, I had three years of absence from a university to work in industry, but that was very unusual and it involved a lot of red tape to get that far. I think that because of this pragmatic approach you have all the big chemical companies of Europe sitting here at one table in DPI.”

fact

Mobility

In relatively new fields like polymeric sensors and actuators progress is spectacular, but it will take some time before products will become feasible. In longer existing fields such as photo-voltaics and organic leds progress is less spectacular, but equally important. Haarer: “The steps forward are more incremental. The insight in the mobility of charge carriers, the modelling and the subsequent improvement of the materials that have been achieved in DPI bring us closer to viable organic solar cells.” Companies such as Shell, Ciba and Degussa are interested in these developments, even though real products still linger at a horizon of ten to fifteen years. Renewable energy sources are and will remain an important research subject of DPI, certainly with the increased attention for sustainability in the research programme.

The impact of organic leds in the display field has been less than expected years ago, but the main reason for that is the enormous drop of prices in lcds. So these areas disappear from the DPI programme and new fields, such as healthcare and 'bio-inspired' materials come up. "But the nice thing is that the physics is similar," says physicist Haarer, "you can make arrays of biosensors with basically the same elements as used to make displays. The troops trained in displays can easily switch over to biosensors." Instead of generating light as a result of applying an electric current organic leds can also be used the other way around: light generates an electric signal. Combinations of such sensors that are selectively sensitive can be used in a lab-on-a-chip that have the potential to make visits to hospitals superfluous. Haarer expects the first products on the market in three or four year from now. "But that will be simple ones, to measure your blood sugar level or something similar."

Progress has also been less spectacular in organic RFID tags, certainly taking the hype of early 2000 into account. At that time the tags were said to be close to being printed and should be readily available soon after, but the efforts to miniaturize the designs and make printing possible still involve a tedious job. Most RFID tags on the market now are based on silicon.

Fuel cells and batteries

One field of functional polymers system that according to Haarer does not receive enough attention both from the European industry and from DPI are fuel cells and batteries. "In Europe we have no hybrid cars. The Japanese are ahead of us in this field, and of the United States for that matter." Companies hesitate to enter the market with materials for membranes for fuel cells for example and universities alone cannot bring about a major change in the materials. The existing membrane, Nafion® from Dupont, can only be used below 100ºC and it is a very expensive polymer. It is even more expensive because fluorinated polymers need special treatment. Investigating the possibilities for a replacement material for an active membrane without these drawbacks would be a useful addition to DPI's programme in Functional Polymer Systems, according to Haarer "Both companies and politicians lack awareness of the importance of the field. And in DPI we could investigate a number of possibilities on a small scale and choose the most promising after the initial phase. A company on its own cannot do that due to the long time scales required."

Apart from membranes and fuel cells there must, of course, also be infrastructure for the fuel distribution before alternatives for gasoline can become a success. But it is not only for the car industry that fuel cells are interesting. Philips has a minor activity in research into fuel cells for music systems, to power loud speakers. And since renewable energy is an important aspect of the DPI programme for the next eight years it should get more attention. Haarer concludes: "Because of diminishing resources for research and a lack of long term vision in this field in most European companies the DPI involvement is more needed than ever."

Van Haare:
"We have been able to get a programme with sufficient critical mass going in a very short time."

Haarer:
"… researchers from industry who have a part time position at a university … that is a very helpful pragmatic approach …"

Better models to improve all-polymer solar cells

Magda Mandoc studied physics in Romania and came to Groningen University (Netherlands) on a Socrates scholarship, an exchange programme for students in Europe. After her project ended, her supervisor asked her whether she would like to continue her research work as a PhD student in the group, which she did. Although it took some adjusting – she had not been so far removed from her family before – Mandoc likes to be in the Netherlands. "After my PhD I would like to go on working in research. I would like to work here, rather than in Romania, because here I have more opportunities. And to be able to make the comparison with academic research, I am curious to see how research is done in industry. Of course, I already have many contacts with researchers in industry via DPI, but it is not like being there, working there yourself. It doesn't have to be in the field of solar cells, I want to learn more, so another device would be fine as well."

Mandoc has been trying to understand and model electron transport in all-polymer solar cells. Her DPI project is finished now and she is busy writing the articles that will make up her thesis, which she will defend later this year. She is part of the group of Professor Paul Blom at the Zernike Institute for Advanced Materials of Groningen University, where world-class polymer electronic devices and simulation tools are being developed.

Mandoc:
"The challenge was to find out how the electron transport takes place."

Magda Mandoc, University of Groningen

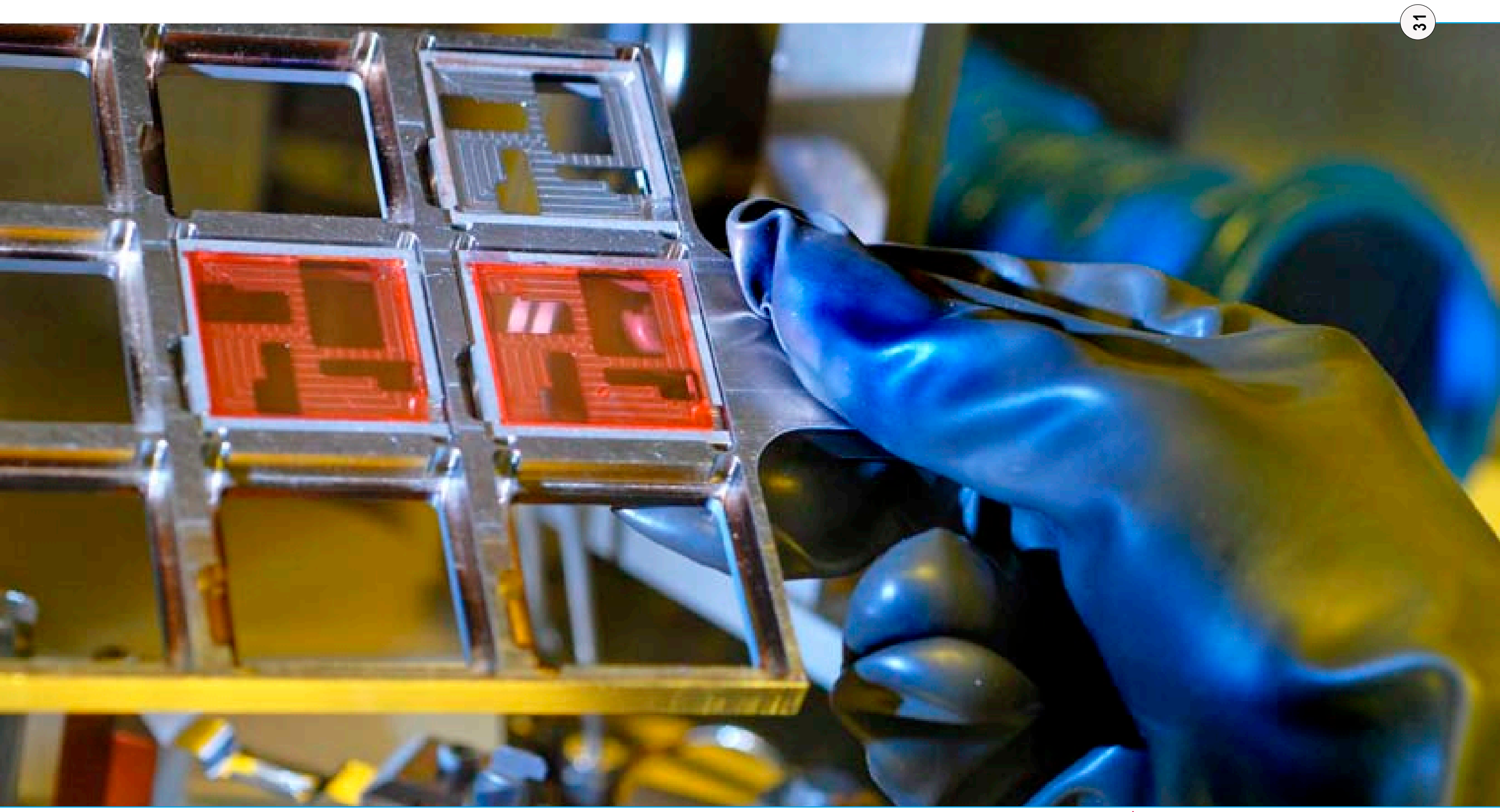
Efficiency

Mandoc explains: “I investigated solar cells made of only polymers; one polymer is the electron donor and another polymer acts as electron acceptor. The efficiencies of such solar cells are not so good. Polymer-polymer solar cells are studied because, contrary to solar cells with for instance fullerene as acceptor material, the acceptor polymer too absorbs light. The maximum charge generation rate is therefore higher than in polymer-fullerene cells. Our latest results concern all-polymer solar cells with an efficiency of 1.5%.” This is not so good compared to the polymer-fullerene solar cells that use this same donor polymer and have an efficiency of 2.5%. There are polymer-fullerene solar cells with an efficiency of almost 5%, but they consist of a different polymer. In the DPI project TNO produces the material, ECN optimizes the solar cells and the group in Groningen studies the device physics.

Mandoc: “At the start of the project these kinds of solar cells were very inefficient. The efficiency was only 0.25% for a standard device and 0.75% for an optimised cell, and we wanted to find out why. The challenge was to find out how the electron transport takes place. We started with the donor polymer. We knew the hole transport process, so when we measured the electron transport we compared the two and made a new model. Next we studied the electron transport in the acceptor polymer and then included it in the solar cell device model. We were quite successful. Our results explain why all-polymer solar cells behave as they do: the electron transport is trap-limited. The energy location of the trap sites with respect to the transport sites determines whether these hamper the electron transport (trap-limited transport) or even participate in it (trap-controlled transport). Compared to hole transport, electron transport is less temperature dependent, something the theory did not explain at the time. But our findings help to understand this. In all-polymer solar cells, due to the fact that small domains exist in the morphology, the splitting of the electron-hole pairs is not so good. The morphology in the solar cells thus plays an important role and by improving it, the efficiency can be increased.”

What Mandoc likes about working in DPI is the collaboration with other people from different origins. “Working with chemists and physicists from academia or from industry gives you insight into the different approaches that are possible, and this raises the chances of success for a project.”

sheet



Facts and figures

The Functional Polymer Systems (FPS) technology area 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. In terms of the latter, the FPS research programme is structured along application lines in the following subprogrammes: polymer lighting and field effect transistors, conductive blends, polymers for information and communication technology, solar cells (photovoltaics), fuel cells and batteries, responsive materials, sensors and actuators.

Subprogrammes

• Polymer lighting and field-effect transistors

The aim of this subprogramme is to gain a thorough fundamental understanding of materials behaviour under operational device conditions. Based on this fundamental knowledge, breakthroughs in device performance are anticipated. The research focuses on improvements in device and materials performance, charge transport, mobility, interfaces, ambipolar FETs, and theoretical device modelling.

• Conductive blends

This subprogramme is focused on conductive filler/polymer matrix composites. The aim is to use very low filler amounts (< vol. 2%) without affecting the processing conditions and other functional properties of the antistatic film. The research focuses on gaining a fundamental understanding of filler network formation to influence percolation threshold and on parameters determining the maximum conductivity level.

• Polymers for information and communication technology

The objective of this subprogramme is the structuring of polymers on the nano and micro scale via ‘top-down’ approaches combined with ‘bottom-up’ techniques based on e.g. self-assembly. In this way new or strongly enhanced properties for optical, electrical and biomedical applications should be generated.

• Photovoltaics

The aim of this subprogramme is to explore new materials and develop a fundamental under standing of all (photo)physical processes occurring in next-generation photovoltaic (PV) technology, namely polymer photovoltaics. Polymer photovoltaics holds a strong potential for large-area cost-effective photovoltaics for sustainable energy production. The research focuses on low band-gap materials and on gaining a thorough fundamental understanding of materials behaviour under operational device conditions.

• Fuel cells and batteries

The aim of this subprogramme is to develop new proton conducting solid electrolyte materials with high temperature operational stability and conductivity in prototype fuel cells. Principles of self-organisation and/or alignment via liquid crystallinity are used to improve mechanical stability and achieve two-dimensional conduction of protons.

• Responsive materials, sensors and actuators

The aim of this subprogramme is to develop new materials and processes that result in a response and/or large displacements upon an external electrical, magnetic, optical and/or chemical trigger. Proof of principle should be demonstrated in prototype devices.

Industry partners

Avery Dennison, Bayer MaterialScience, Ciba Specialty Chemicals, Degussa, DSM, ECN, Merck, Océ Technologies, Philips, Shell and TNO.

Academia and research institutes

The research was carried out in eight institutions: The Universities of Wageningen, Groningen, Delft and Eindhoven (Netherlands), The University of Cologne (Germany), ECN, TNO and the Max Planck Institut für Polymerforschung in Mainz (Germany).

Budget and Organisation

The total costs in 2006 amounted to EUR 3.0 million (budget EUR 2.9 million). The total number of FTEs allocated at the end of 2006 was 30. The 48 researchers involved comprised 26 PhD students, 8 post-doctorate graduates, 7 TNO and ECN senior researchers, 2 research fellows, 2 technical staff members and 3 senior lecturers. Total expenditure on equipment, expensive consumables and special analysis time was EUR 81.000. In 2006 Scientific Chairman (SC) Prof. Dietrich Haarer was actively engaged in scientific development alongside the Programme Area Coordinator (PAC) Dr. John van Haare.

Networking

• The FPS programme committee, consisting of the Programme Area Coordinator (PAC), the industrial partner representatives and four academic subprogramme experts, met three times in 2006 to discuss research programme issues, scientific reporting and inventions/Intellectual Property issues.

• A two day mini-symposium was organised to review all running FPS projects and stimulate cross-fertilization between subprogrammes. The symposium was highly appreciated by the industrial and academic participants.

• Subprogramme thematic meetings, involving industrial experts and DPI researchers, were organised on polymer lighting-FETs-photovoltaics (two), conductive blends (one), polymers for information and communication technology (one), fuel cells and batteries (one), responsive materials, sensors and actuators (one). Extensive thematic half-year progress reports were written and are available on the intranet for the benefit of the industrial partners.

• FPS researchers frequently disseminated research results by attending scientific conferences, submitting papers to academic journals and writing reports on inventions.

Highlights

• Using the Maragoni effect explored in FPS, researchers demonstrated the rotation of microscale objects by nanomotors. This marvellous result was published in Nature.

• Although the Responsive Materials, Sensors and Actuators subprogramme is still in its infancy, admirable research results and developments were achieved in 2006, demonstrating the excellent flexibility of a virtual organisation like DPI.

Publications

In addition to a significant number of contributions to scientific symposia in the form of posters and presentations, the publication of 44 refereed papers as well as two theses reflects the considerable contribution of this TA to international science in this area.

Output

Theses

V.N. Marin
Novel functional materials based on ruthenium(II) and iridium(III) polypyridyl complexes.

B.K.C. Kjellander
Stratified functional films by photo-polymerization-induced mesoscopic phase separation

Scientific publications

R. Eelkema, M.M. Pollard, J. Vicario, N. Katsonis, B. Serrano Ramon, C.W.M. Bastiaansen, D.J. Broer, B.L. Feringa
Nanomotor rotates microscale objects.
Nature
440 (9), 163

T. Offermans, S.C.J. Meskers and R.A.J. Janssen
Photoinduced absorption spectroscopy on MDMO-PPV: PCBM solar cells under operation
Organic Electronics

Z. Chen, J.C.M. Brokken-Zijp, H.P. Huinink, J. Loos, G. de With, M.A.J. Michels
Cross-Linked Epoxy Composites Filled with Intrinsically Conductive Phthalocyanine Nanocrystals. Influence of Filler Amount, Layer Thickness, and Cross-Linkers Used on the Percolation Threshold and Conductivity Level of the Composites
Macromolecules
39, 6115-6124

Z. Chen, J.C.M. Brokken-Zijp, M.A.J. Michels
Novel phthalocyanine crystals as a conductive filler in crosslinked epoxy materials: Fractal particle networks and low percolation thresholds
J. Polymer Science B, Polym. Phys.
44, 33-47

L. J. Huijbregts, H. B. Brom, J.C.M. Brokken-Zijp, M.A.J. Michels, M. de Goeje, M. Yuan
The intrinsic conductivity of nano-sized semiconducting crystals
Physica Status Solidi
3, 259-262

L.J. Huijbregts, H.B. Brom, J.C.M. Brokken-Zijp, M. Kemerink, Z. Chen, M.P. de Goeje, M. Yuan, M.A.J. Michels
The Optimal Structure-Conductivity Relation in Epoxy-Phthalocyanine Nanocomposites
J. Phys. Chem. B.
110, 23115-23122

H.A. Every, E. Mendes, S.J. Picken
Ordered Structures in Proton Conducting Membranes from Supramolecular Liquid Crystal Polymers
Journal of physical chemistry B
110, 23729-23735

H.A. Every, G.J.M. Janssen, E. Mendes, S.J. Picken
Performance Analysis of Sulfonated PPTA Polymers as Potential Fuel Cell Membranes
Journal of power sources
162, 380-387

T.D. Anthopoulos, S. Setayesh, E. Smits, M. Cölle, E. Cantatore, P.W.M Blom, D.M. de Leeuw
Air-stable complementary-like electronics based on solution processed ambipolar organic transistors
Adv. Mat.
18, 1900

E.C.P. Smits, T.D. Anthopoulos, S. Setayesh, E. van Veenendaal, R. Coehoorn, P.W.M. Blom, B. de Boer, D.M. de Leeuw
Ambipolar charge transport in organic field-effect transistors
Phys. Rev. B
73, 205316

T. van Woudenbergh , J. Wildeman, P. W.M.Blom
Bias-dependent current efficiency in polymer light-emitting diodes
Semicond. Sci. and Technol.
21, 387

K.D. Meisel, W.F. Pasveer, J. Cottaar, C. Tanase, R. Coehoorn, P.A. Bobbert, P.W.M. Blom, D.M. de Leeuw, M.A.J. Michels
Charge-carrier mobilities in disordered semiconducting polymers: effects of carrier density and electric field
Physica Status Solidi (c)
3, 267-270

C.Tanase, P.W.M. Blom, D.M. de Leeuw, M. Mulder
Enhanced hole transport in poly(p-phenylene vinylene) planar metal-polymer-metal devices
J. Appl. Phys.
99, 103702

W.F. Pasveer, M.A.J. Michels
Understanding Mott's law from scaling of variable-range-hopping currents and intrinsic current fluctuations
Physical Review B
74, 195129

W.F. Pasveer, P.A. Bobbert, M.A.J. Michels
Universality of ac conductivity: random-site-energy model with Fermi statistics
Physical Review B
74, 165209

K.D. Harris, C.W. M. Bastiaansen, D.J. Broer
A Glassy Bending-Mode Polymeric Actuator Which Deforms in Response to Solvent Polarity
Macromolecular Rapid Communications
27, 1323-1329

C. Sanchez, B.J. de Gans, D.A. Kozodaev, A. Alexeev, M.J. Escuti, C. van Heesch, D.L. Beke, U.S. Schubert, C.W.M. Bastiaansen, D.J. Broer
Polymerization-induced Diffusion as a Tool to Generate Periodic Relief Structures: A Combinatorial Study
Proc. SPIE - Int. Soc. Opt. Eng.
6136, 61360H/1-61360H/12

J.A. Koster, V.D. Mihailetchi, P.W.M. Blom
Bimolecular recombination in polymer/fullerene bulk heterojunction solar cells
Appl. Phys. Lett.
88, 05210

V. D. Mihailetchi, H. X. Xie, B. de Boer, L. J. A. Koster, P. W. M. Blom
Charge Transport and Photocurrent Generation in Poly(3-hexylthiophene): Methanofullerene Bulk-Heterojunction Solar Cells
Advanced Functional Materials
16, 699-708

M.M. Koetse, J. Sweelssen, K.T. Hoekerd, H.F.M. Schoo, S.C. Veenstra, J.M. Kroon, X. Yang, J. Loos
Efficient polymer:polymer bulk heterojunction solar cells
Applied Physics Letters
88, 083504

M.M. Mandoc, B. de Boer, P.W.M. Blom
Electron-only diodes of poly (dialkoxy-p-phenylene vinylene) using hole-blocking bottom elektrodes
Phys. Rev. B
73, 155205

T. Offermans, S.C.J. Meskers, R.A.J. Janssen
Electro-optical studies on MDMO-PPV : PCBM bulk-heterojunction solar cells on the millisecond time scale: Trapped carriers
Organic Electronics
7, 213-221

J. Cremer, P. Bauerle, M.M. Wienk, R.A.J. Janssen
High Open-Circuit Voltage Poly(ethynylene bithienylene):Fullerene Solar Cells
Chem. Mater.
18, 5832-5834

W.J.E. Beek, M.M. Wienk, and R.A.J. Janssen
Hybrid solar cells from regioregular polythiophene and ZnO nanoparticles
Adv. Funct. Mater.
16, 1112-1116

M.M. Wienk, M.G.R. Turbiez, M.P. Struijk, M. Fonrodona, and R.A.J. Janssen
Low band gap poly(di-2-thienylthienopyrazine):fullerene solar cells
Appl. Phys. Lett.
88, 153511/1-3

M.M. Wienk, M.P. Struijk, R.A..J. Janssen
Low band gap polymer bulk heterojunction solar cells
Chem. Phys. Lett.
422, 488–491

A. Alexeev, J. Loos, M.M. Koetse
Nanoscale electrical characterization of semiconducting polymer blends by conductive atomic force microscopy
Ultramicroscopy
106-3,191-9

A. Hadipour, B. de Boer, J. Wildeman, F. Kooistra, J.C. Hummelen, M.G.R. Turbiez, M.M. Wienk, R.A.J. Janssen, and P.W.M. Blom
Organic multi-junction solar cells processed from solution with sensitivity from ultraviolet to the near infrared
SPIE-Int. Soc. Opt. Eng. (Organic Optoelectronics and Photonics II)
6192

V.D. Mihailetchi, H. Xie, B. de Boer, L.J.A. Koster, L.M. Popescu, J.C. Hummelen, P.W.M. Blom
Origin of the enhanced performance in poly(3-hexylthiophene):[6,6]-phenyl C61-butyric acid methyl ester solar cells upon slow drying of the active layer
Appl. Phys. Lett.
89, 012107

P.A.C. Quist, W.J.E. Beek, M.M. Wienk, R.A.J. Janssen, T.J. Savenije, and L.D.A. Siebbeles
Photogeneration and decay of charge carriers in hybrid bulk heterojunctions of ZnO nanoparticles and conjugated polymers
J. Phys. Chem. B.
110, 10315-10321

D. Veldman, J.A M. Bastiaansen, B.M.W. Langeveld-Voss, J. Sweelssen, M.M. Koetse, S.C.J. Meskers, and R.A.J. Janssen
Photoinduced charge and energy transfer in dye-doped conjugated polymers
Thin Solid Films
511-512, 581-586

P.A.C. Quist, T. Martens, J.V. Manca, T.J. Savenije, L.D.A. Siebbeles
Photo-induced charge separation and electron diffusion in MDMO-PPV: PCBM bulk heterojunction.
Solar Energy Materials & Solar Cells
90, 362

J.L. Li, J.S. Wu, A. C. Grimsdale, K. Müllen
Poly(2,7-carbazole) and Perylene Dicarboxydiimide: A Promising Donor/Acceptor Pair for Polymer Solar Cells
Journal of Materials Chemistry
16, 96-100

H. Zhong, X. Yang, B. de With, J. Loos
Quantitative Insight into Morphology Evolution of Thin PPV/PCBM Composite Films upon Thermal Treatment
Macromolecules
39, 218-223

A. Hadipour, B. de Boer, J. Wildeman, F. B. Kooistra, J. C. Hummelen, M. G. R. Turbiez, M. M. Wienk, R. A. J. Janssen, P. W. M. Blom
Solution-Processed Organic Tandem Solar Cells
Advanced Functional Materials
16 (14), 1897-1903

T.J. Savenije, J.E. Kroeze, X. Yang, J. Loos
The formation of crystalline P3HT fibrils upon annealing of a PCBM: P3HT bulk heterojunction
Thin Solid Films
511-512, 2-6

M. Lenes, L.J.A. Koster, V.D. Mihailetchi, P.W.M. Blom
Thickness dependence of the efficiency of polymer:fullerene bulk heterojunction solar cells
Appl. Phys. Lett.
88, 243502

T. Offermans, S.C.J. Meskers, R.A.J. Janssen
Time delayed collection field experiments on polymer: Fullerene bulk-heterojunction solar cells
J. of Applied Physics
100, 074509 1-7

D. Veldman, T. Offermans, J. Sweelssen, M.M. Koetse, S.C.J. Meskers and R. A.J. Janssen
Triplet formation from the charge-separated state in blends of MDMO-PPV with cyano-containing acceptor polymers
Thin Solid Films
511-512, 333-337

L.J.A. Koster, V.D. Mihailetchi, P.W.M. Blom
Ultimate efficiency of polymer/fullerene bulk heterojunction solar cells
Appl. Phys. Lett.
88, 093511

F. Verbakel, S.C.J. Meskers, R.A.J. Janssen
Electronic Memory Effects in a Sexithiophene-Poly(ethylene oxide) Block Copolymer Doped with NaCl. Combined Diode and Resistive Switching Behavior
Chem. Mater.
18, 2707-2712

F. Verbakel, S.C.J. Meskers, R.A.J. Janssen
Electronic memory effects in diodes from a zinc oxide nanoparticle-polystyrene hybrid materiaal
Applied Physics Letters
89, 10210

P.A.C. Quist, T. Martens, J.V. Manca, T.J. Savenije, L.D.A. Siebbeles
Photo-induced charge separation and electron diffusion in MDMO-PPV: PCBM bulk heterojunction.

Solar Energy Materials & Solar Cells
90, 362

P.A.C. Quist, T. Martens, J.V. Manca, T.J. Savenije, L.D.A. Siebbeles
Solution-Processed Organic Tandem Solar Cells
Advanced Functional Materials
16 (14), 1897-1903

Filed patent applications
#530 + #546 K. Hermans, J. Perelaer, C.W.M. Bastiaansen, D.J. Broer
Process for preparing a polymeric relief structure

Reported inventions
#532 F. Fahrni, L.J. Van IJzendoorn, J.M.J. den Toonder, M.W.J. Prins
Microfluidic system based on actuator elements

#530 K. Meerholz, M. De la Rosa
Outcoupling efficiency improvement in OLEDs

#427 B. Serrano-Ramon, C.W.M. Bastiaansen, D.J. Broer
Liquid crystal micro- and nanostructures

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

Environment-friendly, durable coatings with new functions

Whereas in the past the research programme of the Coatings Technology Area was very diverse, it is now firmly based on three pillars: sustainable coatings, functional coatings, and durability and testing of coatings. The projects aim at understanding the phenomena of coatings rather than solving problems of specific coatings. The aim is to generate knowledge that creates the foundation for future systems and technologies.

"Over the last century coatings technology has for a large part been developed by trial and error. Like the paper and rubber industry, the coatings industry is a very specialised and practice-oriented industry with many traditional approaches that are not always based on scientific knowledge. Our projects therefore do not always have to come up with new inventions, it is also important to understand why some coatings perform well and others don't. From that knowledge we can deduce how to improve existing coatings and design new ones." Professor Claus Eisenbach, scientific chairman of the technology area since 2005, aims at creating a platform from which academic knowledge is transferred to the companies to solve problems in the real world and to stimulate novel developments.

Coatings technology is a multidisciplinary field. Progress in the long run will only be made on a scientifically established basis, often generated by studying well designed 'model' systems, and not by short-term successes that may result from a practical approach such as straightforward formulation of materials. The ongoing dialogue between members from industry and academic members reveals relevant questions to be answered. Professor Eisenbach greatly appreciates the constructive cooperation of the industrial members in DPI in this respect.

Sustainable coatings

Dr John van Haare, programme coordinator of the TA, mentions that in accordance with DPI's overall business plan sustainable coatings are an important research subject. "First and foremost we want to reduce the volatile organic compound (VOC) emissions by developing new coatings with at least the same,

but preferably better properties than solvent-based coatings. Powder coatings and waterborne coatings are likely candidates.”

Van Haare: “In a project we showed the feasibility of using encapsulated liquid cross-linkers in powder coatings. It is the purpose of the powder coatings programme to lower the curing temperature, making it possible to apply powder coatings to other substrates such as wood, plastic, and MDF. However, the flow and levelling before curing should not be affected. Moreover, by exploring this concept, the storage stability should not be harmed by preventing flow of powder coatings below 40°C. Powder coatings should display many desired properties within a rather limited temperature regime (40°C – 100°C). The coatings industry is very interested in the patent that resulted from this work. It is a typical example of a project that gives us more insight into the process, even though the exact combination of materials is not directly usable in applications. Coating manufacturers use this knowledge to develop their own coatings.”

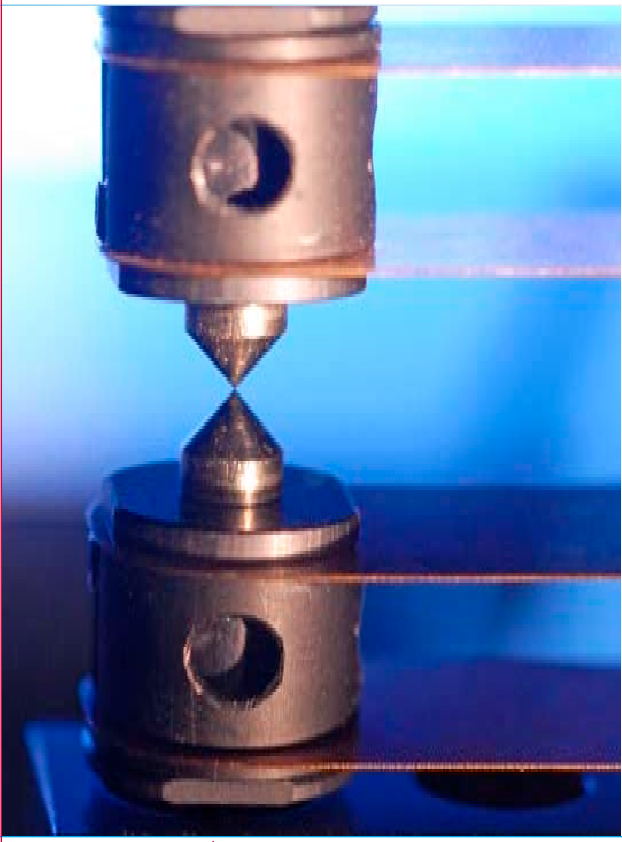
For the other candidate, waterborne coatings, a project was started in 2006 to investigate how drying, film formation, and finally curing of waterborne latex takes place from the surface to deep in the layer.

Sustainable coatings are preferably made from renewable resources. Coatings based on completely renewable resources with the same properties as existing coatings are not easy to realise, but the first results with polymers from renewable resources that are still modified with the aid of existing chemistry look promising, according to Van Haare. Eisenbach adds: “We can deduce from our knowledge of existing systems which bio-based coatings might work and which won’t. And deficiencies, if any, of these bio-based coatings can perhaps be counterbalanced by novel and unusual properties.”

Functional coatings

Modern coatings often offer more than just protection to the substrate they cover. They may consist of a number of layers, each having its own function. Apart from protection against corrosion, the ‘normal’ function of a coating, self-cleaning or self-healing can be thought of, as well as the roughness of the surface or its colour, which might even change upon an external stimulus. DPI is not only exploring such smart coatings but also investigating the possibility of combining layers with such functions in order to reduce the number of coating steps. ”Ideally, only one coating layer that ‘self-organises’ during the curing step and ‘self-structures’ to realise the various functions would be enough,” Eisenbach summarises.

fact



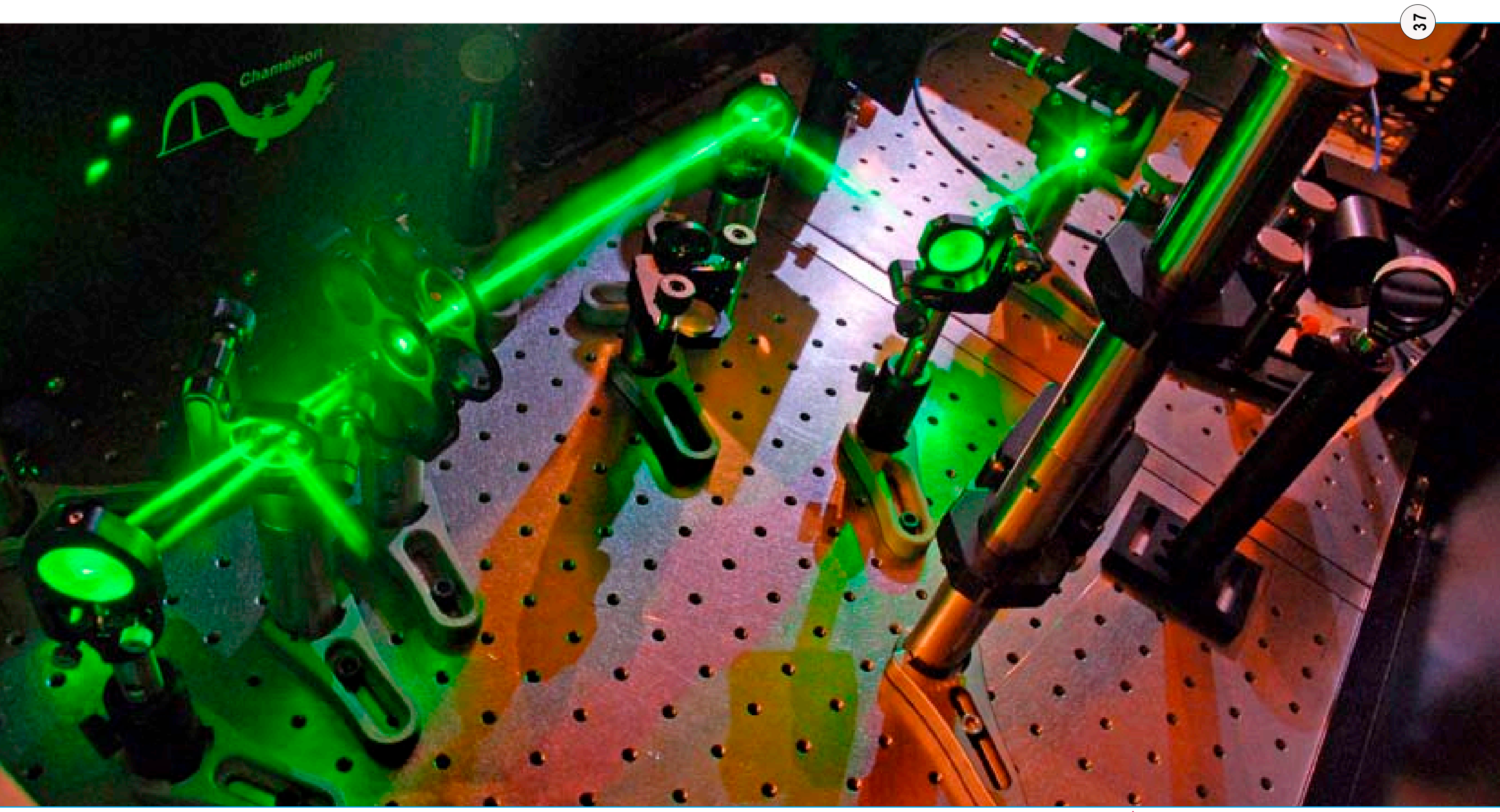
Van Haare mentions an example of such a project: “A coating can be made hydrophobic so that when it rains dirt is removed. This effect can be achieved by adding a top layer only 20 nanometres in thickness. However, if this top layer is damaged the effect disappears. By homogeneously distributing hydrophobic tails in the protective coating instead of adding a top layer, the same effect is achieved. These molecules position themselves with their functional tails towards the coating-air interface. They also do this when striving for a new equilibrium state when the coating is damaged. For that reason it is called a self-replenishing coating.” Combining two functions is also found in projects with modified pigments that co-function as reinforcement particles.

Durability

The third pillar in the programme is durability, extending the lifetime and performance level of existing coatings, and the appropriate testing of coatings. In industry, so-called Florida-Numbers and the outcomes of empirically established scratch tests or salt spray tests indicate whether or not a coating meets the requirements. (Florida Numbers are the number of hours a coating lasts when exposed to the sun and other weather influences in Florida.) However, none of these tests offers insight into the polymer-physical processes taking place under test conditions, or the relationship between chemical and/or physical materials characteristics of the coating and the test results. DPI projects aim at understanding, for instance, why coatings degrade, what the accompanying changes in the molecular structure and the network topology are, and how degradation can be prevented.

Eisenbach: “The tests used so far are too impractical and too numerous. Every end-user has his own set of tests that he requires the coating manufacturer to conduct before the product will be approved for application. The tests often are not comparable, not always reproducible, and have little scientific basis if any at all. Our idea is to reduce the number of tests to two or three with a scientific basis. The results of practically as well as scientifically meaningful tests will allow a focused improvement of existing and a development of novel materials”. A newly developed scratch test with precisely controlled scratch forces and scratch speeds in combination with perfectly pure and well-characterised coating networks will show the relationship between the test data and the morphology and structure of the coating system.

Coating manufacturers are beginning to see the usefulness of uniformity in tests and of an established scientific basis. The coatings companies are aware of the need for pre-competitive research and appreciate DPI’s contributions to advancing coatings technology. This is also becoming evident in review meetings, in which representatives of companies participate frequently and actively. The number of members in the DPI coatings community has remained stable: TNO withdrew as an industrial member in 2006, due to the downsizing of its coatings activities in favour of activities in the Holst Centre, (see LATFE report), but Bayer Material Science joined as a new partner.



Green technology to apply green coatings

Bart Noordover feels like a fish in the water in his research project on new coatings based on renewable monomers. After he received his masters degree at the University of Twente he moved to the Eindhoven University of Technology almost four years ago. That is the place to be if you want to work at the interface between polymer chemistry and coatings, is his opinion. "I like polymers, because it is a very broad field of research. You start with the building blocks, the monomers, and end up with a material with properties that you can measure and optimize for a certain application." One of the things he likes about his work is to apply the knowledge he has acquired in a product. And being part of DPI is an extra advantage to him because of the many contacts with industrial partners. When his project is finished, some time next year, Noordover wants to continue working with polymers, but he prefers the industry above research work at a university.

fact

Bert Noordover, Eindhoven University of Technology

Cross-linking

In his project he investigates if and how polymers made of monomers from renewable resources like maize can be used as powder coatings with at least the same quality as powder coatings made starting from petroleum. One of the partners in this project is Agrotechnology and Food Innovations of Wageningen University, which makes the monomers, for example isosorbide. Noordover polymerizes the monomers into polyesters and grinds these into powders. A 'green' application technique without solvents is the method used to apply the coatings. The powder, which is a mixture of the polyester resin, a cross-linking agent and other additives, is distributed over a panel, to which it adheres electrostatically. In an oven with a temperature of about 180ºC the polyester melts, reacts with the cross-linker and forms a polymeric network with an extremely high molecular weight. This is a smooth homogeneous layer that adheres well to the panel. Noordover: "People often think that, because our raw materials are natural monomers, the coating will change colour very quickly, but you can stabilize the system. It is not easy, because you have to deal with a complicated formulation. Apart from the monomers you have cross-linking agents and all kinds of additives to influence the flow properties or to remove air bubbles."

Functional end-groups

Polymers for powder coating must have special properties. On the one hand the powder should not react and lump when kept at normal room temperatures, up to 40ºC or 50ºC. This means that the glass transition temperature must be higher than 40ºC or 50ºC. On the other hand, the polymers must crosslink fast when heated to 180ºC in the presence of the cross-linker, but not before that. Noordover: "We have found a way to make polymers with the desired functions by giving them the right end groups for cross-linking. We can also use a kind of blocking agent that prevents reactions between the cross-linker and these end groups taking place at lower temperatures. When the polymer is heated to temperatures above 160ºC the blocking agent is removed. In curing experiments that we can do here at the university and for which we still use solvents, it appeared that the resulting coatings are durable and have good mechanical properties." To test if this is also true for coatings applied as powder paints, Noordover has to ask the industrial partners in the DPI project for help. They have the powder application equipment and the expertise to formulate, apply and test these systems. Recently, the coatings were found to have the same favourable properties when applied as an actual powder coating.

Noordover: "It is very useful to have such direct contacts with our industrial partners. Not only because they have the equipment and the expertise in using it, but also because they have a different way of looking at the developments going on at the universities. What we are doing, making coatings from renewable polymer sources, should be economically feasible. Not immediately, of course, but in the long term, say ten years from now. I notice that, when I have been working for a long time at a stretch at the university, I tend to lose that frame of reference."

Noordover:
"You start with monomers and you end up with materials with properties optimized for a specific application "

Facts and figures

The Coatings Technology research area performs frontier research in the general field of organic coatings. The aim is to gain fundamental understandings that lead to innovative coating technologies. The research is pre-competitive and is aimed at achieving sustainability, quality-of-life improvements and economic growth (DPI business plan 2008-2015), thus preparing the coatings industry for the challenges of the future.

Subprogrammes

- **Renewable raw materials, formulation and powder coatings**
  The objectives are threefold:
  - Establish the feasibility of the use of sustainable, renewable resources for the development of alternative monomers and co-monomers for the production of toner and powder coating resins, without compromising the final product properties
  - Gain a fundamental understanding of the colloidal stability of waterborne coatings with regard to shelf-life as well as applications
  - Extend the application field (wood, MDF, plastics) of powder coatings by developing innovative solutions that meet the stringent demands to the cure window with respect to both rheology (levelling) and reactivity (cure) at moderate temperature

- **Functional coatings**
  The objective is to develop new coatings with additional functional properties at the surface as well as in the bulk, besides the protection of underlying layers and decorating effects, which are normally associated with coatings. Preferably, these additional functional properties should be demonstrated using fewer sequential coating layers - ideally, they should be realized in a single coating step. Therefore structure-property relationships are extensively studied in the research field.

- **Durability and testing of industrial coatings**
  The aim is to create a fundamental understanding of the degradation mechanisms of coatings used in outdoor exposure to enhance durability. Furthermore, the programme aims to develop new testing methods for coatings, e.g. methods for testing adhesion, gloss or scratch resistance, which correlate to meaningful physical parameters.

fact

Foto onderschrift

Industry partners

AKZO Nobel, Bayer MaterialScience, Degussa, Dow, DSM, Océ Technologies, Shell and TNO.

Academia and research institutes

The Universities of Amsterdam, Wageningen and Eindhoven (Netherlands), the University of Stellenbosch (South Africa), TNO, Agro Technology and Food Innovations, and the Forschunginstitut für Pigmente und Lacke, Stuttgart (Germany).

Budget and Organisation

The total costs in 2006 amounted to EUR 1.8 million (budget EUR 2.1 million). The total number of FTEs allocated at the end of 2006 was 21. The 28 researchers involved comprised 19 PhD students, 5 post-doctorate graduates and 4 TNO researchers. The total amount spent on equipment, expensive consumables and special analysis time was EUR 56,000. In 2006 Scientific Chairman (SC) Prof. Claus Eisenbach was actively engaged in scientific development alongside the Programme Area Coordinator (PAC), Dr. John van Haare.

Networking

• The CT programme committee, consisting of the Programme Area Coordinator (PAC), the Scientific Chairman (SC) and the industrial partner representatives, met four times in 2006 to discuss research programme issues, scientific reporting and inventions/Intellectual Property issues.

• A general "DPI Coatings Day" was organized at DSM Resins Zwolle where all researchers presented their latest research results and project members and industrial partners had discussions about the programme and future plans. The DPI Coatings Day is highly appreciated by the industrial and academic participants.

• Subprogramme thematic meetings involving industrial experts and DPI researchers were organised and presentations were made available on the intranet for the benefit of the industrial and academic partners.

• The thematic half-year reports, providing management information as well as giving the research groups the opportunity to elaborate on their latest research results, were highly appreciated by the industrial partners.

• Three project kick-off meetings were organised for newly granted projects to discuss the project proposal in detail and achieve mutual agreement between industrial and academic partners on the research plan for the first 12 months.

Clear deliverables and milestones were defined to enable evaluations to be carried out at future project progress meetings.

• For individual projects, bilateral meetings were organised with the relevant industrial partners when necessary and on an informal basis.

• CT researchers frequently disseminated research results by attending scientific conferences and submitting papers to academic journals.

Highlights

• Sixteen scientific proposals were submitted in response to the Call for CT Proposals. Three applicants were granted the opportunity to have an excellent and scientifically sound project carried out on their proposal. The applicants managed to find capable candidates, who started executing the project research plan in 2006.

Publications

In addition to a significant number of contributions to scientific symposia in the form of posters and presentations, the publication of seven refereed papers as well as one thesis reflects that the TA can considerably improve its contribution to the international science in this area.

Output

Theses

D.-J. Voorn
Polymer/platelet nanocomposites particles. Encapsulation of platelets by physical and chemical approaches.

Scientific publicatios

D.J. Voorn, W. Ming, A.M. van Herk
Clay platelets encapsulated inside latex partikels
Macromolecules
39, 4654-4656

B.A.J. Noordover, V.G. van Staalduinen, R. Duchateau, C.E. Koning, R.A.T.M. van Benthem, M. Mak, A. Heise, A.E. Frissen, J. van Haveren
Co- and Terpolyesters Based on Isosorbide and Succinic Acid for Coating Applications: Synthesis and Characterization
Biomacromolecules
7, 3406-3416

D.J. Voorn, W. Ming, A.M. van Herk
Controlled heterocoagulation of gibbsite platelets and latex spheres
Polym. Mater. Sci. Eng. Proceedings
95, 61-62

D.J. Voorn, W. Ming, A.M. van Herk
Encapsulation of platelets by physical and chemical approaches
Macromol. Symp.
245-246, 584-590

V.V. Khatavkar, P.D. Anderson, H.E.H. Meijer
On scaling of diffuse–interface models
Chem. Eng. Sci.
61, 2364-2378

D.J. Voorn, W. Ming, A.M. van Herk
Polymer-clay nanocomposite latex particles by inverse pickering emulsion polymerization stabilized with hydrofobic montmorillonite platelets.
Macromolecules
39, 2137-2143

B. de Ruiter, A. El-Ghayoury, H. Hofmeier, U.S. Schubert, M. Manea
Two-step curing processes for coating application
Progress in Organic Coatings
55, 154-159

Filed patent applications

#451 + #471 B.A.J. Noordover, R. Sablong, R. Duchateau, R.A.T.M. van Benthem, W. Ming, C.E. Koning
Process for the production of a polyester

Reported inventions

#422 D. Senatore, R.A.T.M. van Benthem, J. Laven, G. de With
Powder coating composition

#556 N. Akeroyd, L. Klumperman
Synthesis of crosslinker for coating

#565 M. Ottink, L. Klumperman
Synthesis of functional latexes

High Throughput Experimentation

Time for thinking

Most materials suppliers have by now acknowledged the advantages of the use of robots in the synthesis of new polymers. They are more or less forced to adopt these time-saving strategies for competitive reasons. And in the scientific world, too, robotisation has brought the big advantage predicted four years ago: it has freed up time for thinking.

Cross-linking

"The biggest event in 2006 in the technology area was that our combinatorial compounding set-up – a system that can automatically try out dozens of formulations in parallel – at the German Plastics Institute in Darmstadt is now operational. For my company, Degussa, that was one of the main reasons to join DPI," says Dr Harald Häger, Vice Chairman of the High Throughput Experimentation technology area. The prospect of the combinatorial compounding set-up brought the bigger industrial partners, the materials producers Degussa, Bayer and Ticona, to DPI's table. "Because of the costs involved in such a set-up no company can afford to operate such a system on its own and yet every company will need it. But costs are not the only factor; another factor is that interdisciplinary cooperation between physicists, chemists and computer scientists is not taken for granted in companies. And yet you have to be just as fast as your competitors in bringing new materials to the market."

New legislation

"That the set-up is operational now not only results in more industrial contacts because we can synthesize more different compounds, we can also, more easily than without it, comply with REACH, the European Union's new regulatory framework for chemicals," adds Professor Ulrich S. Schubert, scientific chairman of HTE. Because of this new legislation some additives to materials have to be replaced with others that do not imply safety hazards. Only in some cases is it possible to replace one additive by another on a one-to-one basis, more often the whole formulation is affected. Customers of the big materials companies do not want to pay more for the new materials. Nor do they want other properties of the materials to change when new additives are used. For instance, they do not want the flame-retardant properties to change when they ask for a polymer with a higher modulus. Adding glass fibres gives them that higher modulus but affects the burning properties, so the whole formulation has to be considered. And of course

fact

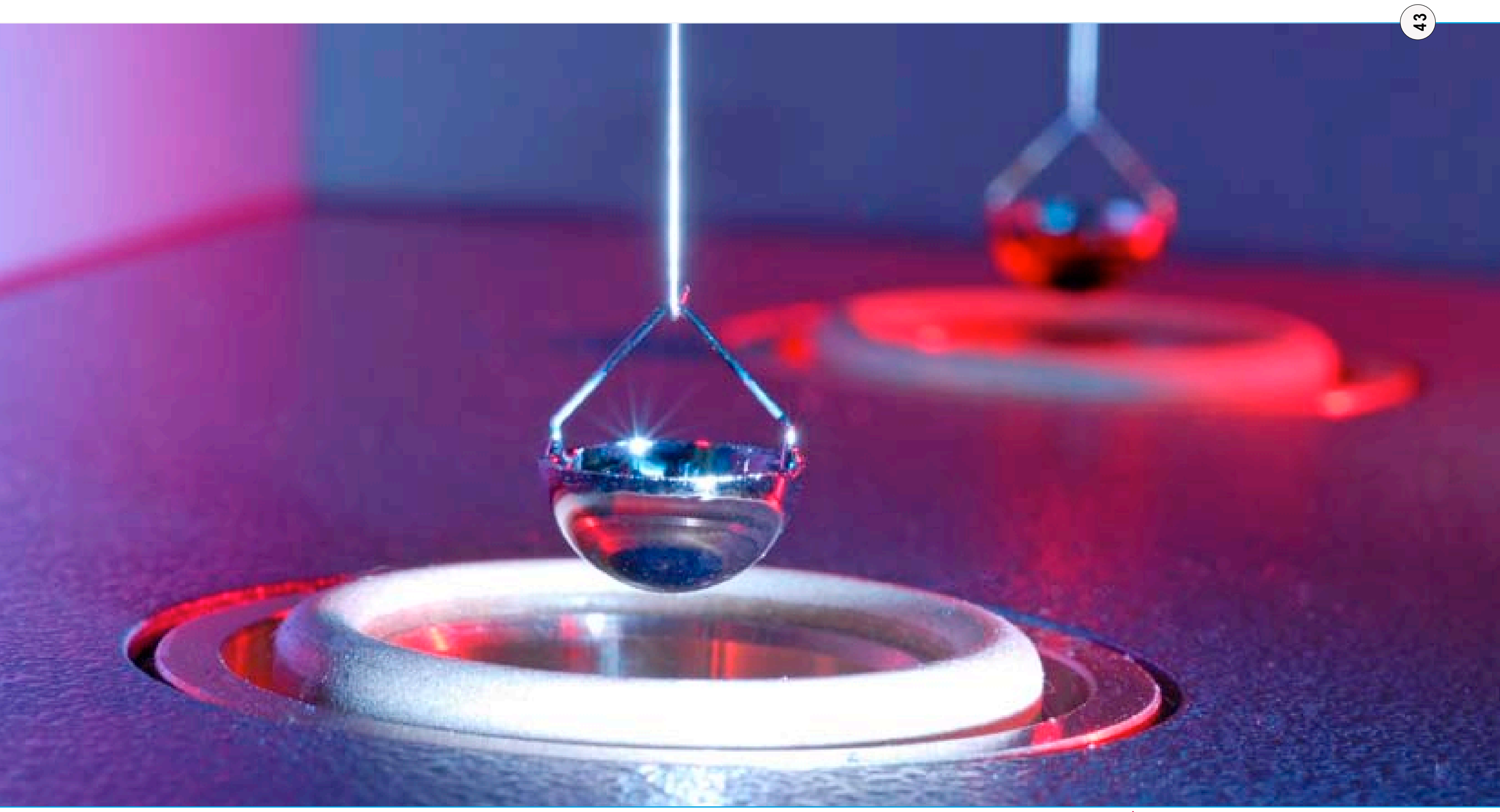
Harald Häger, Degussa

customers do not want to wait for a year to get an answer. Tailoring new materials to specific needs in a short time can only be done by adopting the HTE approach. DPI was and still is ahead of its time with this. “But the scene is changing. I know of a small company in Germany that has plans to provide this kind of service to compounding materials companies. They are developing a similar process,” says Häger, who admits that this new way of working will have to be adopted by the whole industry.

Side effects

HTE saves the industry time and money. Instead of 20 kilograms of one compound, now 20 kilograms of many different compounds are made and only the successful ones are pursued. But this also has consequences for the scientific community. Indeed, as predicted and hoped for four years ago, the HTE approach frees up time to evaluate and characterise the polymers that are synthesised, time to understand the processes so that further syntheses can be tailored even better to resolve specific questions. In addition, PhD students now have time to follow interesting side effects, as the example with ionic liquids shows. In the ‘old’ days, starting up a new PhD project to follow such a lead would have taken years to get results, but when the lead is tackled as a side path in an ongoing PhD project results can be available within six months. The strength of DPI, its network of industrial and scientific experts, can be used to direct PhD students to promising and interesting applications. PhD students feel highly motivated by the feedback meetings to look for applications. Häger gives an example, the so-called coffee-drop effect. “Polymers in a solution tend to assemble at the borders of a drop. This was not wanted and it took a lot of effort to get rid of it. But once the phenomenon was understood it could also be exploited and used in a positive sense to make structures.”

Schubert is not afraid to claim that HTE makes a tenfold increase in efficiency possible. But there is more. “I could even mention that it will free up time for us to look through publications to track down interesting side effects that others have left open. Remember that the Nobel Prize is always awarded for interesting side effects, never for mainstream work,” Häger eagerly explains the great opportunities that the HTE approach offers. He adds that after speeding up the synthesis of new compounds attention should be focused on improving the evaluation process and speeding up measurements. After all, it would be a shame if the time gained in the early stages of the process was lost again in evaluation and measurement.



New possibilities

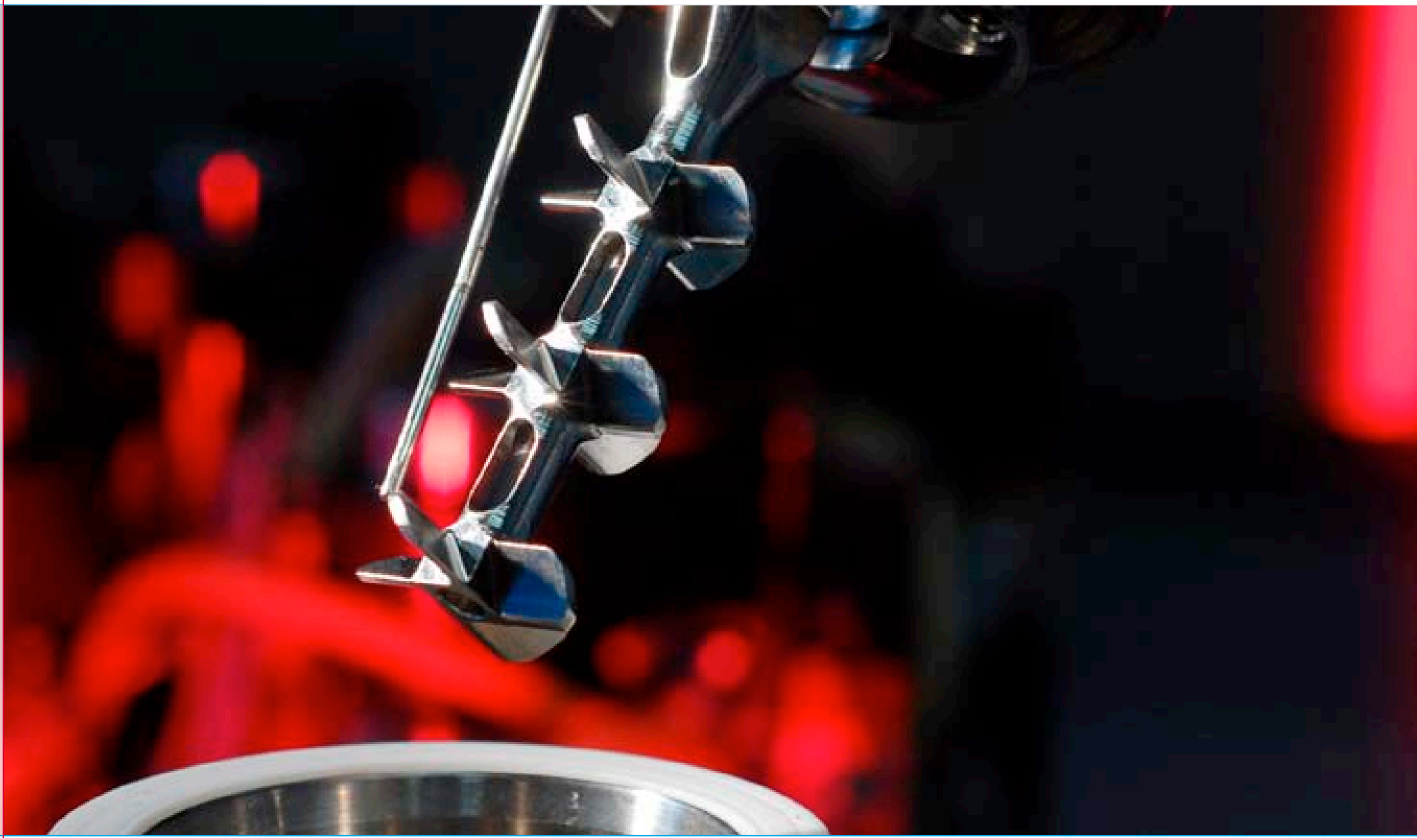
Ink jet printing is another area that is really flying, as Schubert puts it. Four years ago it started with printing simple polymers such as polystyrene. "Conductive polymers for LEDs and displays followed, and now we are printing completely new polymers, synthesised at DPI. For instance, we print conductive lines directly on polymers or flexible substrates. Possible applications are the heating of rear windows of cars made of polymers instead of glass." RFID tags and sensors are also being printed now, so Schubert's group really made headway last year. It has published several articles that had a very high impact, and there were also patents involved. HTE is one of the few areas where at this moment science is very close to potential applications. Schubert continues: "We received an award for a method to print very fine conductive lines of silver particles that can be 'sintered' with microwaves in a few minutes. This method not only saves the energy that would otherwise be consumed by the large ovens normally used for sintering, which need to be heated for several hours, but it also brings more thermosensitive substrates within reach."

Printing is extending its possibilities even beyond printing new materials on other substrates. It will in the future no longer be limited to two dimensions. Three-dimensional printing of new materials, or rapid manufacturing as it is called, will play an increasingly larger role now that with the shorter life cycles of products fewer identical parts will be needed. "3-D printing can be a solution for mouldless manufacturing of parts," Häger explains. "This will not only save the cost of expensive moulds but will also facilitate the manufacture of single unique parts. Given the impact DPI has had in 2D printing, in particular in the scientific community, we see the third dimension as an interesting challenge, which we will gladly take up."

Looking back on the plans and expectations at the start of the HTE technology area four years ago, Schubert is well pleased. "After four years of steady growth, it is now time for a steady flow. We have the highest number of publications per person of all technology areas in DPI. Although we thought that it would take some time before patents were granted, this has happened already. I think HTE definitely has changed people's mindset. We will now focus on finding cooperation with other technology areas of interest to spread our technologies."

fact

Häger:
"We must now focus on improving and speeding up the evaluation methods for the compounds we have realised."



Time for side paths

Carlos Guerrero Sanchez studied chemical engineering in Mexico, where he grew up. Guerrero Sanchez: "I did my final master thesis project in the research centre of DESC, a major Mexican company. They were starting a lab for combinatorial materials research and had acquired a Symyx platform. When I finished my project, they hired me to synthesise and characterise polymeric materials with the new equipment. It was nice at the beginning, but soon I got into a kind of steady state. I wanted to learn more. So I decided to pursue a PhD abroad in order to grow, not only scientifically, but also to get better opportunities." For Mexicans, the United States or Canada are obvious choices for this purpose, but via a conference contact Guerrero Sanchez met Professor Schubert, who was establishing a combinatorial laboratory in the Netherlands. In July 2003 he came to Eindhoven as a PhD student. At first he was a bit concerned about surviving in a country where he did not speak the language, but with time he managed to find his way.

Polymer research

Because of his previous experience in anionic polymerisation, Guerrero Sanchez was asked to implement this into the high-throughput experimental workflow of Schubert's group. Such experimental techniques are very sensitive to water and oxygen. Guerrero Sanchez spent the first few months making the available combinatorial platforms suitable for these reactions. After that, the real research could start. Guerrero Sanchez: "I synthesised 'new' block copolymers and added functional end groups to different polymers via anionic polymerisation, which as far as I am concerned is the most powerful synthetic technique for the preparation of well-defined polymeric materials. Block copolymers are very important materials since they can self–organise to form various nano–structures, which can be used for different purposes. We used relatively inexpensive monomers. The resulting polymers have novel and

Guerrero Sanchez:
"You can design ionic liquids with the required properties for a specific application."

improved thermal and mechanical properties compared to their commodity versions." It is important to Guerrero Sanchez that the results of his research work lead to potential applications.

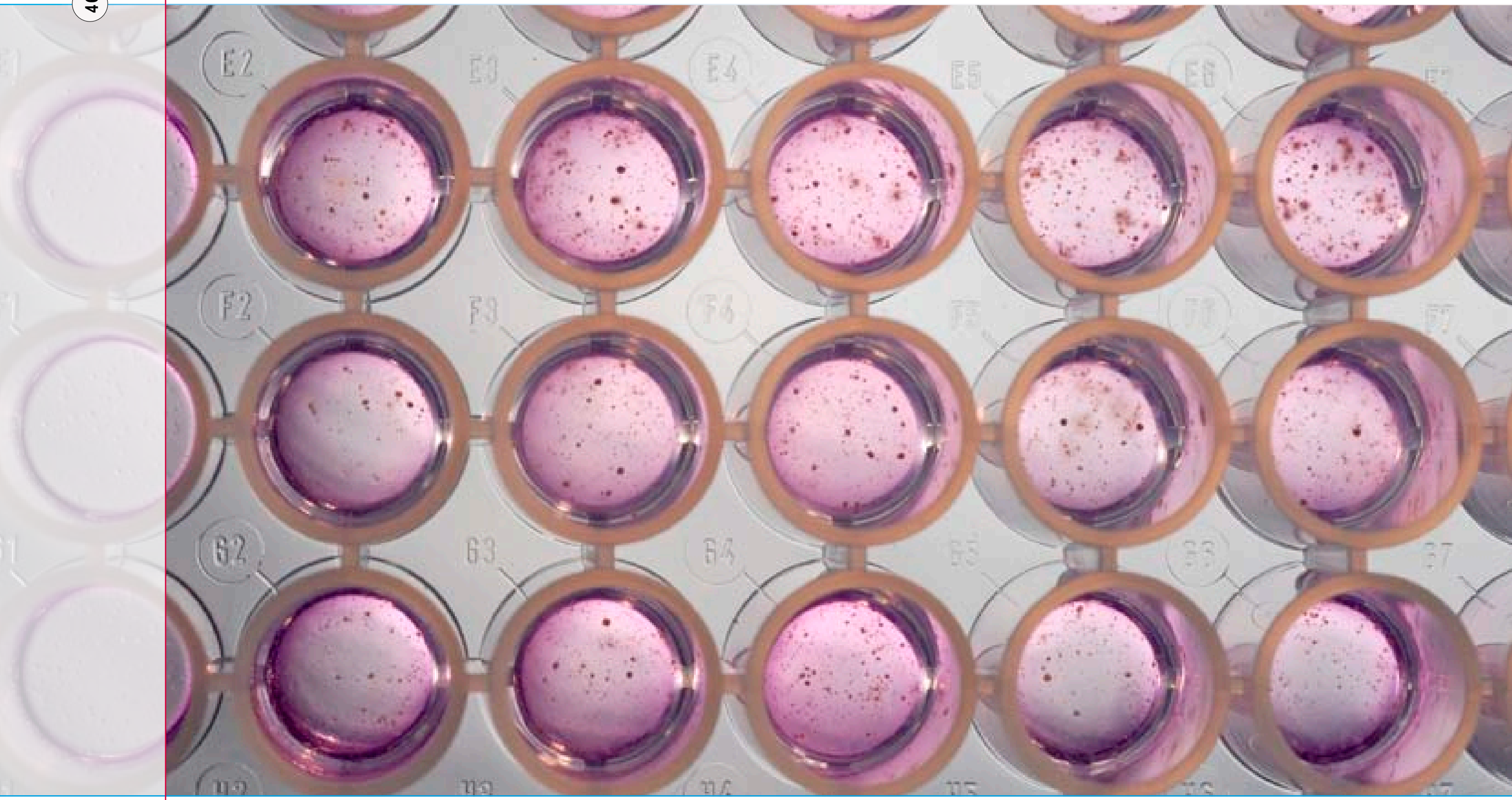
Ionic liquids

The big advantage of the use of a high-throughput workflow is that it can provide extra time to investigate an interesting side path. Professor Schubert suggested that Guerrero Sanchez incorporate ionic liquids into his research plan. Ionic liquids, salts that melt below 100 °C, are a new kind of solvents with special properties: they have negligible vapour pressure and do not evaporate. Ionic liquids can be used instead of organic solvents in order to avoid pollution. They also have negligible flammability, which makes them very stable and safe compounds. Guerrero Sanchez: "An important aspect of ionic liquids is that you can adjust their properties - viscosity, electrical conductivity, melting point, density, miscibility with other substances - to the application by combining different cations and anions. I used them as solvents in different polymerisation reactions, but created a new problem in doing that: you cannot evaporate the ionic liquid or the polymer in order to obtain your end product. But we managed to develop an efficient and suitable approach in order to phase-separate them by solubilising either the ionic liquid or the synthesised polymer in water."

Plastic magnets

Ionic liquids act as surfactants. Guerrero Sanchez used ionic liquids to disperse magnetic particles in a polymer matrix to make 'plastic magnets'. Sensors, membranes and actuators can be controlled with the aid of a magnetic field, and in this specific case also with an electric field. In doing that he found that when you mix the ionic liquid with the magnetic particles, you actually prepare a magnetic fluid, which solidifies reversibly in the presence of a magnetic field. Guerrero Sanchez: "We have filed a patent application for that. You can use these magnetic liquids in dampers for cars, buildings and bridges, and in loudspeakers. Conventional magnetic fluids require several additives and complicated preparation methods to keep the magnetic particles in suspension, which obviously increases their cost. The use of ionic liquids as carriers of magnetic fluids can reduce their production cost. Another advantage is that the properties of the magnetic fluids can also be tailor–made." This is no longer related to polymers, but the HTE approach made this excursion into the fascinating field of magnetic fluids possible.

fact



Facts and figures

High-Throughput Experimentation and Combinatorial Materials Research

High-throughput experimentation (HTE) and combinatorial materials research (CMR) open the way to the rapid construction of libraries of polymers, blends and materials with a systematic variation of composition. Detailed characterization of such libraries will help to develop in depth understanding of structure-property relationships. In the long term, a kind of "materials informatics" is envisioned that allows the design and preparation of tailor-made materials and devices with predetermined properties based on the previously established structure-property relationships. The goal of this DPI technology area is the design, set-up and development of a world-leading centre in combinatorial material research and high-throughput experimentation.

Subprogrammes

- **Synthesis, Catalysis and Formulation**
  The research in this subcluster focuses on the preparation of libraries of (co)polymers and formulations as basis for the determination of structure-property relationships. Library preparation is performed using automated parallel synthesis and dispensing platforms. The main focus for polymer synthesis is on living and controlled polymerizations since well-defined polymers with systematical structural variation are easily accessible.

- **Thin-Film Libraries and Screening**
  This subcluster mainly focuses on detailed understanding and application of thin-film preparation technologies (mainly inkjet printing) and screening of thin film materials properties by automated atomic force microscopy 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).

- **Combinatorial Compounding**
  The programme of the combinatorial compounding subcluster 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 facilitates a one to twofold acceleration for the preparation, characterisation and optimisation of plastic formulations. The utilized combinatorial extrusion line will be supported by in-line and on-line screening techniques (e.g., IR, UV/Vis, rheometry, ultrasonic spectroscopy) as well as data acquisition, analysis and visualisation systems.

- **Materials Informatics and 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 and Screening and Combinatorial Compounding.
  A model is developed for the screening of MALDI matrices to facilitate a faster screening of molecular weights.

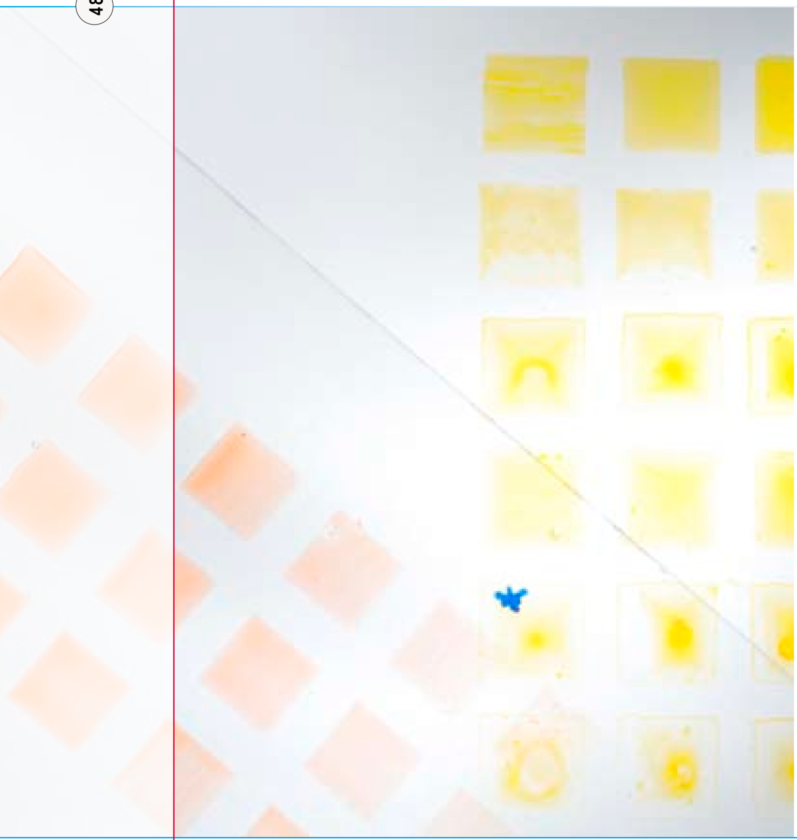
- **Detailed Characterisation Techniques**
  The subcluster detailed characterisation techniques aims to development of detailed characterisation methodologies (mainly microscopic and chromatographic techniques) for specific applications.

Facts and figures

Industry partners
Accelrys, Analytik Jena, AstraZeneka, Avantium, Basell, Bayer, Chemspeed Technologies, Degussa, DOW Benelux, Hysitron, Microdrop Technologies, NTI-Europe, Océ, Ticona and Waters.

Academia and research institutes
Eindhoven University of Technology, Deutsches Kunststoff Institut (Darmstadt), University of Amsterdam and University of Twente.

Budget
The total costs of the technology area High-Throughput Experimentation in 2006 amounted to EUR 2.7 million. About EUR 0.8 million (EUR 0.4 million in 2005) was spent on equipment. The remaining budget was allocated for 35 researchers (25.5 full time equivalents). In 2006 Prof. Ulrich S. Schubert was scientific chairman (SC) of the TA.



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 “Combinatorial and High-Throughput approaches in Polymer Science” with a special focus on microwave-irradiation as emerging technology was organized in June 2006, attracting approximately 150 international participants from industry and academia.

Highlight
During the workshop on Combinatorial and High-Throughput approaches in Polymer Science, speakers from NIST, BASF, North Dakota State University (NDSU) and the University of Graz reported on industrial applications as well as state-of-the-art academic research. In addition, 7 invited lectures and 7 contributed lectures were further discussed the current status of HTE, CMR and microwave irradiation in polymer science.
The equipment manufacturing DPI partner companies provided spotlight presentation on their latest developments. The programme was finalized by hands-on demonstrations in the DPI HTE-laboratory at the Eindhoven University of Technology.

Publications
The research programme of the TA generated 36 scientific publications (and 8 proceedings) in 2006, including contributions in high-ranking scientific journals like Advance Materials and the Journal of the American Chemical Society.
In addition, 7 scientific papers were published in collaboration with other TAs of the DPI.

Inventions
The collaboration with other Technologies Areas resulted in 1 reported inventions and 2 filed patents.

Output
Scientific publicatios

R. Hoogenboom, R.M. Paulus, Å. Pilotti, U.S. Schubert
Scale-up of Microwave-Assisted Polymerizations in Batch Mode: The Cationic Ring-Opening Polymerization of 2-Ethyl-2-oxazoline
Macromolecular Rapid Communications

R. Hoogenboom, M.W.M. Fijten, R.M. Paulus, H.M.L. Thijs, S. Hoeppener, G. Kickelbick, U.S. Schubert
Accelerated pressure synthesis and characterization of 2-oxazoline block copolymers
Polymer
47, 75-84

M.V. Rasa, C. Tziatzios, B.G.G. Lohmeijer, D. Schubert, U.S. Schubert
Analytical Ultracentrifugation Studies on Terpyridine-end-functionalized Poly(ethylene oxide) and Polystyrene Systems Complexed via Ru(II) Ions
Prog. Colloid Polym. Sci.
131,165-171

D. Wouters, A. Alexeev, D. Kozodaev, S. Saunin, U.S. Schubert
Automated scanning probe Microscopy for Combinatorial
Mat. Res. Soc. Symp. Proc.
894, 111 – 117

A.A. Abdallah, D. Kozodaev, P.C.P. Bouten, J.M.J. Toonder, U.S. Schubert, G. de With
Buckle morphology of compressed inorganic thin layers on a polymer substrate
Thin Solid Films
503, 167-176

N.Adams, M. Moneke, S.A. Gulmus, D. Chenouf, M. Rehahn, U.S. Schubert
Combinatorial Compounding
Mat. Res. Soc. Symp. Proc
894, 171-179

C.A. Guerrero Sanchez, R. Hoogenboom, U.S. Schubert
Fast and “green” living cationic ring opening polymerization of 2-ethyl-2-oxazoline in ionic liquids under microwave irradiation
Chem. Commun.
3797-3799

E. Tekin-Kazancioglu, H. Wijlaars, E. Holder, D.A.M. Egbe, U.S. Schubert
Film thickness dependency of the emission colors of ppe-ppvs in the inkjet printed libraries
J. Mater. Chem
16, 4294-4298

M. Moneke
High Throughput Experimentation - A New Way in Compound Development
Trends in Plastics
2-3, 19

H. Zhang, C.H. Abeln, M.W.M. Fijten, U.S. Schubert
High-throughput Experimentation applied to Atom Transfer Radical Polymerization: Automated Optimization of the Copper Catalysts Removal from Polymers
e-Polymers
8, 1-9

C. Guerrero-Sanchez, R.M. Paulus, M.W.M. Fijten, M.J. de la Mar, R. Hoogenboom, U.S. Schubert
High-throughput experimentation in synthetic polymer chemistry: From RAFT and anionic polymerizations to process development
Applied Surface Science
252, 2555–2561

N. Adams, B.J. Gans, de, D. Kozodaev, C. Sanchez, C.W.M. Bastiaansen, D.J. Broer, U.S. Schubert
High-Throughput Screening and Optimization of Photoembossed Relief Structures
J. Comb. Chem.
8, 184-191

R. Hoogenboom, M.W.M. Fijten, S. Wijnans, A.M.J. van den Berg, H.M.L. Thijs, U.S. Schubert
High-Throughput Synthesis and Screening of a Library of Random and Gradient Copoly(2-oxazoline)s
J. Comb. Chem.
8, 145-148

J. Perelaer, B.-J. de Gans, U. S. Schubert
Ink-jet Printing and Microwave Sintering of Conductive Silver Tracks
Advanced Materials
18, 2101-2104

V. Marin, E. Holder, R. Hoogenboom, E. Tekin-Kazancioglu, U.S. Schubert
Light-emitting Iridium(III) and Ruthenium(II) Polypyridyl Complexes Containing Quadruple Hydrogen-bonding Moieties
Dalton Trans.
1636-1644

R. Hoogenboom, F.D. Wiesbrock, H. Huang, M.A.M. Leenen, H.M.L. Thijs, S.F.G.M. van Nispen, M. van der Loop, C.A. Fustin, A.M. Jonas, J.F.M.W. Gohy, U.S. Schubert
Microwave-Assisted Cationic Ring-Opening Polymerization of 2-Oxazolines: A Powerful Method for the Synthesis of Amphiphilic Triblock Copolymers
Macromolecules
39, 4719-4725

R. Hoogenboom, U.S. Schubert
Microwave-assisted cationic ring-opening polymerization of a soy-based 2-oxazoline monome
Green Chem
8, 895-899

R. Hoogenboom, F.D. Wiesbrock, U.S. Schubert
Microwave-assisted Polymerizations: The living Cationic Ring-Opening Polymerization of 2-Oxazolines
Chemica oggi
24, 46049

R. Hoogenboom, H. Huang, C.A. Fustin, J.F.M.W. Gohy, U.S. Schubert
Microwave-assisted synthesis and micellization behavior of soy-based copoly(2 oxazoline)s
Colloid Polym. Sci
284, 1313-1318

F.D. Wiesbrock, U.S. Schubert
Microwaves in Chemistry: The succes story goes on
Chemica oggi
24, 1-4

S. Hoeppener, F. Wiesbrock, R. Hoogenboom, H.M.L. Thijs, U.S. Schubert
Morphologies of Spin-Coated Films of a Library of Diblock Copoly(2-oxazoline)s and Their Correlation to the Corresponding Surface Energies
Macromolecular Rapid Communications
27, 405-411

M. Moneke
Neue Wege bei der Rezepturentwicklung
Kunststoff-Trends
6, 40

M. Moneke, W. Wunderlich
Neue Wege bei der Rezepturentwicklung - Die Additivierung schnell optimieren
GIT-Fachzeitschrift
10, 950

C. Remzi Becer, Renzo M. Paulus, Richard Hoogenboom, Ulrich S. Schubert
Optimization of the nitroxide-mediated radical polymerization conditions for styrene and tert-butyl acrylate in an automated parallel synthesizer
Journal of Polymer Science Part A: Polymer Chemistry
44, 6202-6213

B.J. de Gans, C. Sanchez, D.A. Kozodaev, A. . Alexeev, M.J. Escuti, C.W.M. Bastiaansen, D.J. Broer, U.S. Schubert
Optimizing Photo-embossed Gratings: A Gradient Library Approach
J. Comb. Chem.; (Report);
2, 228-236

B.-J. de Gans, S. Hoeppener, U. S. Schubert
Polymer-Relief Microstructures by Inkjet Etching
Advanced Materials
18, 910-914

N. Adams, J. Clauss, M. Meunier, U.S. Schubert
Predicting thermochemical parameters of oxygen-containing heterocycles using simple QSPR models
Mol. Simul.
32, 125-134

H. Huang, R. Hoogenboom, M.A.M. Leenen, P. Guillet, A.M. Jonas, U.S. Schubert, J.-F. Gohy
Solvent-Induced Morphological Transition in Core-Cross-Linked Block Copolymer Micelles
J. Am. Chem. Soc.
128, 3784-3788

M.A.R. Meier, U.S. Schubert
Successful Approaches in Combinatorial Polymer Research
Soft Matter
2, 371-376

R. Hoogenboom, M.W.M. Fijten, R.M. Paulus, U.S. Schubert
Tailor-made copolymers via RAFT the fast way
ACS Symp. Ser.
944, 473-485

A. Winter, C. Ulbricht, E. Holder, M.T. Rispens, U.S. Schubert
Unusual terpyridines as ligands for novel light-emitting iridium(iii) complexes: synthesis and characterisation
Aust. J. Chem
59, 773-782

C. Guerrero-Sanchez, T. Erdmenger, P. Sereda, D. Wouters, U.S. Schubert
Water-Soluble Ionic Liquids as Novel Stabilizers in Suspension Polymerization Reactions: Engineering Polymer Beads
Chemistry - A European Journal
12, 9036-9045

U. Hangen, S. Downs, J.M. Kranenburg, R. Hoogenboom, U.S. Schubert
Adhesion Studies by Instrumented Indentation Testing
NanoS
1, 18-22

T.Tang, V. Castelletto, P. Parras, I.W. Hamley, S.M. King, D. Roy, S. Perrier, R. Hoogenboom, U.S. Schubert
Thermo-responsive Poly(methyl methacrylate)-block-poly(N-isopropylacrylamide) Block Copolymers Synthesized by RAFT Polymerization: Micellization and Gelation
Macromolecular Chemistry and Physics
207, 1718-1726

M. Rasa, U.S. Schubert
Progress in the characterization of synthetic (supramolecular) polymers by analytical ultracentrifugation
Soft Matter
2, 561-572

M.A.R. Meier, D. Wouters, C. Ott, P. Guillet, C.A. Fustin, J.F. Gohy, U.S. Schubert
Supramolecular ABA Triblock Copolymers via a Polycondensation Approach: Synthesis Characterization, and Micelle Formation
Macromolecules
39, 1569-1576

Filed patent applications
#530 + #546 K. Hermans, J. Perelaer, C.W.M. Bastiaansen, D.J. Broer
Process for preparing a polymeric relief structure

#401 C.A. Guerrero Sanchez, M. Rasa, U.S. Schubert
Magnetic fluids

Reported inventions
#401 C.A. Guerrero Sanchez, M. Rasa, U.S. Schubert
Magnetic fluids

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

Bio-Inspired Polymers

With the help of nature

Since 2006 Bio-Inspired Polymers has been a separate technology area, in which research is carried out on both the production and the potential applications of biotechnological or bio-inspired polymers. The use of enzymatic or microbial catalysis to make polymers, or the use of polymers from renewable resources, may help to make the world less dependent on fossil resources.

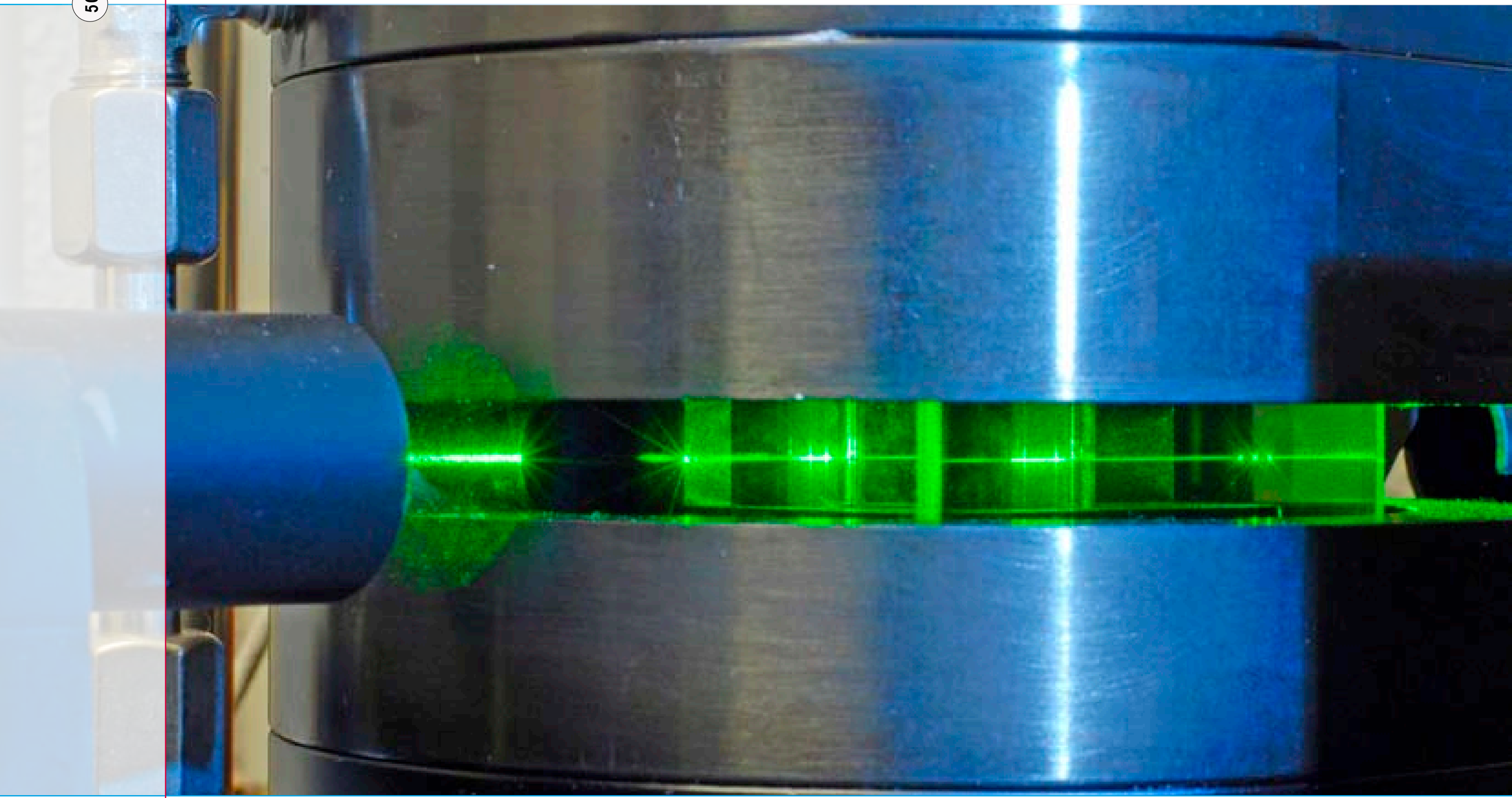
Biotechnology is a very broad field, which is sometimes subdivided into three categories. The first is white or grey biotechnology, which concerns the use of biochemical processes to produce chemicals, polymers or monomers on a large scale. Green biotechnology covers the production of chemicals, monomers or polymers from renewable agricultural resources and red biotechnology encompasses materials for biomedical applications and the biochemistry of living organisms.

Wide range

Programme area coordinator Richard van den Hof, commenting on the wide range of projects now running in DPI: "Most of these have to do with understanding the role of hydrogen bonding both in the formation of structures and in their resulting strengths. The common factor is that we try to learn from nature and bring this into polymer production. Because of their special properties, biological polymers are very interesting for certain applications and we try to determine the relationship between these properties and the polymers' structures. Hydrogen bonding leading to self-assembly and crystalline structures is such a property that is being investigated experimentally and theoretically. Adding ions or salts may shield this hydrogen bonding and can in certain cases make polymers more processable. This applies to both biopolymers and synthetic polymers. 'Bio-inspiration' is the driving force."

Apart from looking into the properties of existing biopolymers, researchers can also make new bio-inspired polymers with specific functions. Monomolecular micelle-like structures, for instance, are in certain circumstances able to encapsulate a small molecule and release it elsewhere. In addition,

fact



the conditions under which existing biopolymers such as cellulose (which is inherently difficult to process) can be used to replace fossil resources is being investigated. In the presence of ionic liquids cellulose may become processable. Van den Hof: “Prof. Schubert suggested tackling this idea using High-Throughput Experimentation, in an attempt to speed up results in this ‘old’ topic. In the meantime others have started or restarted working on it as well, based on their long track record in cellulose research. We have to work hard to stay ahead.”

Another important area of bio-inspired research in this area is enzymatic catalysis. The projects build on the results previously achieved in the Corporate Research TA.

Red

Professor Neil Cameron of Durham University (UK) is a member of the IRC, the Interdisciplinary Research Centre in Polymer Science and Technology, which is a collaboration between the Universities of Durham, Leeds, Bradford and Sheffield (all in the UK) in the field of polymers. His research interests cover the preparation of polymers and polymeric materials of controlled structure and functionality and their subsequent application in situations that have relevance to biology or medicine. Since this technology area in DPI still has no scientific chairman, Van den Hof asked him to contribute to the discussion with his outsider’s view. Cameron more than once stresses the fact that DPI should not forget red biotechnology, which according to him is a very important area in which tremendous advances are about to be made.

Cameron: “Applications such as drug-eluting stents that widen blood vessels and prevent blood clotting at the same time, or scaffolds on which tissue of a living organism can be implanted to develop into new functional tissue again, are just a few examples. You have to look into micelles, vesicles, nanoparticles and other novel kinds of assemblies for delivering and targeting drugs to specific cells. Investments in this type of research will not yield profit in the short term but in five to ten years from now there will be products on the market that will use advanced biomedical polymers, I am sure of that. ” Van den Hof mentions that projects in which the biochemical and biophysical aspects of living material are the central issue are covered by other initiatives in the Netherlands. There is too much non-polymer research involved and thus it does not match well with the DPI conglomerate of companies. But some aspects are also covered in the Corporate Research technology area, the scaffolds for instance, and drug delivery with the aid of specific polymers is covered in Schubert’s project. Cameron: “I see a lot of opportunities in developing materials or molecules for delivering medicines. And that would be a field where the physical chemistry of the molecules themselves still presents us with some interesting challenges.”

Green

The dwindling stocks of fossil resources and the need to shorten the CO_2 cycle for energy, petrochemicals and polymers are challenges that need to be met by developing new technologies based on the world’s natural resources. Cellulose is the most abundant of these polymers. As already mentioned above, it is difficult to process, but again nature can come to the rescue. Cameron: “You might be able to use microbes and enzymes to break down cellulose into useful fragments that you cannot make by doing carbohydrate chemistry. Not only with a view to improving the processability to be able to make new chemicals, but also because these fragments have interesting properties and maybe we can develop high-tech materials from them. We already have examples of fragments that are interesting in biology.

Such fragments play a role in the recognition of compounds that could damage a cell and in the subsequent action to prevent that damage." That same kind of mechanism in other polymers might also lead to self-cleaning surfaces, which would facilitate removing algae from ship hulls, for instance. Fragmented in another way, cellulose might also give us interesting materials that we cannot make in any other ways. Cellulose has for instance liquid-crystal-like properties when modified in the correct way, so maybe very sophisticated materials can be made. The possibilities are countless.

According to Van den Hof industry is currently considering cellulose not as feedstock for energy or synthetic polymer production, but only for structural purposes. Cellulose has always been used as a structural material, mostly in fibres prepared by mechanical methods, but processed in a chemical way and in a polymer physical sense it can result in interesting materials that are strong and inexpensive. "It is not sexy and appealing research, but extremely difficult to do. You need quite a lot of academic disciplines to develop a material for a feasible price on a large scale," Van den Hof adds. "If price is no issue you can do anything you like, but in our world that is of course not sustainable; the economics must be right too. To become independent of oil you need a large-scale process. For a material to be successfully sustainable, the full CO^2 cycle has to be considered, not just biodegradability on its own, as so often happens."

Another green aspect of biotechnology of importance in the polymer field that is has been gaining importance lately is enzymatic processes. These kind of reactions require a different approach and new ideas. Enzymes cannot be used at high temperatures or in all solvents for instance. An interesting project in this context, again in Corporate Research is the project in which supercritical CO^2 is used as a solvent at low temperatures. Cameron: "Biocatalysis and organocatalysis are methods to produce polymers without the often toxic catalysis ingredients used until now. Different enzymes will be used, new methods to mobilize enzymes and reuse them will be developed. There is a drive towards this approach in the UK. And rather than isolating a specific enzyme, you can also take an organism that produces the enzyme and have that do the work for you." "This is not part of DPI research, but we are closely following the biochemistry research on this topic, for instance at the Delft University of Technology. We try to cooperate with these research groups and incorporate the polymer part in our own approach," Van den Hof adds.

fact

Atom-scale simulations to understand materials

At the Max Planck Institute for Polymer Research in Mainz (Germany), two Dutch scientists are trying to unravel the secrets of nature by simulating it, or at least part of it, on a computer. Dr Nico van der Vegt is group leader of the Computational Chemistry group where postdoc Dr Berk Hess simulates how crystalline polymers, nylon 4-6 for instance, dissolve in superheated water, water with a temperature above 100ºC. They are trying to find a theoretical explanation for the experimental results of Dr Sanjay Rastogi at the Eindhoven University of Technology (Netherlands).

Self-assembly

Van der Vegt explains why they want to understand this: "Our interest is first of all fundamental. We want to understand the atomic-scale mechanism of water molecules destroying hydrogen-bonded crystals that are present in synthetic polymers such as nylons. Dissolving a nylon crystal cannot be a process similar to melting an ice cube, where layer-by-layer molecules leave the crystal surface and go into solution. In nylons the polymer chains are folded in hydrogen-bonded sheets oriented perpendicularly to the crystal surface. Water molecules penetrate between these sheets and interfere with inter-chain hydrogen bonds within the sheets. If you understand that mechanism you may also get insight into the reverse process, in which polymers or oligomers of synthetic and biological origin self-assemble in water resulting in new materials with a wealth of interesting properties." To illustrate the unlimited possibilities Van der Vegt

Hess:
"Bio-inspired polymers form an interesting field of research with a lot of potential applications."

Van der Vegt:
"We want to understand not only how hydrogen-bonded structures break up in water, but also how they self-assemble."

Nico van der Vegt, Berk Hess
Max Plank Institute for Polymer Research, Mainz.

mentions the example of the threads in a spider's web: "If you can make these longer and thicker, you have a material stronger than steel."

Coarse-grained model

The behaviour of polymers is not easy to simulate. Length scales and time scales are very long and thus simulations last long and are very complicated. Hess and van der Vegt have tackled this problem by making so-called coarse-grained models: typically ten atoms are taken together in a super atom whose behaviour can be simulated much more easily and orders of magnitude faster. Coarse-grained molecular dynamics simulations can only provide motion pictures of the molecular world with a slightly blurred view of the actual molecules. Van der Vegt and Hess have developed a way to 'zoom back in' by reintroducing the individual atoms in the coarse-grained dynamic movie. The advantage is that they get a dynamic picture of the actual atomic system on very long time scales. Atomistically-detailed molecular dynamics simulations do not give such results. The two scientists validate their models by comparing the results with experimental data that are available for some of the materials they simulate. Hess: "The crystalline polymers that we are interested in are not like the usual picture that people have of polymers: a plate full of spaghetti. Computer simulations of such disordered polymers are relatively straightforward and various methods have been developed over the past ten years or so. The process of organizing molecules in regular structures starting from polymers in solution is something else and more complicated. But if you can do that you can design new materials and structures with interesting new applications. Ions, for instance, play an interesting role. A spider adds ions to the material from which it spins threads to prevent the material from crystallizing in its body."

Both Van der Vegt, trained as a chemical engineer at Twente University (Netherlands), and Hess, a mathematician from Groningen University (Netherlands), have been working in the field of computational chemistry for quite a while. They ended up in Mainz because it is the largest centre where this kind of research is done. Hess will complete his post doc project, his third after defending his thesis in 2000, in about two years' time. He hopes to find a permanent research job at a university, preferably in the Netherlands. Hess: "Bio-inspired polymers form an interesting field of research with a lot of potential applications. I might be lucky to find a company where fundamental research like this is done, but I think the chances to find a place at a university are better."

Fact and figures

Bio-Inspired
January 2006 the new Technology Area Bio-Inspired started. In line with DPI's business plan 2008-2015, sustainability is an important issue for future materials and nature is seen as an important source of inspiration to find new leads and possibilities. Both industry and academia have high expectations of research results in this field. The programme started with a strong emphasis the importance of non-covalent bonding mechanisms, especially through hydrogen bonding, both in synthetic polymers (e.g. polyamides) as well as in polymers from bio-chemical synthesis (controlled protein blocks). Monomolecular micelles with potential use as drug delivering carrier are being investigated as yet another possibility based on self assembly capabilities. Following a call for proposals in 2006, additional fields of interest to be started through projects in 2007 are enzymatic catalysis for the synthesis of high molecular weight polyesters, new routes for the modification and processability of cellulose and modeling of self-assembly, including verification through controlled synthesis of well defined model systems.

Partners industry
Agrotechnology & Food Innovations, Degussa, DSM, Dow, Friesland Foods,

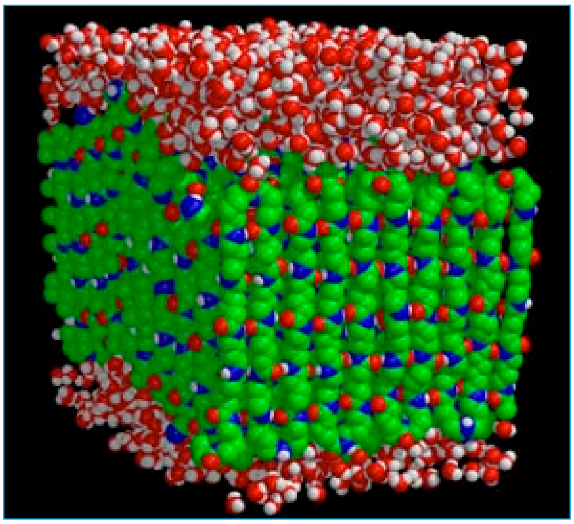
Partners research
Universities of Eindhoven, Wageningen, Leeds and Loughborough, Polymer Technology Group Eindhoven, Max Planck Institut für Polymerforschung.

Budget/realized
Total costs were EUR 203,000 (budget EUR 903,000), spent on equipment EUR 60,000.

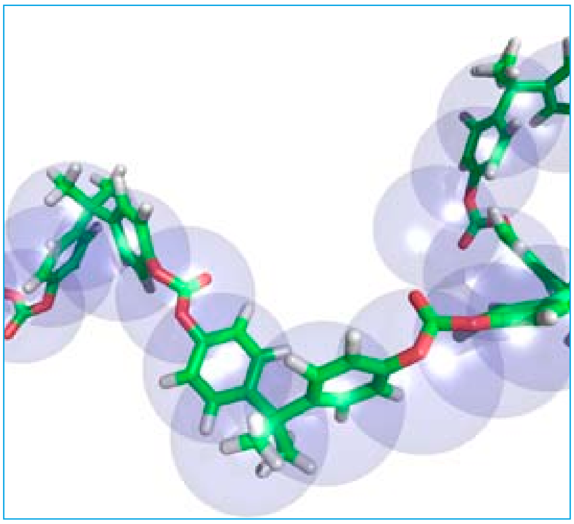
Organisation
The Scientific Chairman position is yet vacant.
Successive Programme Area Coordinators:
Dr. Stefan Schmatloch and Ir. Richard van den Hof.

Networking
A call for proposals and 2 PC meetings were organized in order to define and manage the bio-inspired research programme.

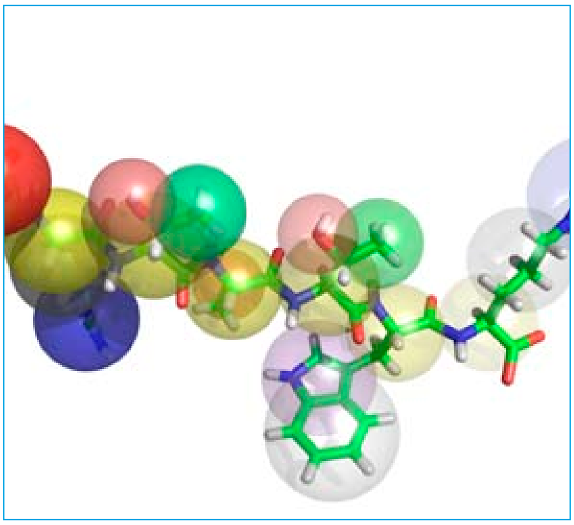
Publications
Publications: see corporate research.
Reported inventions or filed patents: 0



Simulation snapshot of a nylon 4,6 crystal in superheated water



Bisphenol-A Polycarbonate in high-resolution (atomistic) and low-resolution (coarse-grained) representations. These models are developed such that "scale-hopping" is possible in up- and downward directions.



Heptapeptide (DRTSTWR) high-resolution (atomistic) and low-resolution (coarse-grained) representations.

Max Plank Institute for Polymer Research, Mainz.

Turning the knobs intelligently

Meulenkamp:
"We are taking polymer research one step further. We want to understand the fundamentals of the large-area deposition processes."

Large-area thin-film electronics is a new technology area in DPI that will address the follow-up needed to actually make large numbers of products based on laboratory prototypes using processable polymer materials combined with scalable processing technology. Proving a concept is one thing, making a product is quite another. In the processing of materials on a large scale many fundamental problems still have to be solved.

Dr Eric Meulenkamp, department head of the Photonic Materials and Devices Group in Philips Research and one of the industrial programme committee members in this technology area (TA), explains the TA's scope: "In this technology area we are taking polymer research one step further. We will not merely look at the materials properties or a device concept, we will also look at the processes to make large numbers of devices simultaneously on large surfaces. These processes have fundamental aspects that differ from those encountered in small-scale prototype work. Printing is a likely candidate for such processes because of its huge potential. But it will still take hard and inventive work to transfer the concepts proven on a millimetre scale in the laboratory to a large scale in a production plant."

Lombaers:
"We expect that the underlying principles that we plan to find are transferable to other applications and different materials."

Van Mol:
"Real-life production processes have to have a high yield and have to result in reliable, reproducible and affordable products."

Ton van Mol, Holst Centre, Jaap Lombaers, TNO/Holst Centre
Eric Meulenkamp, Philips Research

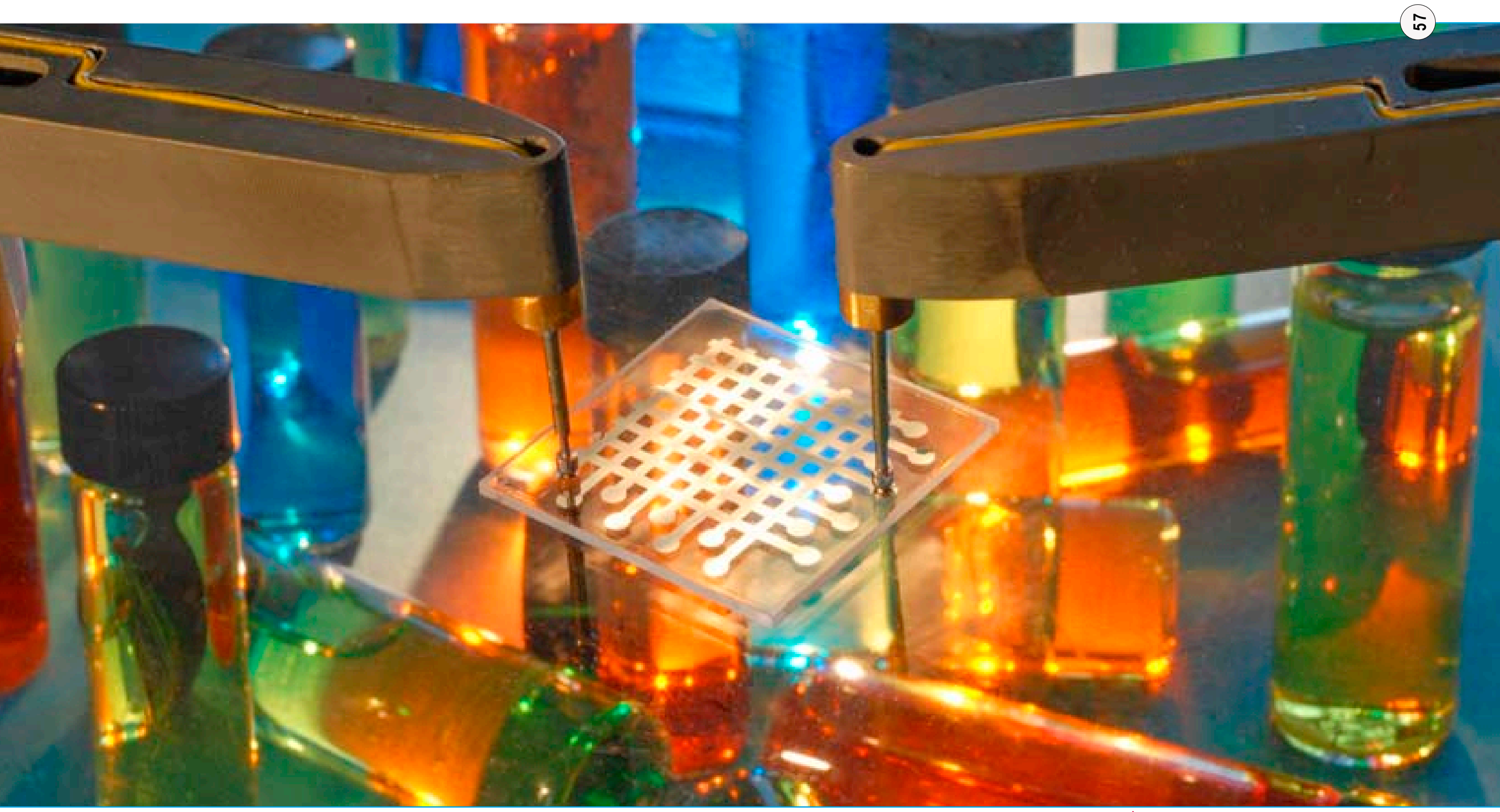
Beyond trial and error

Ton van Mol, leader of the systems-on-foil programme in the Holst Centre, adds: “It is not a matter of simply scaling up the processes that we used in our laboratories to prove a concept. Real-life production processes make heavy demands. They have to have a high yield and have to result in reliable, reproducible and affordable products.” Dr John van Haare, programme area coordinator, points out DPI’s ambitions: “We want to go beyond a trial-and-error programme. We really want to understand what is going on, so that if we change to another combination of materials or another application, we can use the results there as well. Although this programme is moving closer to production compared to other DPI programmes, it is still pre-competitive research.”

The fact that individual companies are not tackling this problem on a large scale at the moment also indicates its generic nature. Yet the small-scale activities of some companies and the interest that other, bigger companies have shown in this technology area indicates that the time is right to address it in a separate TA in DPI. This TA has existed since 1 July 2006, but preliminary research projects took place before that date in the Corporate Research TA.

Range

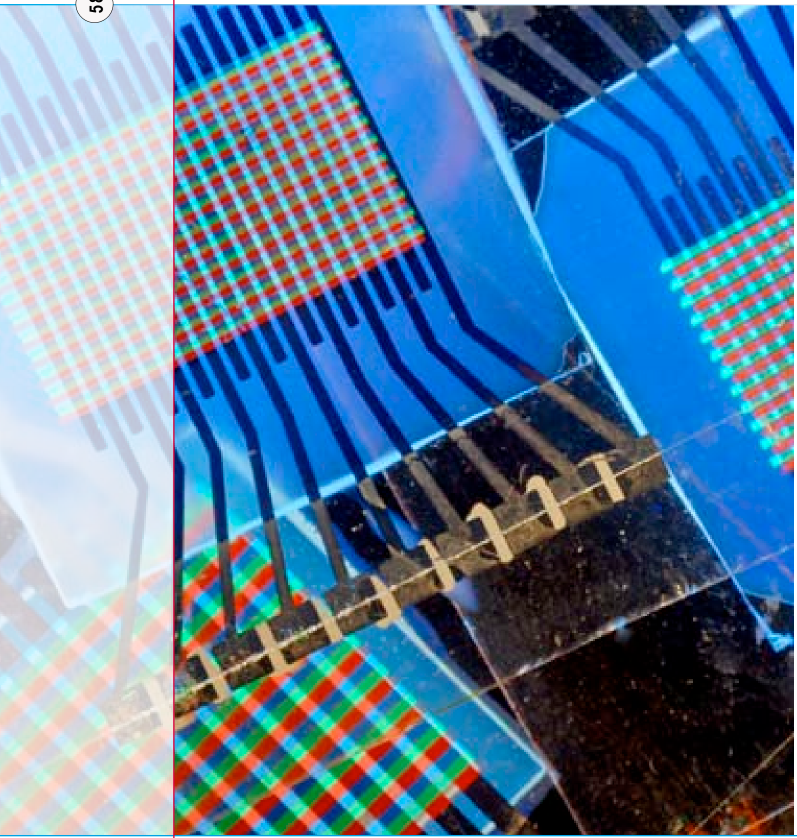
Large-area thin-film electronics comprises a wide range of applications. OLEDs for general lighting or signage, flexible solar cells, arrays of (disposable) sensors, back planes with driver circuits for displays and identification tags are just a few. One of the important driving factors is the cost price per device. Jaap Lombaers, one of the directors of the Holst Centre and a member of the programme committee: “You can think of devices that do not need a flexible substrate to perform their function but will nevertheless be produced on flexible substrates because of the costs involved. But to make this problem controllable, we have decided to limit ourselves to one application area, OLEDs for general lighting and signage. You cannot tackle all applications at the same time, but we hope that the underlying principles that we plan to find are transferable to other applications and different materials.” OLEDs for general lighting and signage open up new possibilities because of their free form factor, their ability to change colour and intensity, and the fact that they are not point sources but surfaces that emit light. You can even make them transparent and attach them to windows that pass the daylight during the day and give off a diffuse light in the evenings. The participants in the discussion



expect full-scale lighting applications in ten years from now, but applications in specific markets will appear long before that.

Mass production

What are the fundamental problems that need to be solved? Firstly, the deposition methods for layers, patterned or otherwise, cannot be transferred directly from the laboratory to a manufacturing environment. In lab situations spin-coating is often used to deposit a homogeneous layer of a polymer, but this cannot simply be extended to the square metres of substrate material that have to be covered in production. You can think of gravure, screen or ink jet printing but then the materials or the formulations will have to be adapted in most cases. Other solvents will have to be used, which means it will need to be known how layers on large surfaces dry, how fast this happens and how this can be influenced. One very important issue that has to be dealt with is the prevention of dust particles that cause short circuits. Contrary to displays, where a short circuit causes malfunctioning of one small pixel, in OLEDs for general lighting a larger surface will not work when a short circuit occurs. It may even be necessary to redesign devices in order to adapt the architecture to the processing windows of the new deposition methods.



And when in the end you have mass produced your device and it works, it has to be shielded from the environment. In a prototype you can add metal covers or glass plates but in mass production, in particular in reel-to-reel processes on flexible substrates, you will need other packaging technologies. Meulenkamp: “The extra difficulty is that all these things depend on each other. If you optimize one aspect, you influence others. So you must turn the knobs intelligently. And to be able to do that, you need to understand the relationships.”

For the answers to all of these problems a fundamental insight into the processes to be chosen is needed. Physical and chemical properties of the materials play a role. Not only physicists, chemists, mechanical engineers but also experts in fluid mechanics, transport phenomena and rheology are needed. Van Haare points out that university groups in these latter fields are not yet represented in DPI. “Recently we made an overview of groups with a solid reputation inside and outside the Netherlands. In the course of this year the first projects will start.”

fact

Reliability

Another important aspect in the production process that codetermines the choice of a specific production process is reliability. To prove that the principle works, it suffices that one of a few devices made in a laboratory works. In industrial production, however, you want a high yield. Van Moll: “In mass production usually the bill of materials determines the cost of the product. If you have a process consisting of six or seven steps, each with a yield of, say, 95%, the total yield will be less than 70% and you will be throwing away a lot of money. You want process steps with a reliability as close as possible to 100%.” Van Haare seizes the opportunity to stress once again that it is impossible to develop a reliable production process without deep insight, and that a trial-and-error approach will not do. “And even if, for some reason or other, you have to accept a lower yield for the time being,” adds Meulenkamp, “you have to understand the fundamentals of the process. You will need to monitor a parameter to decide in-line which devices do not meet the requirements in order to be able to discard them.”

Fact and figures

The Large-Area Thin-Film Electronics focuses on fundamental issues related to processing for large-area deposition and architectures for large-area processing and/or devices. Moreover, Large-Area Thin-Film Electronics opens possibilities for high-risk, high-reward research on the development of new disruptive device concepts showing improved reliability combined with robust processing. The fundamental knowledge generated in this area should facilitate reliable production of solid-state lighting panels and, in the longer term, contribute to the development of thin-film sensor devices.

The Large-Area Thin-Film Electronics technology area was established on 1 July 2006. Having first defined its objectives in consultation with the industrial partners, the TA is currently building its own research portfolio by requesting and granting research proposals and by approaching academic groups with a proven track record in this field.

Subprogrammes

- **Large-area material deposition using solution processing**
  The objective is to study fundamental issues of large-area polymer material deposition using solution processing (gravure, roll-to-roll, screen, etc.) to realise the transition from lab scale to industrial scale and reliably processed devices. Example: most lab-scale devices are made using spin coating, but this processing technique cannot be scaled up to industrial production. Although lab-scale devices have ultimate performance, mass production is currently not feasible because industrial processes and fundamental knowledge about large-area material deposition from solution are lacking.
- **Disruptive-device architectures**
  The objective is developing disruptive-device architectures for more reliable and easier production of large-area solid-state lighting. Current device architectures require very thin films (~ 100 nm) having less than 5% thickness deviation. These architectures place very strict demands on the processing and production of devices, which is currently resulting in poor yields. New device architectures allowing more robust processing and production without affecting device performance (efficiency, homogeneity of light output) would be very welcome.

Industry partners

Philips, OTB and TNO/Holst Centre.

Academia and research institutes

As DPI is currently in the process of requesting and granting research proposals addressing the objectives of the technology area, participating academia and research institutes have not yet been defined. The Programme Committee has defined a list of preferred groups to be approached as they have an established track record in this field.

Budget and Organisation

The total costs for 2006 were EUR 181.000. The total number of FTEs allocated at the end of 2006 was one, because objectives had to be defined first and research proposals had to be requested. In 2006 the Programme Area Coordinators (PAC), Dr. Stefan Schmatloch and Dr. John van Haare, were actively engaged in setting up the technology area and defining the strategy and objectives together with the industrial partners.

Networking

The Large-Area Thin-Film Electronics programme committee, consisting of a Programme Area Coordinator (PAC) and the industrial partner representatives, met two times in 2006 to define and agree the objectives of the research programme and identify/approach academic groups with a proven track record in the field.

Science-driven research for the benefit of all

The Corporate Research technology area fosters enabling science from which all other technology areas benefit. This enabling science deals with new characterisation methods, basic studies of materials structure versus performance and advanced computer modelling techniques to predict properties from molecular structure. On top of this there is a need for developing 'wild ideas', characterised as 'science-driven', 'high risk' and potentially 'high reward'.

The technology area is different from the others in the sense that its programme is not so much determined by requests from industry but by what is on offer in the academic world. In other words, the TA is science-driven. This is, of course, natural for a programme with a long-term view. The TA is financed by taking 10% of the contributions to the other areas and it has proved to be a good breeding ground for new technology areas: 'High Throughput Experimentation' and 'Bio-inspired Polymers' were born here. Richard van den Hof became programme area coordinator of the technology area in October 2006. Both the position of scientific chairman and that of programme area coordinator for this technology area fell vacant at that time. Corporate Research has a programme committee which consists of all scientific chairmen of the other technology areas and is headed by the scientific director of DPI. For the time being the positions of scientific and managing director are combined in one person, Dr Jacques Joosten, which means that a lot of the work comes down to the programme area coordinator. Van den Hof plays a dual role here, since he is also scientific chairman of Engineering Plastics.

Van den Hof: "A lot was going on in the technology area in 2006. Besides characterisation, performance and modelling projects, the ambitions of this area also included the emerging area of biomedical materials and a number of so-called breakthrough projects. These were short projects enabling scientists to demonstrate the feasibility of a particular idea or concept. It became apparent that the breakthrough projects ran the risk of losing their pre-competitive character and therefore, in view of the development of the new DPI business plan, might better be taken care of in a future 'DPI Value Centre' organisation.

Joachim Loos, Eindhoven University of Technology

The biomedical materials area will, most probably, not become a separate technology area because most industries involved have embarked on different initiatives within the Netherlands. Still, polymers will play an important role in biomedical applications. The polymer science groups within DPI will therefore certainly address the issues connected to biomedical applications. From the viewpoint of the industry members these activities will either fit in the Corporate Research technology area or in the respective technology areas."During the programme committee meeting in November the above considerations were adopted as the future direction of the Corporate Research technology area. Key to getting it all in full swing will be, firstly, the appointment (in 2007) of a new scientific chairman, secondly the establishment of much closer communication with the other areas and their industry members and, thirdly, the issuance of a call for proposals in order to fill a project portfolio in accordance with the ambitions.

Characterisation and modelling

In this technology area DPI wants to establish an environment and infrastructure that attracts top scientists who are front-runners in the field of polymer characterisation and modelling. Polymer science will benefit from those competences that are needed in all other technology areas. Predicting the behaviour of polymers in structures from their thermal history and characterisation of polymers with the aid of new methods are two examples that will be described on the following pages. Another enabling technology is structure analysis. The new cryo-TEM and tomo-AFM equipment that is now ready for use at the Eindhoven University of Technology (Netherlands) is of great benefit to all DPI members. Molecular structures can now be studied in three dimensions with a resolution of 1 nanometre. The equipment has been developed by FEI and NTI, respectively, but the group of Professor Bert de With is doing a great job in developing the tools for measuring and interpreting the results.

High risk and high reward

Professor Ludwik Leibler, winner of the Polymer Physics Prize in 2006 and member of the DPI Scientific Reference Committee, stresses the importance of the other part of the technology area, the 'wild ideas', by indicating that Corporate Research has already produced a number of new technology areas, fields of research that now exist in their own right: high throughput experimentation, bio-inspired polymers and large-area thin-film electronics.

Van den Hof: "When someone has a bright new idea that has some connection to what people really need there is always a possibility of a high impact. An example of such a breakthrough is the work by the group of Professor Frank Baaijens at the Eindhoven University of Technology and Professor Jan Feijen at Twente University on bio-active scaffolds." To make heart valves from the body's own substances, scaffolds made of biodegradable material are used on which cells will grow and 'specialise' into the strong, fibrous structure that is needed. This is achieved by 'training' these cells under circumstances similar to those occurring in the heart itself. This tissue then gets stronger and grows to become a complete heart valve. The biomaterial of the scaffolds degrades and disappears as the heart valves grow. This happens in

Joachim Loos, Eindhoven University of Technology bioreactors for the time being, but later perhaps also in living creatures. Van den Hof: "What is interesting is that the project started with a study of the blood flow in hearts to determine what the ideal shape of the valves would be to prevent clotting. The idea to build a heart valve came in the picture in a later stage." "And I think that this project was successful," adds Leibler, "because of the fact that different groups with experts in biology, chemistry and fluid mechanics were involved. Such a unique cooperation is what DPI was set up for."

Cooperation

DPI actively promotes cooperation between different groups from different universities. In a project in which Wageningen University (Netherlands) and the University of Technology in Eindhoven were involved, very interesting di-block copolymers were made. In one reactor – not yet in one go, but that will be the next step – an enzymatic polymerisation reaction resulted in an acrylic group at one end of a polymer and a radical polymerisation reaction gave a polyester type group at the other end. The molecular weight is well-controlled in this reaction, something which is impossible in classical polymerisation reactions. Self-assembly of such molecules can subsequently lead to structures with interesting applications. They can for instance result in controlled drug release from vesicles or in conducting channels to transport charge carriers in solar cells. Van den Hof: "It is a good thing that DPI does not allow polymer research to be pushed aside by the nano and bio hypes. There is a nice connection between them that would otherwise be missed out." "Polymer science is extremely important for the chain of knowledge, to make other things possible. We have to safeguard this, in particular when other disciplines are more fashionable," adds Leibler. Polymerisation in supercritical CO^2 is another approach with very promising results. At a temperature of 31.1° and a pressure of 73.8 bar supercritical CO_2 can be used instead of toxic solvents. Because of this low temperature biocatalysts can be used. Professor Steven Howdl in Nottingham (UK) is working in this field.

A new call for proposals will be sent out in the near future to fill the portfolio with high-risk/high-impact projects again. Van den Hof: "You cannot plan this research, sometimes something else than originally intended results from it. Like with the project of Professor Stephen Picken in Delft on ionic liquids that resulted in a self-healing ionomer. We will also have to think about the criteria that we will apply for approval. Of course the projects should have to do with polymers, but I would like to broaden the field. However, we cannot take up all possibilities."

Assembling the jigsaw

Corporate research is DPI's technology area where 'wild ideas' are tried out and where projects are carried out that do not naturally belong to one of the other technology areas. Polymer analysis belongs to the latter category. Professor Peter Schoenmakers is head of the Polymer Analysis research group at the University of Amsterdam. Over the last two years his group has been involved in a DPI project to analyse natural polymers in addition to the synthetic polymers they were already analysing.

Excipients

Schoenmakers: "The instigator of this project is the pharmaceutical industry. They use polymers for the same purposes as elsewhere, to package medicine for instance. Polymers are also used in the life sciences, because of their mechanical properties in artificial joints. However, polymers that are used inside the human body must meet very strict requirements with respect to stability and reactivity. It can easily take 13 to 15 years before a newly synthesised compound is approved for use inside the human body. For natural polymers that period can be shorter. A number of cellulose-derived polymers have already been approved.There is thus a great interest in using cellulose-like materials for excipients, the inactive ingredients added to a drug to dilute it or give it form or consistency." To optimise the use of natural polymers as excipients an in-depth analysis of these materials and their properties is needed. They have to be stable when shelved but when introduced in the body they must dissolve in a reproducible and controlled way.

Schoenmakers' research group has a wide experience in analysing polymers with a high molecular weight and was therefore the natural choice to tackle this

Schoenmakers:
"It is fascinating to reconstruct the polymer structure and its behaviour from what you know about the separated fractions."

subject in DPI. Even when the chemical composition of a polymer with a high molecular weight is the same for different batches, the polymer can still have a number of degrees of freedom that result in different properties. The viscous behaviour of branched polymers for instance differs from that of linear ones. Chemical analysis of a block copolymer does not reveal whether the structure is regular or completely random, and this difference can result in different solution behaviour. If the molecular structure is known exactly the behaviour can be predicted.

Separation

Schoenmakers explains how the molecular structure is unravelled: “One way or the other you have to separate these large molecules to be able to obtain information about the structure. We have invested in multidimensional techniques to separate polymers more than once. You can physically separate polymers or chemically cut them into pieces. Hydrolysis, complete chemical fragmentation into monomers, is not useful here. There is also enzymatic fragmentation: enzymes break up large molecules by reacting at specific places along the chain. This method is used a lot in the analysis of proteins and cellulose derivatives, but it is rather laborious. At this stage we are not using such methods. We prefer to stay closer to home, closer to the physical properties that determine the behaviour of the polymer. We have been lucky that our choice of solvent has resulted in a good and reproducible separation. Subsequently, we use other techniques to analyse the fractions. These measurements can be correlated with solution parameters, such as cloud points. We are not there yet, but I think that we are close to having a fast and reliable method to predict solubility on the basis of the molecular structure.” Further characterisation will be done by separating the fractions again on the basis of their size, analysing these with methods such as Matrix-Assisted Laser-Desorption Ionisation mass spectrometry or Nuclear Magnetic Resonance spectrometry, and reconstructing information about the original polymer from these data.

Reconstructing the information of the polymer from the fragments and what you know of them, assembling a jigsaw if you like, is the challenge that makes this field of research so interesting and fascinating for Schoenmakers. After a career in industry - he worked for nine years in chemical analysis in Philips Research and another nine years in polymer analysis with Shell - he is very happy in his present position. He agrees with Professor Haarer (see FPS technology area) that the Dutch system, with excellent industrial researchers working as part-time professors in academia, helps to propel the dialogue between industry and universities to a level where successes can and will be achieved.

fact

Hans Wolfgang Spiess, Eindhoven, Max-Planck-Institut für Polymerforschung

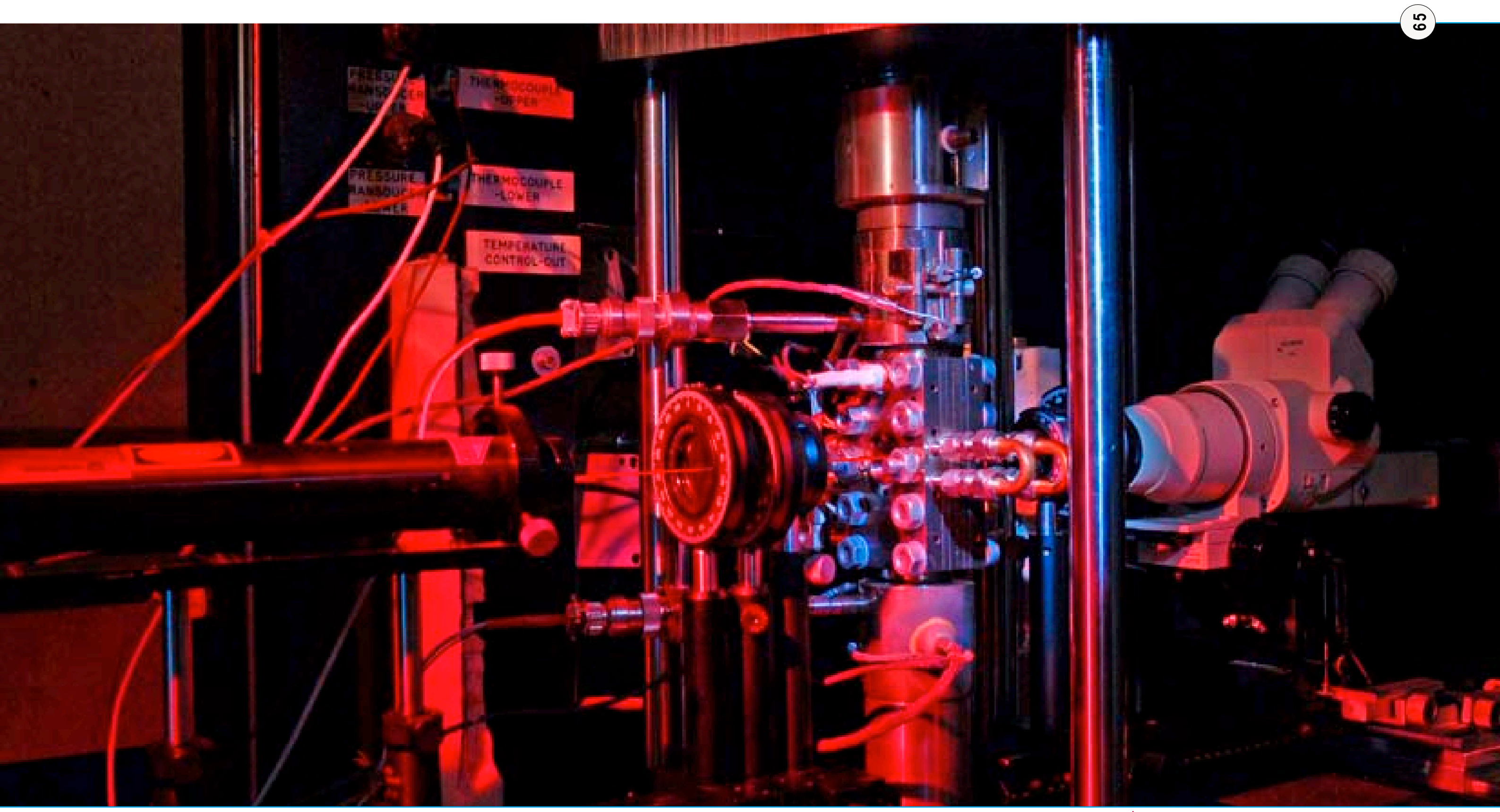
Lifetime predictions of polymer products

"Not unlike human beings, freshly made polymers are ductile and tough but in time become fragile and brittle." Prof. Han Meijer, who heads the Polymer Technology group in the Mechanical Engineering department of Eindhoven University of Technology, reads this quote from the opening chapter he wrote in a recently published book to illustrate the need for the kind of work he does. "We would like to be able to predict when this happens, that is what our work is about."

Two years ago Tom Engels started his PhD project, a natural continuation of his masters work in the field of solid polymers. Engels: "We try to predict the structural properties via the change in physical properties of polymer products directly from their processing history. The products we focus on are made of transparent amorphous polymers shaped in an injection moulding or extrusion process. We investigate both short-term failure - when products are loaded to their maximum - and long-term failure - answering questions like how long products can take an allowed load. These answers are important in deciding when to replace pressurized gas pipes, for example, and they can also help to shorten certification procedures." Meijer, Engels' supervisor, gives another example. "The cover of an air bag has to break in a well-defined way when the air bag is to be released, but it is supposed not to fragmentize upon brittle failure caused by exposure to sunlight and high temperatures."

History

One of Engels' predecessors had established how the yield stress, the stress that causes a permanent deformation and whose evolution in time controls how and when the polymer breaks, depends on temperature and time. However, he did not include the influence of the production process in his assessment. "Yet, this history has an enormous influence on the final product's performance," says Engels. "Polymers look like solids at room temperature but they behave as fluids. They strive for an equilibrium situation and reach that after a very long time that depends on their history. This process is called physical aging." To get a better grip on the aging process, you have to know how a product has been made, and to which temperatures and stresses it has been exposed. In aging



experiments products are exposed to higher temperatures and stresses and from the results it is calculated how they will behave under normal circumstances. "The nice thing is," adds Meijer, "that the controlling shift and acceleration parameters for a certain polymer do not depend on its molecular weight distribution and thus need to be measured only once. So if you subsequently know the temperature and stress history of a product, you can predict when it fails. You have to take into account that parts of products may have a different history: the walls cool faster than the inside, for instance. With our models we are the only group in the world that can predict lifetimes following from the fabrication process quantitatively without performing any mechanical test on the product."

Material providers and polymer processors, in particular those that want to use their products under high temperatures and stresses, are interested in this work. They can use the results and the methods to optimize their processes and guarantee the accompanying lifetime of their products. For example: can a mould temperature that is 100 degrees higher result in a 100 times longer product lifetime? The methods can also be used the other way around, to determine the age of products without affecting the product.

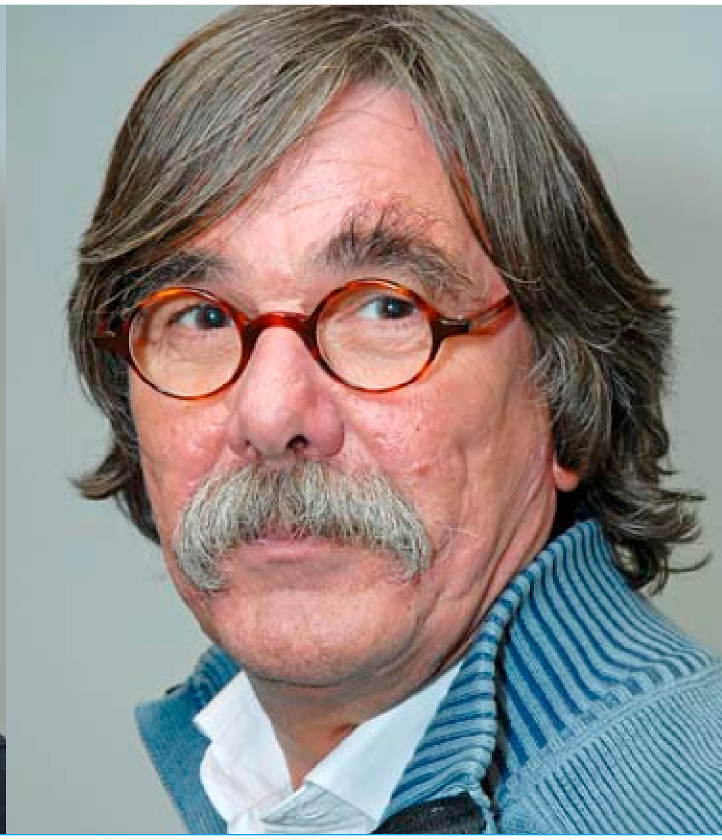
Small quantities

Meijer: "We started with amorphous polymers. Semi-crystalline polymers are more difficult, because their anisotropy is determined by the flow in the mould and is influenced by time. The mathematical description is more complex because of this direction sensitivity. But building on our amorphous results we will tackle this problem as well. In the even longer term we would like to couple the macroscopic properties to molecular ones. Our hope is to determine in due time how material properties change through the addition of small quantities of additives that influence the arrangement of polymer chains in both processed crystalline and amorphous polymers."

Meijer's group also uses the expertise to quantitatively characterize the behaviour of thin-film materials and to better understand wear and friction. Only very small amounts of material are needed, and therefore materials as produced in small quantities via for instance High-Throughput Experimentation suffice. Materials can be evaluated and optimized for certain applications long before large amounts are made and this can, of course, save money and development time.

Tom Engels, Eindhoven University of Technology

Han Meijer, Eindhoven University of Technology



Facts and figures

Corporate Research
The Corporate Research area performs enabling and strategic research in relevant fields for the whole DPI programme.

Enabling Science
The Enabling science programme is primarily science-driven and operates at the forefront of scientific knowledge and capabilities of polymer science.

Subprogramme
- Structure vs performance: modeling different length scales, fluid dynamics (rheology) and solid-state properties (bulk materials and surface properties).
- Polymer characterization: surfaces and interfaces (applying mainly microscopic techniques) and molecular characterization (SEC techniques, cross-linked architectures and networks, and analysis of polymer distribution)

Emerging technologies
With emerging technologies DPI fosters research on science-driven research in its embryonic phase if it holds a promise of a new technology area in the future. Companies are entitled to make a direct financial contribution to this part of the corporate research programme.
• In 2006 two new Technology Areas were launched after an initial period of research within the Corporate Programme: Bio-Inspired and Large Area Thin Film Electronics.
• Polymers for biomedical applications (tissue engineering novel hybrid scaffolds, heart-valve engineering, intervertebral discs) is another emerging area that most probably will not find continuation as a separate area but will be of great interest within existing areas because of its impact on new application possibilities

Engels:
"The temperature and stress histories of processed polymers have an enormous influence on their lifetime."

Meijer:
"We are the only group in the world that can predict polymer product lifetimes quantitatively."

Strategic projects
These are projects that cannot be easily accommodated with the TAs but have the potential for short-term implementation by the industrial partners. Breakthrough technological opportunities and capabilities with sometimes a high-risk/high-impact nature make part of this programme.

Subprogramme
• Mesoscopic chemistry and physics and breakthrough technologies: microwave synthesis and improved strategies for knowledge capture and data handling.

Partners industry
All DPI industry partners have access to the Corporate Programme results since funding is accomplished by contribution from all Technology Areas

Partners research
University of Amsterdam, Eindhoven University of Technology, University of Maastricht, University of Twente, University of Wageningen, Agrotechnology and Food Innovations, NWO/Dubble, Leibniz Institut für Polymerforschung Dresden, University of Leeds, National Technical University of Athens, University of Maastricht, University of Stellenbosch

Budget/realized
Total costs were EUR 1.7 million (budget EUR 1.9 million), spent on equipment Eur 150,000.

Organisation
Number of FTE is 19, Scientific Director Prof.Dr. Thijs Michels / Dr Ir Jacques Joosten a.i. Successive Programme Area Coordinator: Dr. S. Schmatloch, Prof. Dr. Thijs Michels, Ir Richard van den Hof.

Networking
2 Programme Committee meetings were organized in 2006.

Publications
25 scientific publications 92 theses.
Reported inventions and patent applications: none

Output
Theses

M.A.R. Meier
Facing current challenges in (supra)macromolecular science

J.T.A. Kierkels
Tailoring the mechanical properties of amorphous polymers

Scientific publicatios
M.A.R. Meier, H. Hofmeier, C.H. Abeln, C. Tziatzios, M. Rasa, D. Schubert, U.S. Schubert
First GPC Results of Terpyridine based Chain Extended Supramolecular Polymers: Comparison with Viscosity and Analytical Ultracentrifugation
e-Polymers
16, 1-7

A.A. Martens, F.A. de Wolf, M.N. Neeleman, G. Eggink, M. Cohen-Stuart
Producing designer peptide block copolymers by biological means
Dutch Polymer Days (KNCV-PTN-NWO), Lunteren, the Netherlands proceedings

M.A.R. Meier, M. Filali, J.F. Gohy, U.S. Schuber
Star-shaped block copolymer stabilized palladium nanoparticles for efficient catalytic Heck cross-coupling reactions
J. Mater. Chem
16, 3001-3006

C.A. Fustin, C. Colard, M. Filali, P. Guillet, A..S. Duwez, M.A.R. Meier, U.S. Schubert, J.F. Gohy
Tuning the Hydrophilicity of Gold Nanoparticles Templated in Star Block Copolymers
Langmuir
22, 6690-6695

M. Raa, B.G.G. Lohmeijer, H. Hofmeier, H.M.L. Thijs, D. Schubert, U. S. Schubert, C. Tziatzios
Characterization of Metallo-Supramolecular Block Copolymers by Analytical Ultracentrifugation
Macromolecular Chemistry and Physics
207, 2029-2041

P.D. Anderson, D.J. Ternet, G.W.M. Peters, H.E.H. Meijer
Experimental/numerical analysis of chaotic advection in a three-dimensional cavity flow
International Polymer Processing
04, 412-420

E.J.H. Boelen, C.S. J. van Hooy-Corstjens, M.J. J. Gijbels, S.K. Bulstra, A. van Ooij, L.W. van Rhijn
Preliminary evaluation of new intrinsically radiopaque hydrogels for replacing the nucleus pulposus
Journal of Materials Chemistry
16, 824-828

E. Klimov, W. Li, X. Yang, G.G. Hoffmann, J. Loos
Scanning Near-Field and Confocal Raman Microscopic Investigation of P3HT-PCBM Systems for Solar Cell Applications
Macromolecules
39, 4493-4496

M.A.R. Meier, U.S. Schubert
Selected Examples of Successful Approaches in Combinatorial Materials Research
Soft Matter
2, 371- 376

Z. Li, W. Han, D. Kozodaev, J. Brokken-Zijp, G. de With, P.C. Thuene
Surface Properties of poly(dimethylsiloxane)-based inorganic/organic hybrid materials
Polymer
47, 1150 –1158

W.R. Hwang, M.A. Hulsen
Toward the computational rheometry of filled polymeric fluids
Korea-Aust Rheo J
18, 171-181

Barosan, P.D. Anderson, H.E.H. Meijer
Application of mortar elements to diffuse-interface methods
Computers & Fluids
35, 1384-1399

A.V. Lyulin, J. Li, T. Mulder, B. Vorselaars, M.A.J. Michels
Atomistic Simulation of Bulk Mechanics and Local Dynamics of Amorphous Polymers
Macromolecular Symposia
237, 108-118

P.J.A. Janssen, P.D. Anderson, G.W.M. Peters, H.E.H. Meijer
Axisymmetric boundary integral simulations of film drainage between two viscous drops
J. Fluid Mech
567, 65-90

M. de Geus, L. Schormans, A.R.A. Palmans, C.E. Koning, A. Heise
Block copolymers by chemoenzymatic cascade polymerization: A comparison of consecutive and simultaneous reactions
J. Polym. Sci. A: Polym. Chem.
44, 4290-4297

W.R. Hwang, M.A. Hulsen
Direct numerical simulations of hard particle suspensions in planar elongational flow
J. Non-Newtonian Fluid Mech.
136, 167-178

A.N. Zdravkov, G.W.M. Peters, H.E.H. Meijer
Film drainage and interfacial instabilities in polymeric systems with diffuse interfaces
Journal of Colloid and Interface Science
296, 86–94

W.R. Hwang, G.W.M. Peters, M.A. Hulsen, H.E.H. Meijer
Flow-Induced Crystallization of Particle-Filled Polymers
Macromolecules
296, 86–94

J. Li, T. Mulder, B. Vorselaars, Alexey V. Lyulin and M.A.J. Michels
Monte Carlo Simulation of Uniaxial Tension of a Well-equilibrated Polyethylene Glass
Macromolecules
39, 7774-7782

P.Y.W. Dankers, Z. Zhang, E. Wisse, D.W. Grijpma, R.P. Sijbesma, J. Feijen, E.W. Meijer
Oligo(trimethylene carbonate) based supramolecular biomaterials with tunable properties
Macromolecules
39, 8763-8771

A.V. Lyulin, M.A.J. Michels
Simulation of Polymer Glasses: from Segmental Dynamics to Bulk Mechanics
J. Non.-Cryst. Solids
352, 5008-2012

C.Tzoumanekas and D.N. Theodorou
Topological Analysis of Linear Polymer Melts: A Statistical Approach
Macromolecules
30, 4592-4606

T.A.P. Engels, L.E. Govaert, G.W.M. Peters, H.E.H. Meijer
Processing-induced properties in glassy polymers: Application of structural relaxation to yield stress development
Journal of Polymer Science Part B: Polymer Physics
44-8, 1212-1225

I.Bazhlekov, P.D. Anderson, H.E.H. Meijer
Numerical investigation of the effect of insoluble surfactants on drop deformation and breakup in simple shear flow
J. Colloid Interface Sci.
298, 369-394

P.D. Anderson, B.J. Keestra, M.A. Hulsen
On the streamfunction–vorticity formulation in sliding bi-period frames: Application to bulk behavior for polymer blends
Journal of Computational Physics
212, 268-287















DPI Annual Meeting, November 2006, hosted by Dow (Terneuzen, NL)

DPI Annual Meeting, November 2006, hosted by Dow (Terneuzen, NL)