

## Top-level partnerships

**At the end of 2007 the Dutch Minister of Economic Affairs, Maria van der Hoeven, gave a positive response to the Polymer Innovation Programme. For the Dutch Polymer Institute and for the DPI Value Centre this meant that the strategic plan we had drawn up was approved, including a financial commitment for the next four years. Via a rolling model the plan will annually be extended by one year, which means we will have a constant four-year time horizon. Interim assessments will be used to evaluate progress against the stated ambitious targets. It goes without saying that we are very pleased with the commitment made by the Ministry of Economic Affairs.**

### New projects

Since DPI was already in the starting blocks, the approval meant that many of our projects suddenly gained momentum. In 2007 calls were issued for the various technology areas. Following a careful selection process, more than 50 projects were launched in 2008. These represent about 35% of the proposals submitted. We are currently working hard to fill the vacancies for the various projects. It took us only four months to fill as much as 60% of the vacancies. This is a result to be proud of. It indicates that young scientists are eager to be part of the DPI brand and work with DPI's partners.

### Job market opportunities

As a result of their work on projects for DPI, young scientists have plenty of opportunities in the job market. As our annual report shows, many of our scientists found jobs with our industrial partners after completing their PhD projects. The contacts with industrial companies that our scientists develop during their studies make it easier for them to switch to an industrial working environment. For example, they have become familiar with commercial ways of thinking and have learned to set feasible targets. DPI projects are projects that are primarily of scientific interest, their direction being determined by our partners from industry. Within the DPI framework, challenging academic concepts can be explored and developed with total freedom.

### Excellence

Excellence is one of our core values. This means we hire scientists of the highest quality and expect their work to be of the highest standard. In March, NOWT (Netherlands Observatory of Science and Technology) published its report 'Science and Technology Indicators 2008' comparing the quality of publications from various Dutch knowledge institutes. It was the first time NOWT included Leading Technology Institutes in its analysis. According to the report, publications from the Dutch Polymer Institute have a very high scientific impact factor – twice as high as the world average. This proves that our efforts to promote excellence are bearing fruit, thanks to the work of DPI staff departments, Scientific Chairmen, researchers and the Scientific Reference Committee. This will certainly greatly enhance the reputation of our work. We will continue along the same lines in the years to come. The high impact score shows that it is possible to carry out top-level research that is industrially relevant. DPI focuses on broader scientific issues that require long-term research.

### Cradle to cradle

A special highlight in 2007 was the Annual Meeting held in November, also the 10th anniversary of our institute. This meeting was hosted by DSM in Maastricht (NL). Professor Michael Braungart, one of the originators of the Cradle to Cradle concept, had been invited as keynote speaker. Braungart challenged the DPI community to help reduce fossil fuel usage, energy consumption and waste generation in chemical processes over the next few years. DPI is taking up this challenge in collaboration with the National Chemistry Board. The ambitions we have defined in our plans include a 30% reduction in fossil-fuel usage within 10 years and equally ambitious goals in the fields of waste reduction and energy conservation.

DPI's portfolio of approved projects reflects the sustainability philosophy. Over the next years, the new technology area of Bio-Inspired Polymers will give concrete shape to the C2C formula. A new line of research is the development of plastics that are suitable for upcycling (as opposed to recycling, in which materials are re-used in a cascade of ever

lower-grade applications and finally end up in roadside marker posts). We want plastics that can be reused as if they were virgin raw materials, 'back to building blocks'. This calls for close collaboration between polymer experts, biotechnologists and catalysis experts, as well as new partnerships with centres of excellence.

### Impact

It is hard to quantify our industrial impact in absolute terms. But our partners clearly have faith in us, as is evident from the fact that they endorse our new business plan, including its financial consequences. The number of patents generated by our research is increasing, but at the same time we have a number of patents that are 'for sale'. We want to avoid spending a disproportionate amount of money on maintaining a patents portfolio. That is why we transfer patents to our partners (industrial companies or knowledge institutes) after at most 2.5 years, and if they are not interested we offer them to third parties. Knowledge transfer constitutes a large part of DPI's added value for our industrial partners. As this annual report shows, many of our scientists have found a job with DPI partners after their studies. Once they have done a DPI project, they find it easier to apply for jobs in industry. The knowledge institutes among our partners greatly value this aspect because it makes it easier for them to hire scientists (PhD students and Post-Docs).

### DPI Value Centre

The DPI Value Centre that we started up in September has many contacts with small and medium-sized enterprises. Through the DPI Value Centre a lot more Dutch companies now have access to the knowledge that we have built up in the field of polymers. Since September, over 40 companies have found their way to the DPI Value Centre. The first successes have already been achieved, as you can read in this annual report. "Not by re-inventing the wheel, but by using our network. We know most of the players in this sector, we know the Dutch infrastructure and together with established stakeholders we know how to get access to top level experts and funding", says Arie Brouwer, director of the DPI Value Centre. "In this way we can really help companies make a big step forward. That's our mission. Innovating together."

### European Polymer Innovation Programme

In September 2008 the new Polymer Innovation Programme will officially be launched in The Hague (Netherlands). The Dutch minister of Economic Affairs, Maria van der Hoeven, will press the button. In this programme, too, we will demonstrate that collaboration pays. Not just within the Netherlands but also outside our national borders. We have taken the first step towards collaboration with North-Rhine Westphalia (Germany). We are also aiming for a closer involvement of the Belgian region of Flanders in our research. It is up to us to give shape to the Polymer Innovation Programme that we have set up. This programme revolves around the Triple P concept (people, planet, profit or, as we have formulated it in our business plan, quality of life, sustainability and economic growth). Innovating together, joining forces, working together on a unique Knowledge and Innovation Community (KIC), at an international top level. That is what we stand for, and it will continue to be our mission for the years to come!

Jacques Joosten  
Managing Director,  
Dutch Polymer Institute



# Annual Report 2007

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## Summary of financial data 2007

### Income (x EUR million)

Contributions from industrial partners	4.64	27%
Contributions from knowledge institutes	3.83	22%
Contributions from Ministry of Economic Affairs	8.95	51%
<b>Total income</b>	<b>17.4</b>	<b>100%</b>

### Expenditure (x EUR million)

By nature			By Programme Area		
<b>Personnel costs</b>	11.17	69%	Polyolefins	2.12	13%
<b>Depreciation</b>	3.26	22%	Performance Polymers	1.93	12%
<b>Other costs</b>	1.53	9%	Functional Polymer Systems	2.53	16%
			Coating Technology	2.10	13%
			High-Throughput Experimentation	3.18	19%
			Bio-Inspired Polymers	0.74	4%
			Large-Area Thin-Film Electronics	0.29	2%
			Corporate Research	1.48	11%
			Knowledge Transfer	0.19	1%
			Organization and support	1.40	9%
<b>Total expenditure</b>	<b>15.9</b>	<b>100%</b>	<b>Total expenditure</b>	<b>15.9</b>	<b>100%</b>

## 2007 Key Performance Indicators

### Number of industrial partners

End 2006:	35
End 2007:	36

### Number of partner knowledge institutes (universities etc.)

End 2006:	30
End 2007:	32

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

End 2006:	28%	
End 2007:	EUR 4.120.339 cash + EUR 424.586 in kind	27%

### Contribution Ministry of Economic Affairs

End 2007:	50%
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### Number of patents filed by DPI

In 2006:	7
In 2007:	9

### Number of patents licensed or transferred to industrial partners

In 2006:	0
In 2007:	0

### Number of patents to be transferred

Interest shown by funding partners:	13
Offered to third parties:	17

### Track record DPI reseachers

Left in total	56
Employed by partner knowledge institute	11
Employed by non-partner knowledge institute	11
Employed by partner industrial company	14
Employed by industrial non-partner company or start-up	16
Returned to native or foreign country	19
Unknown	4

### European governmental funding (% of total funding)

In 2006:	0%
In 2007:	0%

### Participation of foreign knowledge institutes (% of total expenditure)

In 2006:	11.4%
In 2007:	22.8%

### Research output

	2006	2007
Scientific publications:	196	152
PhD theses:	19	18

### Overhead costs as % of total expenditure

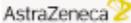
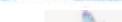
In 2006:	10.7%
In 2007:	8.7%

### Expenditure for knowledge transfer

In 2006:	EUR 291,000
In 2007:	EUR 248,000

# Partners

## Industry

-  Accelrys
-  Agrotech & Food Innovations
-  Akzo Nobel
-  AstraZeneca
-  Avantium Technologies •
-  Avery Dennison •
-  LyondellBasell
-  BASF
-  Bayer Bayer MaterialScience
-  Borealis
-  Braskem
-  Chemspeed Technologies
-  Ciba Specialty Chemicals Inc.
-  Evonik Degussa GmbH
-  Dow Benelux
-  DSM
-  ECN
-  FGK Forschungs Gesellschaft Kunststoffe
-  Friesland Foods
-  Sabic Innovative Plastics
-  Hysitron •
-  Merck
-  Microdrop Technologies
-  Nano Technology Instruments - Europe
-  Philips
-  Océ Technologies
-  OTB Engineering
-  National Petrochemical Company Iran
-  Sabic
-  Shell
-  SKF
-  Symyx
-  Teijin Aramid
-  Ticona •
-  TNO
-  Waters

## Ministry

-  Dutch Ministry of Economic Affairs

## Knowledge Institutes

-  Delft University of Technology
-  Eindhoven University of Technology
-  University of Twente
-  University of Amsterdam
-  University of Groningen
-  Leiden University
-  Maastricht University
-  Radboud University Nijmegen
-  University of Utrecht
-  Wageningen University and Research Centre
-  Agrotech & Food Innovations
-  Energieonderzoek Centrum Nederland ECN
-  NWO
-  Polymer Technology Group Eindhoven
-  TNO
-  Stellenbosch University
-  National Technical University of Athens
-  University of Ottawa •
-  University of Manitoba •
-  University of Cambridge •
-  University of Leeds
-  University of Liverpool •
-  Loughborough University
-  University of Nottingham
-  Queen Mary & Westfield College, University of London
-  Bergische Universität Wuppertal •
-  Deutsches Kunststoff Institut (DKI)
-  Universität Duisburg-Essen •
-  Forschungsinstitut für Pigmente und Lacke (FPL)
-  Innovent •
-  Friedrich-Schiller-Universität Jena
-  Universität zu Köln
-  Leibniz-Institut für Polymerforschung Dresden
-  Max-Planck Institut für Polymerforschung
-  Universität Ulm •
-  Westfälische Wilhelms-Universität Münster •
-  Universita degli Studi di Perugia •
-  Università degli studi di Napoli Federico II
-  ESPCI
-  ESCPE-Lyon

- new per 2007
- left in 2008

## Organization

### Supervisory Board

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Prof.dr.ir. C.J. van Duijn,  
Eindhoven University of Technology (NL)  
Prof.ir. K.C.A.M. Luyben,  
Delft University of Technology (NL)  
Prof. T.C.B. McLeish, University of Leeds (UK)  
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Dr. H.M. van Wechem, Shell International (NL),  
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### Council

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### Scientific Reference Committee

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Prof.dr. L. Leibler, Ecole Supérieure Physique et  
Chimie Industrielles, Paris (F)  
Prof.dr. H. Siringhaus, Cavendish Laboratory,  
Cambridge (UK)  
Prof.dr. B. Voit, Institut für Polymerforschung,  
Dresden (G)

### Executive Board

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Scientific Director a.i.

### Programme Area Coordinators

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Coating Technology, Large-Area Thin-Films Electronics  
Ir. R.P.A. van den Hof, Bio-Inspired Polymers a.i.,  
Corporate Research a.i.  
Prof.dr. U.S. Schubert, High-Throughput  
Experimentation a.i.  
Dr. J.E. Stamhuis, Polyolefins, Performance Polymers

### Scientific Programme Chairmen

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Prof.dr. C.D. Eisenbach, Coating Technology  
Prof.dr. D. Haarer, Functional Polymer Systems  
Ir. R.P.A. van den Hof, Performance Polymers  
(*co-Chairman*), Bio-Inspired a.i.  
Dr.ir. J.G.H. Joosten, Corporate Research a.i.  
Prof.dr.ir. J.W.M. Noordermeer, Performance  
Polymers (*co-Chairman*)  
Prof.dr. U.S. Schubert, High-Throughput  
Experimentation

### Organisation Staff

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

### DPI Value Centre

Ir.drs. A. Brouwer, Managing Director  
(per September 2007)

## Intellectual Property Rights

### 10 years of DPI patents

DPI has built up a substantial patent portfolio since its start in 1997. The first DPI inventions originate from 2000. After a few years of research, the programme had delivered a total of five inventions, most of which were filed as priority application in early 2001. The first grant occurred in 2004, the rest followed in 2005 and the following years. In the meantime the patent portfolio has grown steadily. At year-end 2007 there were a total of 65 filed priority applications.

The maintenance of a patent portfolio makes heavy demands on an organization's financial resources. Therefore, DPI will only file a patent application if at least one of its industrial partners is interested. Otherwise the subject matter will be published, unless the knowledge institute where the invention took place wants to file a patent application. In order to further enhance the opportunities for exploitation of the patents developed within the DPI research programme, DPI changed its Intellectual Property (IP) policy in 2006. Within the new IP framework

DPI can after a few years' time transfer its patent applications to partner companies, the knowledge institute that carried out the research or any other parties that might be interested in the technology. After a start-up phase in 2006/2007, DPI is currently negotiating the transfer of quite some patent applications with partners and third parties.

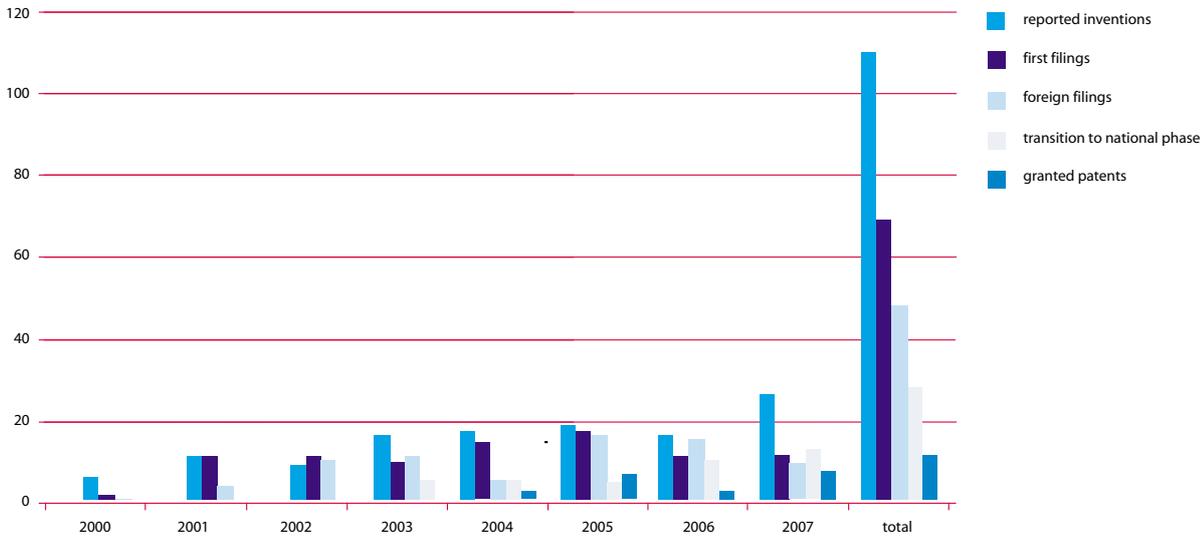
### DPI inventions and patents

DPI experienced quite a good year in terms of patents and inventions. A total of 27 invention disclosures were submitted in 2007, which represents a growth of 80% compared to 2006. Out of these submitted inventions, 9 patent applications have been filed. This percentage is consistent with the overall rate of DPI inventions that are submitted as patent applications.

This brings DPI to an average of 1.5 inventions per million euros spent in 2007. The number of patent applications per million euros spent in 2007 is 0.5. This is comparable to the results of other research organizations and industrial R&D of a similar nature.

### *DPI award winners during DPI annual meeting 2007*





### Intellectual Property awards

In 2007, at our annual general meeting in Maastricht (Netherlands), we granted a total of 28 Certificates of Invention to the inventors of 17 patent applications filed in the academic year 2006-2007. We grant

Certificates of Invention in order to honour researchers who have made an invention that has proved to be of interest for our partners. The Certificates of Invention carry a cash prize of € 500.

The first DPI patent application originates from project #103 'Chemistry of half-sandwich catalysts', which was executed at the University of Groningen by PhD student Patrick Deckers and project leader Bart Hessen within the Polyolefins Technology Area. It concerns a catalyst system based on a titanium complex for the selective trimerization of olefins and was filed on 22 February 2001.

The patent application was subsequently filed in nine countries via the PCT route in August 2003. (The Patent Cooperation Treaty (PCT) is an international patent law treaty, concluded in 1970. It provides a unified procedure for filing patent applications to protect inventions in each of its contracting states; 139 States have signed this treaty today). The first patent was granted by the Singapore patent office on 31 October 2005, followed by grants from the Chinese and US patent offices. In the other six countries, the patent application is still being examined.

DPI is currently negotiating the transfer of this patent family with one of its partners.

The first reported invention of 2007 originates from project #451 'Bio-based building blocks for coating and toner resins', executed at Eindhoven University of Technology by PhD student Bart Noordover and supervisors Rob Duchateau, Rolf van Benthem, and Cor Koning within the Coating Technology Area.

The invention concerns a bio-based polycarbonate for coating applications, among other things. Bio-based in this case means based on renewable resources such as starch from corn. An additional advantage of these polycarbonate coatings is that they hardly show any discoloration.

The patent application was filed on 13 September 2007. A total of five partner companies have indicated their interest in this patent application.

## DPI Value Centre off to a successful start

During the first half of 2007 the plans for the DPI Value Centre were finalized and preparations were made to start up the organization. On 26 September the DPI Value Centre was officially launched during the Kunststoffenbeurs (Plastics Fair) in Veldhoven (Netherlands). Immediately after this launch the Centre embarked on a pilot phase (lasting until mid 2008) and was officially founded as a legal entity: a foundation separate from the Dutch Polymer Institute.

While the financing for the plans, the launch and a part of the pilot were made possible by the financial support of Brainport, an organization that aims to stimulate new economic activity in the Eindhoven region, the approval of the Polymer Innovation Programme by the Dutch Ministry of Economic Affairs in December 2007 gave a second financial boost. The requested action lines in this programme related to the activities of DPI Value Centre comprised a total of EUR 13.55 million for the period 2008-2011.

### How does the DPI Value Centre work?

The DPI Value Centre (VC) supports innovative SMEs (including start-ups) in the field of polymers who have new ideas and want to know

- their business opportunities; the VC brings them into contact with experts in the field who can give support on demand;
- whether their ideas are technically or economically feasible; the VC defines a feasibility or development project and brings the SME into contact with experts who can execute it;
- whether other companies can help them to execute production; the VC helps the SME find partners and set up a joint project for the development of new polymer applications.

Furthermore, the VC takes new polymer-related knowledge to innovative companies and asks them whether they are interested. By actively finding inter-ested companies and setting up projects with them, valuable knowledge is transferred into business. The Perkalite® project, the first major project of the DPI Value Centre that started in 2007, is an example of this approach. During this project a consortium of companies around Perkalite®, a product developed by Akzo Nobel, was set up. After several consultations, twenty companies were found to be willing to start a joint project (see box).

What differentiates the DPI Value Centre from other support organizations is the combination of the following elements:

- Exclusive focus on the creation of new business related to polymer applications
- Ability to connect the right expertise within the unique polymer sector network. Besides the Dutch Polymer Institute and its 70-plus funding partners, this network includes partners such as
  - NRK (Dutch Rubber and Plastics Industry Federation), Platform BBB (bio-based business) and BCPN (association of companies and organizations involved in compostable products)
  - Knowledge Institutes: PTG/e (Polymer Technology Group Eindhoven), United Brains (partner of Fontys Hogescholen, TU/e, TNO, ROC)
  - Syntens (non-profit organization providing innovation support and acting as partner)
  - Incubator3+, TechnoPartner (support programmes for start-up companies)
- Ability to act as a closely involved partner when stimulating new business. The DPI Value Centre is capable of finding the right answer to a business question by connecting the right expertise and staying closely involved until results are achieved.
- Ability to support in focused financing for polymer-related projects. The DPI Value Centre helps in financing of the necessary support, workshops and business development, feasibility and innovation projects.

In 2008, a separate funding scheme for feasibility and innovation projects will start ('Subsidieregeling Polymeren').

## Two examples from practice

### Akzo Nobel and plastics sector jointly looking for applications for organic clay

#### *Broad collaboration across the chain*

In the near future twenty plastics and rubber converters will try out Perkalite®, a new breakthrough additive developed by Akzo Nobel. This synthetic organic clay is an outstanding flame retardant, filler and barrier material and has an excellent heat resistance. The Dutch Rubber and Plastics Industry Federation (NRK) and the DPI Value Centre have jointly set up the project. It is the first time such a broad cross-chain collaboration project is set up in the Netherlands. The DPI Value Centre provides support in arranging meetings, formulating plans, coordinating partnerships and financing and starting up projects. It aims to initiate more projects of this kind in 2008.

### Unique security label

Validus Technologies has developed a unique security label comprising a set of extensive safety codes for authenticating products and documents in various ways. Currently the focus is on the pharmaceutical industry, where the security label helps prevent drug copying. However, the technology can be applied in a much broader field and is suitable for other markets as well. Nico Verloop, director of Validus Technologies: "It is difficult for a start-up company to secure itself a place in the market. To find investors you need more than a lab model. In the initial phase we got a lot of support from Incubator3+. The DPI Value Centre helped us with their knowledge and experience, provided technological support in the development of a pilot production line and helped us gain access to financial support. Meanwhile, the Technostarter Fund for the South of the Netherlands (TechnoStars) and Gavilan have also invested in us to set up a production facility and launch the product on the market. Our security label is still unique, but one day others will catch up. That is why we need to stay alert and continue to focus on further developing the product. That is the only way to maintain our unique position in the marketplace."

### Launch DPI Value Centre, Kunststoffbeurs, Veldhoven (NL)





*Gerrit Peters: "Our field, rheology and computational rheology, is typically one where well-trained people can be of immediate use in industry."*

## Like any other commodity?

Some plastics are commodity products used in all sorts of mechanical and packaging applications. They have been with us for so long and are produced in such high quantities that research hardly seems necessary any more. Yet several research groups covering the complete chain of knowledge, from catalysts and polymerization up to and including processing of the polymers, are working in the field and improving processes step by step. DPI creates the conditions.

The production of polyolefins, the most important of which (in volume terms) are polypropylene and polyethylene, may seem an old process, but it is also a very precise process. "Polyolefins are commodity products. The production process has been 'tamed' and great breakthroughs are not to be expected. However, in the past ten to fifteen years we have implemented a number of small but important improvements, and many small steps can also make a big difference, including moneywise, because of the large volumes. A lot of expertise and knowledge is still needed to keep the production speed and the process yield at their present high levels. Polyolefins are produced at impressive production rates, yet the specifications are very narrow so you will always need knowledgeable people who know the details of the process." Dr. George Evens, who retired from DSM/Sabic a few years ago but is still involved as a consultant in DSM's activities in the field, holds strong views on this topic. According to him DPI's role in the polyolefins field is undeniable and indispensable.

Dr. Jochem Pater, leader of the Fundamental Research group on Ziegler-Natta catalysts at Lyondell-Basell in Ferrara, Italy, adds: "If you have problems with polymerization reaction engineering of polyolefins you may have trouble finding a group that does high-quality and relevant research in this field. I did my PhD at the University of Twente in the Netherlands with professor Weickert, but since that group stopped it has been difficult to find that expertise in Europe. One of the roles of DPI in my view is to ensure that research in the different fields of interest to polyolefins production has sufficient critical mass to support industry." His message: the process may be 'complete', the catalysts may be at their maximum, yet improvements in the process to optimize the materials for a specific application or a production process tailored to a particular product are still possible and needed.

### Supertanker

Dr. Gerrit Peters, associate professor in the Polymer Technology Group at Eindhoven University of Technology (Netherlands), is someone who approaches polyolefins from the application side. "A product's performance depends not only on the materials it is made of, but also on the process to make it. If you understand how, you can ask materials suppliers to make specific materials, optimized for a specific product or process.

Very small modifications of the molecules or a different molecular weight distribution can result in very different mechanical properties." Even the production process for the raw material influences the end result. The relation with the reactor in which the raw material is produced, possible new combinations of catalysts, chain shuttling... there are plenty of ways to influence the properties of the end product. "But convincing companies of these possibilities is a slow process. The polyolefins community is like a supertanker, it takes a while to change its course", adds Evens.

Progress is gradual and spectacular breakthroughs are rare. Still, research is needed and DPI is needed for that research, is the general opinion. Looking back at ten years of DPI, Pater formulates it as follows: "The added value of the cooperation with others, universities and industries, goes beyond the short term. The network that enables us to participate in scientific discussions on a high level and the development of strong academic groups that supply industry with qualified researchers are long-term results of DPI cooperation that are of interest to my company."

**Jochem Pater: "The role of DPI is to ensure that research in polyolefins has sufficient critical mass to support industry."**



Evens looks back at the early years of DPI. "DSM's goals were twofold. We wanted to build a high-profile and well-recognized knowledge centre in the Netherlands in the polyolefins field, as relatively little money was being invested in polyolefins research at the time and universities did not focus on it. And we wanted to be able to hire good people who already had a background in the field so that we would not need to train them ourselves. DPI has met these two objectives to a large extent." It took a while for universities and industry to get used to each other and to speak the same language. Industrial partners had to indicate very clearly what the fields were in which they wanted to look for improvements and they had to learn how to start such partnerships. All the time they sat at the table with their competitors and did not want to show their weaknesses or their specific interests. It took some time to find a workable approach. It also took some time to find a good way to distribute the available money in a generally accepted and well-balanced way.

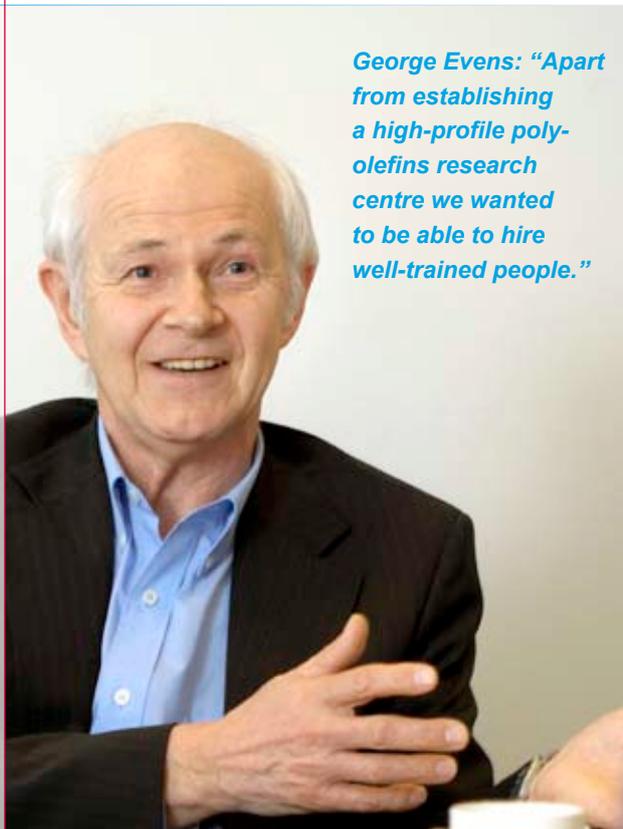
### Inconceivable

Looking at it from the other side, Peters' experience is slightly different. "In our view an adequate organization, put in place quickly and smoothly, enabled us to get a number of projects funded. Being able to hire not one but several PhD students

at the same time enabled us to build up critical mass in a short time so that our research programme really had an influence in the field. But there were also things that needed more time. In the chain of knowledge catalyst chemists and injection moulding experts are a world apart. Now, after ten years, we have almost reached the point where we can have the materials producers make materials with built-in specific properties by asking them the right questions. I now talk to professor Busico (Polyolefins), which would have been inconceivable five years ago. I have contacts with people in industry who are really helpful. In their labs they allow me to do experiments for which we do not have the right equipment."

The network, the availability of trained personnel and the critical mass of research groups are three of the original objectives DPI has met. These are complemented with two other goals of DPI: the build-up of an infrastructure and technical results. It is perhaps not so surprising that 'technical results' are mentioned last. Evens: "No miracles have happened in the field of catalysts and polymerization, but we have gained insight and that was our objective." Being a member of DPI means being a member of a community involved in a programme, not participating in only one project with a specific goal. "Still", says Peters, "we take industrial problems as a guideline. In a broad subject field you always have to make choices for research vehicles and there is no reason why these cannot be the ones of special interest to industry." Pater mentions an example of such a choice: "The modelling work by the Computational Fluid Dynamics group of Hans Kuipers at the University of Twente is focused on polymerization reactors because of the DPI programme. Without DPI, the models would have been the same, but they would have been less realistic and less directly applicable to polyolefins production." "But", adds Peters, "if Basell wants to use them in the future, they will have to hire people who can use them. Our field, rheology and computational rheology, is typically one where well-trained people can be of immediate use in industry. Because the knowledge is not yet available there." That is quite different from what Evens and Pater have just observed about DPI researchers coming to industry: they have the right background, but have to learn how to tackle specific problems in practice. After all, the production processes involve hundreds of variables.

*George Evens: "Apart from establishing a high-profile polyolefins research centre we wanted to be able to hire well-trained people."*



Luigi Balzano

## Crossing borders

**Innovation in polymers involves not only research in chemistry. Physics and mechanical engineering also play role. This interdisciplinary aspect is what attracts Luigi Balzano to DPI.**

After his studies in chemical engineering at the University of Naples (Italy), Luigi Balzano came to the Netherlands for his PhD project. "I wanted to acquire research experience outside of Italy. The Netherlands was an obvious choice because this country has a special reputation when it comes to research on plastic materials, not least because of the stamp that DPI has put on this research. DPI projects typically start from fundamental science but in the end they are aimed at solving real-life problems. In such projects you are given the chance to cross borders between disciplines. That I find a very attractive aspect."

After completing his PhD project, Balzano wanted to pursue an academic career and again chose for a DPI project, now as a Post Doc. His choice was now even more motivated. "I am passionate about science. The fact that research leads to useful products is motivating and satisfying, of course, but I also like to know and understand things. I am equally happy when my research solves a purely scientific problem. This is in line with the goals of DPI, one of which is to generate excellent knowledge. By publishing in high-quality journals we contribute to the image of DPI and attract other scientists and other companies. The fact that I can combine different fields - physics, chemistry and mechanical engineering - in one project definitely played a role. The advances in polymers today only come from the combination of disciplines. I could have joined a company, as I had some offers from industrial partners involved in my PhD project, but for now I prefer the freedom that working at a university gives me."

### Unique

In the group where he is working now a unique machine was built to investigate the relationship between process parameters and material properties. Balzano gets very excited when he tells about it: "We have the capability to apply shear to a molten polymer subjected to high pressures and then cool it down very fast. No one else in the world can do these experiments. In a smart way we can select processing conditions and materials optimized for a

certain application. I am the materials scientist studying the physical parameters in relation to the chemical composition of the materials. Mechanical engineers were involved in the making of the machine and chemists are involved in the optimization of the composition. The industrial partners participating in this project provide us with the materials, sometimes with special additives or with a special molecular weight distribution."

Balzano started this project early 2008. He is confident that he will be able to find another interesting position after this. The fact that he knows a lot of people from both industry and academia and that they know him will be of great help. Whether this position will be in industry or at a university in the Netherlands or elsewhere is still an open question. "The nice thing about the Netherlands is that there is no real boundary between an academic career and a career in a company. There is a continuous exchange between the two."

Luigi Balzano investigated the crystallization of polyolefins in flows during his PhD project at the Eindhoven University of Technology. In his present Post Doc position at the same university but in another group he is interested in the relationship between process parameters and product properties in polymer production processes.



*Luigi Balzano: "The advances in polymers today only come from the combination of disciplines."*

## Facts and figures

### Polyolefins: the never-ending story

#### Objectives

Polyolefins are the only class of macromolecules which can be produced catalytically with precise control of stereochemistry and, to a large extent, of (co)monomer sequence distribution. Therefore, as with the letters of the alphabet, the number of constituent elements which can be assembled into meaningful organized structures is infinite. In fact, polyolefin-based materials range from ultra-rigid thermoplastics to high-performance elastomers, having in common little else than the full atom economy in their synthesis, low cost, excellence in performance, long life cycle and ease of recycling. The research programme of this Technology Area studies polyolefin semantics in full width and depth, aiming at proficiency in the composition of ever new polyolefin best-sellers.

#### Subprogrammes

- **Catalysis**  
Investigation, screening and development of novel homogeneous and heterogeneous catalyst systems, new approaches for the immobilization and activation of heterogeneous and single site catalysts for polyolefin (co)polymerization.
- **Polymer Structure, Properties and Processing**  
Understanding, modelling and predicting structure-processing-property relationships of polyolefin polymer systems.
- **Polymer 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 polymerization processes.
- **New Methods and Exploratory Research**  
New characterization and polymerization methods, high-throughput screening and experimentation, embryonic research and concept development.

#### Partners industry

Borealis, Braskem, Dow, DSM, LyondellBasell, NPC Iran, Sabic, Shell, Symyx and Teijin Aramid.

#### Partners research

Delft University of Technology, Eindhoven University of Technology, University of Groningen, University of Twente, University of Amsterdam (all in the Netherlands), University of Naples Federico II and University of Perugia (Italy), ESPCE Lyon (France), University of Ottawa and University of Manitoba (Canada)

#### Budget and organization

Overall expenditure in 2007 was € 2.1 million (budget: € 2.4 million). Expenditure on equipment was € 660,000; a major investment was made in HTE PO catalyst screening equipment. The total number of FTEs allocated at the end of 2007 was 12 (25 researchers). Professor Busico is Scientific Chairman of the Technology Area and dr. Jan Stamhuis is Programme Area Coordinator.

#### Publications and inventions

In 2007 21 reviewed papers and one thesis were published in this Technology Area. In addition, three inventions were reported and one patent application was filed.

#### Projects

- #387: Advanced characterization of Ziegler-Natta catalysts on flat surfaces
- #495: Single-site catalyst immobilization using magnesium chloride supports
- #633: Understanding structure/performance relationships for non-metallocene olefin polymerization catalysts
- #635: Measuring active site concentration of olefin polymerization catalysts
- #638: Thermally stable olefin polymerization catalysts by reversible intramolecular alkyl shuttling
- #639: Quantity and quality of active sites in immobilized and solid olefin polymerization catalysts
- #132: The influence of melt memory in crystallization of polyolefins
- #637: Influence of entanglements on the flow behaviour of polyolefins
- #634: Characterization of the specific density of semi-crystalline polymers
- #354: Investigation of catalytic gas-phase olefin polymerization reactors, radioactive particle tracking and CFD studies
- #507: Comparison of slurry and gas-phase polymerization for HDPE: kinetics, chemical composition, molecular weight distribution

- #536: Dynamically controlled polymer structures
- #547: Experimental and computational study of high-pressure fluidization of polymeric materials
- #632: Experimental and computational study of dense gas fluidized beds with liquid injection
- #636: The study of the influence of the support, support preparation and initial conditions on olefin polymerization
- #641: High-throughput computational pre-screening of catalysts
- #642/643: Development of high-temperature 2-dimensional liquid chromatography for the characterization of polyolefins (jointly with the Corporate Research Technology Area)
- #644/645: High-throughput experimentation approaches to Ziegler-Natta-type catalytic olefin polymerizations (jointly with the HTE Technology Area)
- #646/647: New functionalized materials by Rh and Pd mediated carbene homopolymerization and olefin/carbene copolymerization (jointly with the Performance Polymers Technology Area)

## Output

### Theses

N. Kukalyekar  
Bimodal Polyethylenes for one pot synthesis; Effect of flow induced crystallization on physical properties

### Scientific publications

Andoni, J.C. Chadwick, H.J.W. Niemantsverdriet, P.C. Thüne  
A flat model approach to Ziegler-Natta catalysts for propylene polymerization and a preparation method of well-defined crystallites of MgCl<sub>2</sub>-supported catalysts  
*Macromol. Symp.* 260, 140-146

Andoni, J.C. Chadwick, H.J.W. Niemantsverdriet, P.C. Thüne  
A preparation method for well-defined crystallites of MgCl<sub>2</sub>-supported Ziegler-Natta catalysts and their observation by AFM and SEM  
*Macromol. Rapid Commun.* 28, 1466-1471

N. Kukalyekar, R. Huang, S. Rastogi, J.C. Chadwick  
Are MgCl<sub>2</sub>-immobilized Single-Center Catalysts for Polyethylene really Single-Center? Confirmation and Refutation using Melt Rheometry  
*Macromolecules* 40, 9443-9450

Di Martino, G. Weickert, T.F.L. McKenna  
Contributions to the Experimental Investigation of the Nascent Polymerisation of Ethylene on Supported Catalysts, Part I: A Quenched-Flow Apparatus for the Study of Particle Morphology and Nascent Polymer Properties  
*Macromolecular Reaction Engineering* 1, 165-184

Di Martino, G. Weickert, T.F.L. McKenna  
Contributions to the Experimental Investigation of the Nascent Polymerisation of Ethylene on Supported Catalysts, Part II: Influence of reaction condition  
*Macromolecular Reaction Engineering* 1, 229-242

Di Martino, J.-P. Broyer, D. Schweich, C. de Bellefon, G. Weickert, T.F.L. McKenna  
Design and Implementation of a Novel Quench Flow Reactor for the Study of Nascent Olefin Polymerisation  
*Macromolecular Reaction Engineering* 1, 284-297

R. Huang, C.E. Koning, J.C. Chadwick  
Effects of hydrogen in ethylene polymerization and oligomerization with magnesium chloride-supported bis(imino)pyridyl iron catalysts  
*J. Polym. Sci., Part A: Polym. Chem.* 45, 4054-4061

Mohammad A. Ali, Ben Betlem, Brian Roffel, Günter Weickert  
Estimation of the Polymerization Rate of Liquid Propylene using Adiabatic Reaction Calorimetry and Reaction Dilatometry  
*Macromolecular Reaction Engineering* 1, 3, 353-363

J.C. Chadwick, R. Huang, N. Kukalyekar, S. Rastogi  
Ethylene polymerization with combinations of early- and late-transition metal catalysts immobilized on MgCl<sub>2</sub> supports  
*Macromol. Symp.* 260, 154-160

L. Balzano, S. Rastogi, G.W.M. Peters  
Flow induced crystallization in iPP-DMDBS blends: implications on morphology of shear and phase separator  
*Macromolecules* 41(2), 399-408

Dirk R. Lippits, Sanjay Rastogi, Günther W. H. Höhne, Brahim Mezari, and Pieter C. M. M. Magusin  
Heterogeneous Distribution of Entanglements in the Polymer Melt and Its Influence on Crystallization  
*Macromolecules* 40(4), 1004 – 1010

Andoni, J.C. Chadwick, S. Milani, H.J.W. Niemantsverdriet, P.C. Thüne  
Introducing a new surface science model for Ziegler-Natta catalysts: Preparation, basic characterization and testing  
*Journal of Catalysis* 24, 129-136

A.K. Yaluma, J.C. Chadwick, P.J.T. Tait  
Kinetic and active centre studies on the polymerization of propylene using MgCl<sub>2</sub> supported Ziegler-Natta catalysts and 1,3 diether donors  
*Macromol. Symp.* 260, 15-20

Audrey Di Martino, Günter Weickert, François Sidoroff, Timothy F. L. McKenna  
Modelling Induced Tension in a Growing Catalyst/Polyolefin Particle: A Multi-Scale Approach for Simplified Morphology Modelling  
*Macromolecular Reaction Engineering* 1, 3, 338-352

Mohammad A. Ali, J. Stroomer, Ben Betlem, Günter Weickert, Brian Roffel  
Molecular Weight Distribution Broadening of Polypropylene by Periodic Switching of Hydrogen and Catalyst Additions  
*Journal of Applied Polymer Science* 108

Mohammad A. Ali, Ben Betlem, Günter Weickert, Brian Roffel  
Nonlinear Process Model Based Control of a Propylene Polymerization Reactor  
*Chemical Engineering and Processing* 46, 554-564

T. Schimanski, J. Loos, T. Peijs, B. Alcock, P.J. Lemstra  
On the overdrawing of melt-spun isotactic polypropylene tapes  
*Journal of Applied Polymer Science* 103, 2920-2931

Claudia Stern, Achim Frick, Günter Weickert  
Relationship between the structure and mechanical properties of polypropylene: Effects of the molecular weight and shear-induced structure  
*Journal of Applied Polymer Science* 103, 1, 519-533

S. Rastogi, D.R. Lippits, G.W.H. Höhne, B. Mezari and P.C.M.M. Magusin  
Role of the Amorphous Phase in Melting of Linear UHMW-PE: Implications for Chain Dynamics  
*J. Phys.: Condens. Matter* 19, 205122, 1-21

R. Huang, C.E. Koning, J.C. Chadwick  
Synergetic effect of a nickel diimine in ethylene polymerization with immobilized Fe-, Cr-, and Ti-based catalysts on MgCl<sub>2</sub> supports  
*Macromolecules* 40, 3021-3029

S. Rastogi, D.R. Lippits, A.E. Terry, P.J. Lemstra  
The role of the interphase on the chain mobility and melting of the semi-crystalline polymers; a study on polyethylene  
*Lect Notes Physics* 714, 285-327

*Filed patent applications*  
#455 V. Van Axel Castelli, R. Cipullo, S. Ronca, M. Amore, V. Busico, M. Gahleitner  
Compatibilized polyolefin compositions

*Reported inventions*  
#132 L. Balzano, N. Kukalyekar, G.W.M. Peters, S. Rastogi, P.J. Lemstra  
All polyethylene nano-composites

#505 P.J. Lemstra, T. Peijs, J. Loos, B. Tuerlings, C. Reynolds  
Polymer-polymer composites

#455 V. Van Axel Castelli, R. Cipullo, S. Ronca, M. Amore, V. Busico, M. Gahleitner  
Compatibilized polyolefin compositions



*Cor Koning: "The supply of high-calibre people is perhaps even more important than the actual project results."*

## Materials are matter put to use

Polymers that are used in products because of their structural properties are called performance polymers. They can for instance be used as a lightweight or easier-to-maintain alternative to metals, or they can be chosen because of their look and feel. A performance polymer's success in such applications depends on several factors, including not only the processing technology for the polymer but also the production technology for the product. DPI is a platform for discussing and influencing developments in this field.

Professor Sybrand van der Zwaag leads the Fundamentals of Advanced Materials group at Delft University of Technology (Netherlands). He is interested in materials used for applications in space. Both metals and polymers play a role in his work and for this reason he is involved in both DPI and the Materials Innovation Institute (M2I), the former Leading Technology Institute for Metals. Van der Zwaag: "I have learned that concepts in metals and polymers differ from each other. The kinetics of large molecules are, of course, essentially different from the kinetics of atoms. But now you see that polymer processing at ultra-high temperatures approaches the low-temperature regime of metal processing. This offers interesting opportunities in the form of composites and laminates."

For instance, Boeing is developing airplanes made of composite materials but for the time being it seems to be one of the few companies in the aerospace industry using such materials. An industry traditionally set up to process metals with the infrastructure to do this will not easily change to other materials. Van der Zwaag: "It is not just a composite's performance compared to metal that counts; the total cost of ownership –

product cost and maintenance cost throughout its lifetime - also plays a role in the decision. DPI can be involved with a portfolio of materials, but we should also look into the technological aspects." A real impact of new materials in industry is, after all, only possible when mass production methods are developed that comply with the industries' requirements. When a sub-assembly that formerly consisted of several metal parts can be made from polymer in a single step, this may seem an advantage. But if the technology for subsequent processing of the sub-assembly is not compatible with polymers, for instance if the polymer part cannot be coated in the same way as the metal assembly, the new material will not be used by industry despite all its advantages.

### Technology development

This aspect, the development of technology after a new material with better properties has been developed, is also one of the points dr. Josien Krijgsman, Polymer Properties scientist at DSM, brings to the table. She did her PhD project at the University of Twente (Netherlands) in the field of crystallization of polymers with a high glass transition temperature.

*Josien Krijgsman, DSM Geleen (NL)*



**Sybrand Van der Zwaag:**  
“Because DPI has the experience to identify good research groups it can be of use to companies changing their focus.”



“With hindsight I now see that in my PhD project the member industries, which were really interested in the properties of the materials that we developed, did not take the next step, namely develop that into a process. I think DPI can and should play a greater role in the transfer of research results to industry in that sense. With the extensive knowledge available within DPI a follow-up research project to come to more practical synthesis routes and processes could have been a solution.” Professor Cor Koning, who leads the Polymer Chemistry group at Eindhoven University of Technology, does not entirely agree with her. “It would be good to involve someone from the academic world for a while, but technology development is the responsibility of industry. They can do that better themselves. To give an example: some time ago we developed a new coating based on renewable raw materials, but we declined the request from industry to take this one step

further. It was no longer a challenge for us.” Whether or not the development work is continued by an industrial company depends largely on the price of the raw materials. If this goes down sufficiently, companies will take the step, is Koning’s opinion. (see the annual report 2006, pages 38-39).

Another example of a DPI project which has ‘landed’ well in the participating companies is the addition of nano-silica particles to polymers to improve their processability (see the annual report 2005, page 10). It is likely that in some cases a company starts a parallel project to investigate the more application-directed aspects of a technology investigated in the fundamental DPI project. “And what we should not forget in this respect”, adds van der Zwaag “are the indirect successes such as characterization and visualization technologies which are developed in DPI

projects and are subsequently used by companies to improve or speed up their own research and development projects. Such successes are not always visible to the outside world but they certainly exist."

### Research lines

An important point of attention in DPI is how to secure the continuity of research lines. In particular in a mature field such as materials research, four years (the duration of a PhD project) is not enough to bring about a serious change. Lines of research should be continued over longer periods. At the same time DPI has to go along with partner industries changing their product portfolios by attracting new groups with different fields of expertise. Van der Zwaag: "Because DPI has the experience to identify good research groups it can be of use to companies wanting to change their focus and looking for reliable and competent new external partners. This means that the groups participating in the DPI programme will also show changes with time." Koning remarks that new expertise is not always needed: "The research tools may remain the same when a company starts activities in a different part of the market. It is also our responsibility as research groups in DPI to keep these tools sharp to be able to employ them in a different field."

Of course it is also the responsibility of academia to start new research lines. Van der Zwaag has some interesting suggestions for research on performance polymers. "The combination of structural and functional properties in one material can lead to such interesting applications as airplane wings made of a photovoltaic material that can contribute to the energy supply of the plane. It may not be possible to combine the desired stiffness with the best photovoltaic materials but even if the yield is not optimal it will still be an interesting line of research." Another aspect of polymers that according to Van der Zwaag deserves attention is that they are often chosen for applications in which look and feel are important. It would be interesting to relate these choices to the molecular properties of the polymers and subsequently be able to design materials with a desired look and feel.

A useful return of DPI projects apart from the technical results is that after their DPI projects PhD student are very attractive employees for the industries involved. Krijgsman: "Within DSM we are constantly looking for good scientists. The network of DPI is an important source of new employees.

While working in a DPI project you get an idea of the atmosphere in the companies that are partners in this project and this may help you to decide for which company you would like to work after your PhD project." Koning adds: "People who are capable of addressing a problem at the molecular level but who at the same time understand and speak the language of all the specialists in the chain of knowledge will always be needed in industry. This supply of high-calibre people is perhaps even more important than the actual project results."

Yet the three participants in the discussion are of the opinion that the participating industries do not always get the most out of their involvement in DPI. There are a lot of meetings – cluster meetings, technology area meetings, annual meetings. But these are all organized in a way that reflects the organizational structure of DPI. Van der Zwaag suggests: "Perhaps a day devoted to a certain company will help to intensify contacts. This company could then choose from all the DPI projects leaders whom they would want to meet."

Koning ends the discussion by stating that from an organization that supplied money to make all his research dreams come true DPI has now become a discussion platform that he would not want to miss.



*Josien Krijgsman: "I think DPI can and should play a greater role in the transfer of research results to industry."*

Montserrat (Montse) Alvarez Grima

## Keeping in touch

The network of industrial and academic contacts that DPI provides helped Montserrat Alvarez Grima during her PhD project to get an idea of what it would be like to work in industry.

*Montse Alvarez Grima:*  
"DPI is a good platform to boost a very open and motivating research atmosphere and offers the opportunity to build a very valuable network."

Montse Alvarez Grima studied chemistry in Barcelona (Spain) at the Institut Quimic de Sarria of Universitat Ramon Llull. For her Master's thesis she worked in the Netherlands for nine months, in the rubber technology group of prof. Jacques Noordermeer at the University of Twente. "I liked the atmosphere in the group and the freedom that researchers have here in the Netherlands, so when I was offered a PhD position in Twente I did not have to think long about accepting it." It was a DPI project in which Dutch companies such as DSM and Akzo Nobel were involved as industrial partners. She valued their input. "The contact persons from the companies were almost always present at project meetings which were held four or five times a year. They were interested in the project, very open and very helpful. As a PhD student you tend to think very scientifically, of course, but your lack of experience in the field limits your vision. Their input provided me with a broader view. For example, they suggested experiments that not only gave me scientific answers I would not have gotten otherwise, but also helped me bring my research into applications closer to reality. As a result of this good interaction, we filed two patent applications at the end of my PhD research. The discussions between people from different companies who not always have the same ideas and interests sometimes resulted in a very interesting and fruitful interaction from which I learned a lot. In a way, it prepared me for working in a company, where I also often have to defend my point of view."

### Profile

After defending her thesis she decided that she would like to work in industry. One of the possible companies to work for was DSM. She knew about the company through her contacts during the DPI project and through professor Noordermeer, who is a part-time consultant at DSM. "I heard about DSM's Technology Talent Pool and I applied for it. I went to DSM for one day, where I was interviewed. We listened to company presentations and we had some workshops in small groups. During such an event the company gets to know you and you get to know the company. When your profile looks good and a job fitting with your background turns up, they invite you to apply for that job. DSM might have consulted the contact persons of my project, but they were not directly involved in the application process. What did help me to decide to apply for a job in the first place was that I knew the company and knew its values

and the quality of its research work. When I started working I already knew some faces and that was also nice."

Although she cannot really compare it with working in Spain, her home country, since working at DSM is her first work experience after finishing her PhD, Grima thinks that the atmosphere in the Netherlands, in both universities and companies, is very open and motivating. "DPI offers a good platform to boost that positive atmosphere. The organization is well-structured and it offers the opportunity to build a network which is very valuable to me and to anyone working in the polymer field. Through DPI I know a lot of people in universities and companies, also outside the Netherlands. And now that I am a DSM contact person in other DPI projects I can help PhD students with their projects. In addition, through these contacts I also keep in touch with what is going on at the universities. It keeps me fresh."

During her PhD project Montse Alvarez Grima studied new co-agents for peroxide cure of saturated elastomers which provided a combination of the advantages of peroxide and sulphur vulcanization. At DSM she is now working in research in the field of performance materials, as project leader for Petroleum Additives.



*Montse Alvarez Grima,  
DSM Geleen (NL)*

Michael de Graaf, Ellen Donkers  
Pavel Shutov

## The human element

Dow Benelux BV has been involved in DPI from the start. It is no surprise to find a few former DPI project champions among the company's employees. Ellen Donkers and Michael de Graaf defended their theses at Eindhoven University of Technology (Netherlands) in 2006 and 2002, respectively. Both are currently doing product development work in the New Products Group of Dow's Core R&D organization, where they try to relate structure parameters to desired end properties of polymer materials. Pavel Shutov, who worked as a Post Doc on a DPI project at the University of Groningen (Netherlands), is looking into the role renewable materials can play in foams.

Donkers: "When you start working for Dow you can participate in the Research Assignments Program. Young, newly appointed researchers typically work on four different projects in four different research groups, spending a few months in each group. Both Pavel and I successfully completed this programme. The idea

is that you get to know the organization, the different product groups and the way of working at the different locations. And of course you build up a network of R&D and business unit people involved in these projects. After each project there is an evaluation phase in which you report what you liked and what you didn't like in the project. The people you worked with report back about their experiences with you. You can give a preference for a next project. I worked in product and process R&D and TS&D departments and went to Tarragona in Spain." In her DPI project Donkers was involved in a project with Kraton, which was one of the DPI partners at that time. "I felt more part of Kraton than of DPI, probably because DPI's rubber technology activities mostly took place at the University of Twente in the Netherlands, and I was working in Eindhoven."

"It really is a great experience and very good for your network. I worked in projects in the Netherlands and Germany that dealt with polystyrene, synthetic rubber and polyether polyols among other things. By working in a few different projects and getting an idea of what it would be like to work there, you can make a conscious choice and will end up in a place where you feel at ease and really want to work", Shutov adds.

*Pavel Shutov: "It really is a great experience and very good for your network."*



## Open innovation

For De Graaf DPI was his natural environment. He did his PhD project in the group of professor Piet Lemstra. After this he worked for two years in what used to be the Kunststoffsuis and is now called PTG (Polymer Technology Group) Eindhoven, a DPI partner. During that period he met dr. Rudy Koopmans of Dow, who convinced him to join Dow. Like his colleagues, De Graaf is a firm believer in networking. "In Dow we advocate a sort of open innovation attitude. When I am stuck with a question I can approach any colleague, wherever they are located in R&D. Together we develop new products. We join forces and share our knowledge. The only condition in developing products is that they have to be profitable for Dow."

In their present jobs the three Dow employees have deviated from the line of research they pursued at university. Shutov first moved from fundamental research into applied science as a Dow employee after doing a Post Doc in Groningen. At Dow he is now involved in large-scale synthesis, processing and testing of low-cost renewable green chemicals. "But", as Donkers formulates it, "It does not matter that you do not build on the specialism of your university project while working here. You learn the methodology at university; you apply it here but not necessarily in the same field of research." De Graaf agrees with this. "Through my experience at DPI and the Kunststoffsuis I learned how companies work, including small and medium sized ones. I learned the variety of questions they had. In my first job at Dow I had a relatively large administrative task and was involved with research from the sideline. Now I am in R&D again, and happily so."

The key points of DPI's value to Dow are that Dow gets direct access to exploratory type research done at leading European universities and research institutes. Also, through the DPI platform Dow has been able to start a number of separate bilateral research projects. Furthermore, DPI gives Dow access to many PhD students and Post Docs and over the years this has resulted in quite a number of new hires of former DPI people into the company – people such as Ellen, Pavel and Michael. They are part of the 'Human Element' that Dow considers all-important.

Ellen Donkers worked on block copolymers with polar and non-polar blocks during her DPI project at Eindhoven University of Technology. At Dow she is now involved in an exploration effort to identify suitable



*Ellen Donkers: "You learn the methodology at university; you apply it here but not necessarily in the same field of research."*

*Michael de Graaf: "Together we develop new products. We join forces and share our knowledge."*

market opportunities for a newly developed material and gain an understanding of structure-property relationships in thermosets.

Michael de Graaf investigated transmissive and emissive amorphous polymer waveguides in his DPI project at Eindhoven University of Technology. He is now involved in concept development for high-throughput experimentation and identifying processing improvements and new market areas for a novel Dow proprietary polymer.

Pavel Shutov did a PhD project in the field of element-organic and inorganic semiconductor chemistry in Marburg (Germany) and completed a Post Doc project at the University of Groningen on boralumoxane activators for metallocene catalysts. He is now working to establish a feasible production process for polyols using 50% wt. renewable materials.



## Facts and figures

### Objectives

Performance Polymers (PP) are able to fulfil part and assembly performance requirements through close cooperation between polymer supplier, converter and end-user. This requires a thorough understanding of polymerization, polymer modification as well as polymer processing, properties and design. This is reflected in the strategy and objectives of the Performance Polymers Technology Area, which include investigations related to fundamental issues in the value chain using a 'chain of knowledge' approach.

### Subprogrammes

- **Polymer and network chemistry and modification**

Studies related to important industrial and societal issues, i.e. an increase in the use of sustainable materials on the one hand and cost and energy reductions in polymerization and network formation on the other. New concepts for monomer and polymer molecular structure to achieve step changes in the balance of flow, static and dynamic mechanical and other functional properties.

- **Processing for properties**

Understanding of the relationship between the molecular structure, processing and properties of polymers. Studies of the processing effects of intermolecular interactions, e.g. hydrogen bonding. Processing and vulcanization studies of elastomer blends. Investigations to elucidate friction and wear mechanisms for thermoplastic and elastomer systems.

- **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, friction and wear of fibre-reinforced thermoplastics and elastomers.

- **Stability and long-term performance**

Investigations of the chemical and physical ageing mechanisms and their interplay with the ultimate objective of predicting lifetime and realizing fit-for-use design over the entire life cycle.

### Partners Industry

BASF, Bayer, Evonik Degussa, Dow, DSM, GE Plastics (now Sabic IP), LyondellBasell, Océ Technologies, Shell, SKF, Teijin Aramid.

### Partners research

Delft University of Technology, Eindhoven University of Technology, University of Groningen, University of Twente (all in the Netherlands), Deutsches Kunststoff Institut DKI (Germany), ESPCI Paris (France), IPF Dresden (Germany), Queen Mary University of London and University of Birmingham (UK).

### Budget and organization

Expenditure in 2007 totalled € 1.9 million (budget: € 3.0 million). A total of € 0.3 million was spent on equipment; a major investment was made in mini-processing equipment.

The total number of FTEs allocated at year-end 2007 was 18 (36 researchers). Ir. Richard van den Hof and professor Jacques Noordermeer acted as Scientific Chairmen of the Performance Polymers Technology Area and dr. Jan Stamhuis was Programme Area Coordinator.

### Publications and inventions

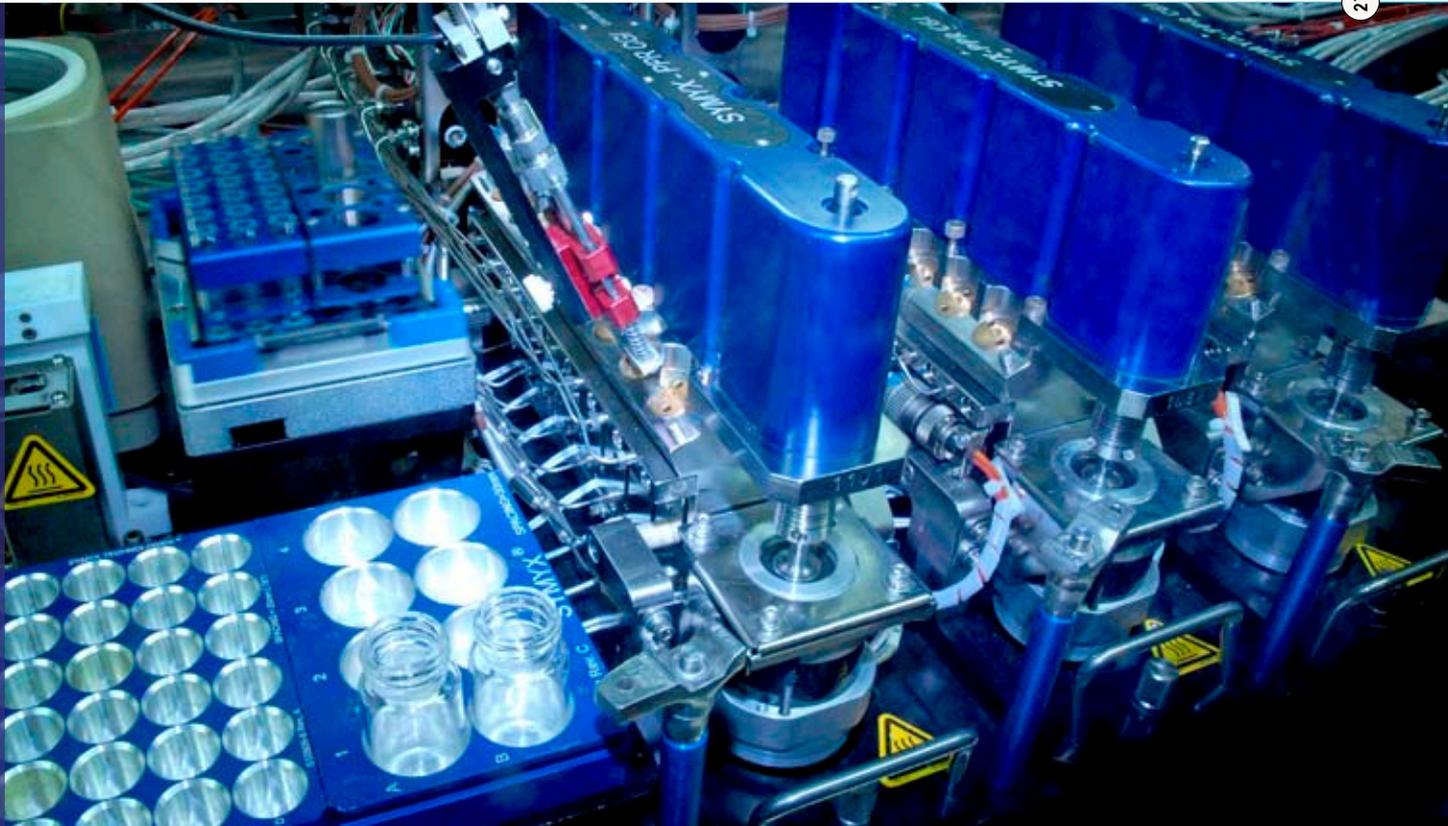
A total of 37 reviewed papers and 6 theses were published in the Technology Area. Eight inventions were reported and two patent applications were filed.

### Projects

- #356: Investigations on blending, reinforcement and curing in EPDM/ NR/ BR rubber compound for the tire side-wall application
- #432: Improved catalysts for controlled propylene oxide polymerization
- #479: Tri-block copolymers with crystallizable amide segments
- #537: Sub-micrometer thermoplastic vulcanizates
- #580: Modification/crosslinking of saturated elastomers using functionalized azides
- #585: The 'sticky blocks' concept, furnishing EPs with enhanced processability
- #647: New functionalized materials by Rh and Pd mediated carbene homopolymerization and carbene/olefin copolymerization (jointly with the Polyolefins Technology Area)

- #649: Thermoplastic elastomers via living radical graft polymerization from functional elastomers
- #651: Smart surface modifiers for engineering plastics
- #653: Bio-degradable thermoplastic polyurethanes from renewable resources
- #656: Green rigid blocks for engineering plastics with enhanced performance
- #650: Molecular modelling of cavitation in polymer melts and rubbers
- #317: Low surface energy rubber materials based on (per)fluorinated polyethers
- #584: Micro friction and wear of polymers
- #654: Effects of the nano-scale structure of polymer surfaces on their adhesion and friction properties
- #460: Influence of pressure on hydrogen bonded polymers; polyamides and polyurethanes
- #582: Encapsulation of reactive chemicals for the design of self-healing engineering plastics
- #583: Dispersion of fillers in engineering polymers for thermal, electrical and rheological properties
- #616: Flow of particle-filled viscoelastic fluids in complex geometries
- #623: Fundamental aspects of nano-composites
- #648: Graphene-based nano-composites
- #652: Rubber/silica nano-composites via reactive extrusion
- #664: Sustainable elastomers and thermoplastics by short-cut fibre reinforcement

*High-throughput experimentation in polyolefins research at the University of Naples Federico II (I)*



## Output

## Theses

M. Mikrut  
Low Surface Energy Rubber Materials. Relationship between network architecture and tack of silicone rubbers

N. Grossiord  
A latex-based concept for making carbon nanotube/polymer nanocomposites

M. Montserrat Alvarez Grima  
Novel Co-agents for Improved Properties in Peroxide Cure of Saturated Elastomers

J. Devroede  
Study of the THF formation during the TPA-based synthesis of PBT

F. Romana De Risi  
The role of co-agents in peroxide cured thermoplastic vulcanizates. Exploring fundamental routes towards corresponding dynamically vulcanized PP/EPDM blends

M. van der Mee  
Thermoreversible Cross-linking of elastomers; a comparative study between ionic interactions, hydrogen bonding and covalent cross-links

## Scientific publications

J. Meuldijk, A.J.M. van Dijk, R. Duchateau, C.E. Koning  
A novel production route for Nylon-6: Aspects of catalysis and process development  
Macromol. Symp. 239, 164-173

K. Sahakaro, N. Naskar, R.N. Datta, J.W.M. Noordermeer  
Blending of NR/BR/EPDM by reactive processing for tire sidewall applications. I. Preparation, cure characteristics and mechanical properties  
Journal of Applied Polymer Science 103, 2538-2546

K. Sahakaro, A.G. Talma, R.N. Datta, J.W.M. Noordermeer  
Blending of NR/BR/EPDM by reactive processing for tire sidewall applications. II. Characterization  
Journal of Applied Polymer Science 103, 2547-2554

K. Sahakaro, R.N. Datta, J. Baaij, J.W.M. Noordermeer  
Blending of NR/BR/EPDM by reactive processing for tire sidewall applications. III. Assessment of the blend ozone- and fatigue-resistance in comparison with a conventional NR/BR blend  
Journal of Applied Polymer Science 103, 2555-2563

J. Yu, K. Lu, E. Sourty, N. Grossiord, C.E. Koning, J. Loos  
Characterization of conductive multiwall carbon nanotube/polystyrene composites prepared by latex technology  
Carbon 45, 2897-2903

N. Grossiord, J. Loos, J. Meuldijk, O. Regev, H.E. Miltner, B. van Mele, C.E. Koning  
Conductive carbon-nanotube/polymer composites: spectroscopic monitoring of the exfoliation process in water  
Comp. Sci. & Techn. 67, 778-782

D.P.N. Vlasveld, W. Daud, H.E.N. Bersee, S.J. Picken  
Continuous fibre composites with a nanocomposite matrix: Improvement of flexural and compressive strength at elevated temperatures  
Composites Part A: Applied Science and Manufacturing 38, 730-738

J. Yu, N. Grossiord, C.E. Koning, J. Loos  
Controlling the dispersion of multi-wall carbon nanotubes in aqueous surfactant solution  
Carbon 45, 618-623

W.G.J. van Pelt, J.G.P. Goossens  
Depolymerization behavior of thermoplastic poly(urethane) (TPU) and its dependence on initial molecular weight  
Anal. Chim. Acta 604, 69-75

E. Tufekcioglu, R.P. Koster, D.P.N. Vlasveld, R. Jongboom  
Designing sustainable products using bio-based nanocomposites  
Plastics Encounter @ ANTEC 2007- Proceedings of the 65th Annual Technical Conference and Exhibition 914-917

Nadia Grossiord, Paul van der Schoot, Jan Meuldijk, Cor Koning  
Determination of the surface coverage of exfoliated carbon nanotubes by surfactant molecules in aqueous solution  
Langmuir 23, 3646-3653

F.R. Risi, J.W.M. Noordermeer  
Effect of methacrylate co-Agents on peroxide cured PP/EPDM thermoplastic vulcanisatie  
Rubber chemistry and technology 80, 83-99

M. Prusty, B.J. Keestra, J.G.P. Goossens, P.D. Anderson  
Experimental and computational study on structure development of PMMA/SAN blends,  
Chem. Eng. Sci. 62(6), 1825-1837

D. Husken, J. Feijen, R.J. Gaymans  
Hydrophilic segmented block copolymers based on poly(ethylene oxide) and monodisperse amide segment  
Journal of polymer science, part A 45(19), 4522-4535

J.M. van der Schuur, R.J. Gaymans  
Influence of morphology on the properties of segmented block copolymers  
Polymer 48(7), 1998-2006

W.B. Wennekes, R.N. Datta, J.W.M. Noordermeer  
Investigation on the adhesion between treated reinforcing cords and rubber  
Kautschuk und Gummi, Kunststoffe 60, 20-23

W.B. Wennekes, J.W.M. Noordermeer, R.N. Datta  
Mechanistic investigations into the adhesion between RFL-treated cords and rubber. Part I: the influence of rubber curatives  
Rubber chemistry and technology 80, 545-564

W.B. Wennekes, J.W.M. Noordermeer, R.N. Datta  
Mechanistic investigations into the adhesion between RFL-treated cords and rubber. Part II: the influence of the vinyl-pyridine content of the RFL-latex  
Rubber chemistry and technology 80, 565-579.

A.J. Zielinska, J.W.M. Noordermeer, A.G. Talma  
Modification and crosslinking of saturated elastomers using functionalized azides  
XIIth International Science and Technology Conference: Elastomers 2007, 14-16 November, Warsaw, Poland

J.A.W. van Dommelen, W.A.M. Brekelmans, L.E. Govaert  
Multiscale modelling of the mechanical behaviour of oriented semicrystalline polymers  
Materials Science Forum 539, 2607-2612

N. Grossiord, H.E. Miltner, J. Loos, J. Meuldijk, B. van Mele, C.E. Koning  
On the crucial role of wetting in the preparation of conductive polystyrene-carbon nanotube composites  
Chem. Mater. 19, 3787-3792

J. Loos, N. Grossiord, C.E. Koning, O. Regev  
On the fate of carbon nanotubes: morphological characterizations  
Comp. Sci. & Techn. 67, 783-788

M. Diepens, P. Gijsman  
Photodegradation of bisphenol A polycarbonate  
Polym. Degr. Stab 92(3), 397-406

G.J.E. Biemond, J. Feijen, R.J. Gaymans  
Poly(ether amide) segmented block copolymers with adipic acid based tetra amide segment  
Journal of applied polymer science 105(2), 951-963

A.J.M. van Dijk, T. Heyligen, R. Duchateau, J. Meuldijk, C.E. Koning  
Polyamide synthesis from 6-aminocapronitrile, Part 1: N-alkyl amide formation by amine amidation of a hydrolyzed nitrile  
Chem. Eur. J. 13, 7664-6772

M.A.G. Jansen, L.H. Wu, J.G.P. Goossens, G. De Wit, C. Bailly, C.E. Koning  
Preparation and characterization of poly(butylene terephthalate)/poly(ethylene terephthalate) copolymers via solid-state and melt polymerization  
Journal of Polymer Science Part A: Polymer Chemistry 45, 882-899

W.C.J. Zuiderduin, J. Huetink, R.J. Gaymans  
Pre-yield tensile set of a semi-crystalline polymer, its blend and composite  
Journal of materials science 42, 4131-4135

R.P. Koster, E. Tufekcioglu, D.P.N. Vlasveld  
Product design support for nanocomposite materials application  
Plastics Encounter@ANTEC 2007 - Proceedings of the 65th Annual Technical Conference and Exhibition 864-868

M.M. Alvarez Grima, J.G. Eriksson, A.G. Talma, R.N. Datta  
Property improvement in Peroxide Vulcanization. A synergistic concept of co-agents for scorch delay  
Kautschuk und Gummi, Kunststoffe 60, 235-240

K. Sahakaro, N. Naskar, R.N. Datta, J.W.M. Noordermeer  
Reactive blending, reinforcement and curing of NR/BR/EPDM compounds for tire sidewall applications  
Australian Plastics & Rubber Institute Journal 12-22

K. Sahakaro, N. Naskar, R.N. Datta, J.W.M. Noordermeer  
Reactive blending, reinforcement, and curing of NR/BR/EPDM compounds for tire sidewall applications  
Rubber chemistry and technology 80, 115-138.

J. Krijgsman, G.J.E. Biemond, R.J. Gaymans  
Segmented copolymers of uniform tetra-amide units and poly(phenylene oxide) by direct coupling  
Journal of applied polymer science 103, 512-518.

R. Duchateau, W.J. van Meerendonk, S. Huijser, B.B.P. Staal, M.A. van Schilt, G. Gerritsen, A. Meetsma, C.E. Koning, M.F. Kemmere, J.T.F. Keurentjes  
Silica-grafted diethylzinc and a silsesquioxane-based zinc alkyl complex as catalysts for the alternating oxirane-carbon dioxide copolymerization  
Organometallics 26, 4204-4211

S.J. Picken, D.P.N. Vlasveld, H.E.N. Bersee, C. Ozdilek, E. Mendes  
Structure and mechanical properties of nanocomposites with rod and plate shaped nanoparticles  
Philippe Knauth & Joop Schoonman (Eds.), Nanocomposites: Ionic Conducting Materials and Structural Spectroscopies Springer. 10

M. Prusty, B.J. Keestra, J.G.P. Goossens, P.D. Anderson  
Structure development of PMMA/SAN blends  
Chem. Eng. Sci. 62, 1825-1837

M.A.G. Jansen, L.H. Wu,  
J.G.P. Goossens, G. de Wit, C. Bailly,  
C.E. Koning  
The Preparation and Characteriza-  
tion of Copolymers of Poly(butylene  
terephthalate) and Poly(ethylene  
terephthalate) via Solid-State  
Polymerization and Melt  
Polymerization  
J. Pol. Sci., Pol. Chem. Ed.  
45, 882-899

R.M.A. l'Abée, J.G.P. Goossens,  
M. van Duin  
Thermoplastic Vulcanizates by  
Reaction-Induced Phase Separation  
of a Miscible Poly(e-caprolactone)/  
epoxy system,  
Rubber Chem. Technol  
80(2), 311-323

*Filed patent applications*  
#582 S.D. Mookhoek,  
S. van der Zwaag, H.R. Fischer  
Polymeric material comprising  
multiple cavities

#416 N. Grossiord, C.E. Koning,  
J. Loos, A.J. Hart  
Carbon nanotube reinforced polymer

*Reported inventions*  
#380 J. Devroede, R. Duchateau,  
G. de Wit, C.E. Koning  
Synthesis of poly(butylene  
terephthalate)

#416 N. Grossiord, C.E. Koning,  
J. Loos, A.J. Hart  
Carbon nanotube reinforced polymer

#583 S.G. Vaidya, S. Rastogi  
High conductivity polyaniline  
compositions

#356 H. Zhang,  
J.W.M. Noordermeer, R. Datta,  
A. Talma  
Grafting of EPDM

#582 S.R. White, S.D. Mookhoek,  
S. van der Zwaag, H.R. Fischer,  
N.R. Sottos, B.J. Blaiszik  
Multi-capsule system

#603 + #460 J.A.W. Harings,  
Y. Deshmukh, E. Vinken, S. Rastogi  
Polyamide with reduced crystallinity

#582 S.D. Mookhoek,  
T.J. Dingemans, H.R. Fischer,  
S. van der Zwaag  
Self-healing polymers

#537 R.M.A. l'Abée,  
J.G.P. Goossens, M. van Duin,  
A. Spoelstra  
Sub-micrometer thermoplastic  
vulcanizates

Lada Kurelec, Technical Marketing HDPE Pipe, SABIC Europe

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*Jan Kroon: "It is very important that research groups with complementary backgrounds find each other and need each other."*

## Renewable energy from organic photovoltaic devices

Global energy consumption is expected to be double between now and 2050. At the same time, harmful emissions have to diminish. To realize this, a variety of renewable energy sources will have to be used, with solar energy contributing to the energy mix. What could be the role of organic photovoltaic devices in this field? And what needs to be done to make this possible?

The research to answer these questions is carried out in the Organic Photovoltaics cluster of the Functional Polymer Systems Technology Area. Dr. Jan Kroon, coordinator of polymer solar cell research in the Energy Research Centre of the Netherlands (ECN), starts the discussion: "Ninety per cent of solar cells sold today are based on silicon technology. Yet there is a need for a less expensive technology and organic photovoltaics hold that promise. Silicon may go down in manufacturing costs from the present € 2/Watt-peak to well below € 1/Watt-peak, but a technology that could realize substantially less than € 0.50/Watt-peak certainly has great potential. It is, however, a high-risk, high-potential research project. The technology that is developed should eventually compete with fossil fuel based electricity generation, which currently costs € 0.30/Watt-peak."

Joost Smits, who works with Shell Global Solutions International in Innovation and Research, adds: "It is not just the cost price that determines whether a technology can be introduced successfully. Organic solar modules can be lighter than inorganic ones, they can be flexible and this opens up niche markets. Foils on windows or worked into clothes can realize applications you cannot have with silicon solar cells. This is a good starting point for further development of the technology and for reducing the cost price of the devices. I do not think that organic cells will replace silicon cells, because silicon cells have a higher efficiency and a much longer lifetime. In addition, the current PV industry benefits from economies of scale. A new technology does not have that advantage." However, in specific applications where its efficiency and lifetime are sufficient, the technology may enter the market and from there it could penetrate further.

### Different

Looking at what still has to be done to realize viable organic solar cells, Professor Paul Blom, who leads the research group on Physics of Organic Semiconductors at the University of Groningen (Netherlands), says: "It will take another five to ten years to get the efficiency and the lifetime of organic solar cells to 10% and 10 years, respectively. By that time a large part of the market will be claimed by silicon and organic solar cells will not replace silicon cells, just as organic electronic circuits will not replace silicon chips. These will remain different markets with different applications. There is a big difference between the two though: organic electronic circuits will never reach the performance of silicon chips because of a fundamental

limit in the charge carrier mobility in organic material. For the efficiency of solar cells there is no such limit that prevents organic cells from reaching the same efficiencies as inorganic cells. But the inorganic ones simply have a head start." Apart from the lifetime and efficiency aspects it also has to be demonstrated that the technology to make large organic cells on a large scale is available and sufficiently economical.

The possibilities for improving lifetime and efficiency depend largely (but not entirely) on the materials from which the devices are made. Improving the presently used materials can result in an efficiency of 7% or 8% and by using cells in a tandem configuration the efficiency could become more than 10%. By using different materials that absorb sunlight in different parts of the spectrum the efficiency can be further improved. Blom: "The problem is that when you change one property of a material to make it better, another property is usually worse than it was. The field is progressing through a steady stream of small improvements rather than because of spectacular breakthroughs." Progress is being made not only in understanding the physical processes in the devices, but also in the tools to visualize the morphology of the material. If a material does not perform as expected, there usually is something wrong with the morphology. The next step will be to try to unravel why the morphology is as it is. That will help to ultimately control the material synthesis completely.

### Critical mass

An EET project in the late 1990s put solar cell research in the Netherlands on the map, but it was due to DPI's support that it could continue after 2003. Blom: "Thanks to DPI we have been able to continue the photovoltaics research over the past six years." In neighbouring countries solar cell research gained ground, while in the Netherlands the infrastructure and the expertise built up in the EET project was threatened to be lost. And it would have been lost if DPI had not decided to support this research field. Smits: "You need critical mass and a sustained effort for a research project to be successful. It is a long-term research programme of course."

The organic photovoltaic project is successful because all links in the chain of knowledge are represented: making the materials, understanding the photo physics and the device physics, scaling up the process and testing the products. Kroon is very much in favour of such an approach: "It is very important that research groups with complementary backgrounds find each other.

They need each other in such large-scale projects as the EET project and the integrated projects in DPI with numbers 323, 326 and 524. It will become more difficult to achieve that kind of cooperation in the near future. There are two reasons: instead of one integrated project, which would have our preference, a number of smaller projects have been granted. In addition, the supply of new materials in sufficient quantities is stagnating. It is difficult to work together if you cannot all use the same materials." Blom adds: "In the integrated project, we kept each other well informed to prevent situations where two groups did the same research. Today, when some of us work with materials owned by companies that want to keep them secret, this will be more difficult. But it is not just the secrecy that troubles us. The synthesis of new materials is difficult and therefore less reproducible, which means that we cannot work with exactly the same materials. Fortunately we have a basis to start from: we know the added value of each other's contributions in the past."

#### Leading

Despite the challenges that the materials supply brings along, Blom, Kroon and Smits agree that the Netherlands has a leading position in organic photovoltaics, in particular in morphology, device

physics and characterization. It would be a pity if that leading position suffered from a lack of good new materials. DPI hopes to convince materials suppliers to make their materials more readily available for research purposes. In the end everyone will profit from a better understanding. Blom stresses this: "If I were a chemical company, I would make a new material, patent it and then distribute it to as many research groups as possible to get as much information about it as possible. Then it might even become a standard."

Whether companies will do this depends for a large part on the answer to the question who earns the money at the end of the day: the materials supplier or the device maker? It is a delicate balance. Kroon: "This might explain the reluctance of some materials suppliers to make their materials available. I am not sure these companies get back what they expect from DPI. I do not even know what they expect or want in return for their financial contribution." Blom wonders about the low profile of some industrial DPI members: "Even if companies participate only to be informed about what is happening in the field, you would expect them to ask questions, to invite researchers to the company and ask them to explain their results to a larger group than the one or two people directly involved. But this hardly ever happens. That kind of interest I miss a bit."

*Paul Blom: "Thanks to DPI we were able to continue the photovoltaics research the past six years."*



*Joost Smits: "You need a critical mass for a research project to be successful."*

*Cristina Tanase: "It is nice to see how all the things I learned and the experiences accumulated from other projects come together in a device."*



Cristina Tanase

## One step further

**Cristina Tanase left her home country Romania in 2001 to do a PhD project at the University of Groningen (Netherlands), where she worked for four years in the Physics of Organic Semiconductors group headed by Professor Paul Blom. After defending her thesis it seemed a natural step to join Philips Research to continue working in the same field.**

Tanase enthusiastically explains what her DPI project in Groningen was about. "Starting from organic semiconducting materials and their properties we wanted to understand how the devices made of these materials worked. I studied two types of devices, organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). We found a connection

between the charge transport in these devices and demonstrated that the strong increase in mobility with increasing charge density is responsible for the large mobility differences observed between OLEDs and OFETs. This had not been shown before and it was not obvious. The charge transport characteristics are also very much related to the morphological and energetic disorder present in the polymer film. The morphology, and consequently the charge transport, is very different in different directions."

When Tanase started her project the clean room in Groningen where devices could be processed was not yet ready, so she did experiments with OFETs made in the clean room of Philips Research, one of the DPI partners in her project.

It must have been a very close and fruitful collaboration, since Dago de Leeuw of Philips Research eventually became her co-supervisor when she defended her thesis. Did that help her to get her present job? "In a way it did, but not directly. Of course, I knew people, they knew me and I was familiar with their way of working, but like everybody else I wrote an open application. After one day of interviews Philips Research decided I could come to work for them and I could choose between two positions: one building on the expertise I had acquired in Groningen and another in a completely different subject field. I preferred the first one. Remaining in the same subject field but working in a different environment was enough of a change for me."

#### Broader task

Tanase is implying that there are differences between working in a university and working in industry, even when this work is in a research environment. "At the university I focused on a very small research area. I tried to gain a fundamental understanding of processes taking place in materials. Here at Philips Research I have a much broader task. Together with my colleagues I work on developing new technologies for OLEDs. I have to take more of an overall view and connect different topics. It is nice to see how all

the things I learned during my PhD project and the experiences accumulated from other projects come together in an application, in a device."

For Tanase the choice to work for an industrial company and not pursue an academic career was clear. Her involvement with DPI and its industrial partners helped her to make that choice. "I had been thinking about what I wanted to do after my PhD and my choice was clear - to go one step further from fundamental research towards more application-oriented work in an industrial environment.

I also knew that I did not want to go and work in a factory right away, so the choice for Philips Research was a logical one. After a few years working in this field I will move on to maybe another subject, which will probably be more in the direction of technology development. But what I will be doing twenty years from now... I don't know, it depends. I like my job and I like my two children... the two are not in conflict with each other.

Cristina Tanase did her PhD project at the University of Groningen, where she investigated charge carrier transport in organic electronic devices. She is now working at Philips Research and is involved in developing new technologies for organic light-emitting diodes.

**PHILIPS**

*Cristina Tanase Research Scientist Photonic materials & devices, Philips Research and Frank Pasveer, Senior Scientist System in package devices, Philips Research*



## Facts and figures

### Objectives

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 four sub-programmes.

### Subprogrammes

- **Polymer lighting and field-effect transistors**

The aim of this sub-cluster 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, the influence of self-assembled monolayers at interfaces and theoretical device modelling. Furthermore, this sub-cluster is open to cutting-edge research on highly conductive (transparent) electrodes based on conductive blends with low filler grades (< 2 vol%).

- **Polymers for information and communication technology**

The objective of this sub-cluster is the structuring of polymers on 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 (solar cells)**

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

- **Responsive materials, sensors and actuators**

The aim of this sub-cluster 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. Furthermore, new materials and devices for selective sensing of gases, time-temperature, biofluids, etc. are targeted and, last but not least, actuating principles of materials and corresponding devices are explored. This subprogramme always strives for proof of principle demonstration in prototype devices.

### Partners industry

The Netherlands: Avery Dennison, DSM, ECN, Océ Technologies, Philips, Shell and TNO Science and Industry. Germany: BASF, Bayer MaterialScience, Evonik Degussa, Merck. Switzerland: Ciba.

### Partners research

The Netherlands: the universities of Wageningen, Groningen, Delft, and Eindhoven; ECN, TNO Science and Industry. Germany: the universities of Cologne, Bayreuth, Münster, Wuppertal, Duisburg-Essen, and Ulm; Max Planck Institute für Polymerforschung Mainz.

### Budget and organization

The total cost in 2007 amounted to € 2.5 million (budget € 3.2 million). The total number of FTEs allocated at the end of 2007 was 23 (41 researchers). Total expenditure on equipment, expensive consumables and special analysis time was € 255,000. In 2007 prof. Dietrich Haarer was actively engaged in scientific development as Scientific Chairman, alongside the Programme Area Coordinator dr. John van Haare.

### Publications and inventions

The publication of 27 refereed papers as well as six theses, in addition to a significant number of contributions to scientific symposia in the form of posters and presentations, reflects the considerable contribution of this Technology Area to international science in this area. The significantly reduced publication output compared to 2006 is a result of the renewal of half of the FPS research programme during 2007. Seven inventions were reported and three filed patents. New projects were staffed at the end of 2007.

## Projects

- #435: Tunable conductivity levels in nano filler/polymer matrix composites
- #437: Synthesis of semi-conducting polymers
- #516: Complementary logic circuits by combining ambipolar field-effect transistors with surface-modified electrodes
- #518: Singlet to triplet exciton formation in polymeric light-emitting diodes
- #529: Conductive block copolymer systems with extremely low wt% of carbon nanotubes
- #627: Air-stable n-type field-effect transistors
- #628: Tuning the (electro)luminescent properties of a polymeric film by controlling intermolecular and/or intramolecular interactions
- #629: Polymer lighting with new triplet emitters and multi-layer structural design
- #304: New routes for the structuring of polymers
- #426: Functionalized phase gradings
- #427: Maskless lithography with liquid crystals
- #530: Photo-embossing of polymeric bi-layers
- #630: Functional polymer based nano and micro optics for solid-state lighting management
- #324: Polymer-Polymer Photovoltaic cells
- #524: Polymer-fullerene solar cells and low band-gap donor materials for photovoltaics
- #631: Triplet recombination in polymer solar cells
- #660: Bulk heterojunction polymer: zinc oxide solar cells from novel organozinc precursors
- #661: Structurally defined conjugated dendrimers and hyperbranched polymers in solar cells
- #522: Towards a push-and-pull muscle fibre: an electroactive polymer composite
- #523: Memory devices: zinc oxide nano-particles in a polystyrene matrix
- #532: Polymer MEMS – an integrated approach towards activated surfaces for microfluidic systems and pro-active devices
- #624: Electronic noses for high-volume system in foil applications
- #625: Polymeric sensors in smart packaging
- #626: Hardening of elastomers (and gels) in response to magnetic fields

*Joost Smits, Shell Research laboraties Amsterdam (NL)*



## Output

### Theses

G. Palaniswamy  
Amorphous Electron-Accepting  
Materials for Organic  
Optoelectronics

L.J.A. Koster  
Device physics of donor/  
acceptor-blend solar cells

Zhili Li  
Mesoscopic adhesion of  
poly(dimethylsiloxane) – self  
adhesion, effects of fillers, surface  
modification and thin top layers

P.A.C. Quist  
Photo-Physical Processes in  
Materials for Photovoltaic Applicati-  
ons based on Conjugated Polymers

J. Li  
Photovoltaics from Discotic Liquid  
Crystalline HBCs & Poly(2,7-  
Carbazole)s

C.M. van Heesch  
Polarization-Selective Diffraction  
for display applications

*Scientific publications*  
B.R. Pauw, E. Holder, V. Marin,  
B.G.G. Lohmeijer, U.S. Schubert  
Capillary zone electrophoresis of  
iridium(III) and ruthenium(II) poly-  
pyridyl complexes in non-aqueous  
solvents  
Analytical Letters  
40, 163-171

P.W.M. Blom, C. Tanase,  
T. van Woudenberg  
Charge transport and injection  
in conjugated polymers  
Semiconducting Polymers, ed. by  
G. Hadziioannou and G. Malliaras,  
Wiley-VCH Verlag book  
1, 385

M.M. Mandoc, W. Veurman,  
L.J.A. Koster, M.M. Koetse,  
J. Sweelssen, B. de Boer,  
P.W.M. Blom  
Charge transport in MDMO-PPV:  
PCNEPV all-polymer solar cells.  
J. Appl. Phys.  
101, 104512

M. Zhang, C. Yang, A.K. Mishra,  
W. Pisula, G. Zhou, B. Schmaltz,  
M. Baumgarten, K. Müllen  
Conjugated Alternating Copolymers  
Containing Both donor and Acceptor  
Moieties in the Main Chain  
Chem. Comm.  
1704-1706

L.H. Slooff, S.C. Veenstra,  
J.M. Kroon, D.J.D. Moet,  
J. Sweelssen, M.M. Koetse  
Determining the internal quantum  
efficiency of highly efficient polymer  
solar cells through optical modeling.  
Appl. Phys. Lett.  
90, 143506

M.M. Mandoc, F.B. Kooistra,  
J.C. Hummelen, B. de Boer,  
P.W.M. Blom  
Effect of traps on the performance  
of bulk heterojunction organic solar  
cells.  
Appl. Phys. Lett.  
81, 263505

B. Roodenburg, P.G. Malchev,  
T.I. Valadas Leitao, S.W.H. de Haan  
Electrical characterization of  
conductive polymer films related  
to pulsed power applications  
Proceedings IET Symposium on  
Pulsed Power. Stevenage: IET.  
53-58

F. Verbakel, S.C.J. Meskers,  
and R.A.J. Janssen  
Electronic memory effects in diodes  
of zinc oxide- nanoparticles in a  
matrix of polystyrene or poly  
(3-hexylthiophene).  
J. Appl. Phys  
102, 083701/1-9

F. Verbakel, S.C.J. Meskers,  
R.A.J. Janssen  
Electronic memory effects in zinc  
oxide nanoparticle - polystyrene  
devices with a calcium top electrode.  
Mater. Res. Soc. Symp. Proc.  
965E, 0965-S09-II

T. Offermans, S.C.J. Meskers,  
R.A.J. Janssen  
Excited state spectroscopy of  
MDMO-PPV:PCBM solar cells  
under operation.  
Org. Electron.  
8, 325-335

M. Zhang, H.N. Tsao, W. Pisula,  
C. Yang, A. K. Mishra, K. Müllen  
Field-Effect Transistors Based on  
Benzothiadiazole-cyclopentadithio-  
phene Copolymer  
J. Am. Chem. Soc.

C.L. van Oosten, K.D. Harris,  
C.W.M. Bastiaansen, D.J. Broer  
Glassy photomechanical  
liquid-crystal network actuators  
for microscale devices  
Eur. Phys. J. E  
23 (3), 329-336

K. Hermans, F.K. Wolf, J. Perelaer,  
R.A. Janssen, U.S. Schubert,  
C.W.M. Bastiaansen, D.J. Broer  
High aspect ratio surface relief  
structures by photoembossing  
Appl. Phys. Lett  
91 (17), 174103/1-174103/3

P.T.K. Chin, C. de Mello Donega,  
S.S. van Bavel, S.C.J. Meskers,  
N.A.J.M. Sommerdijk,  
R.A.J. Janssen  
Highly luminescent CdTe/CdSe  
colloidal heteronanocrystals with  
temperature-dependent emission  
color  
J. Am. Chem. Soc.  
129 (48), 14880-14886

K. Asadi, F. Gholamrezaie,  
E.C.P. Smits, P.W.M. Blom,  
B. de Boer  
Manipulation of charge carrier  
injection into organic field-effect  
transistors by self-assembled  
monolayers of alkanethiols  
J. Mater. Chem.  
19, 1947

S.C. Veenstra, J. Loos, J. Kroon  
Nanoscale structure of solar cells  
based on conjugated polymer  
blends.  
Progress in photovoltaics  
15, 727

E. C. P. Smits, S. Setayesh,  
T. D. Anthopoulos, M. Buechel,  
W. Nijssen, R. Coehoorn,  
P. W. M. Blom, B. de Boer,  
D. M. de Leeuw  
Near-Infrared Light-Emitting  
Ambipolar Organic Field-Effect  
Transistors  
Advanced Materials  
19, 734

M.M. Mandoc, L.J.A. Koster,  
P.W.M. Blom  
Optimum charge carrier mobility  
in organic solar cells.  
Appl. Phys. Lett.  
90, 133504

M.M. Mandoc, W. Veurman,  
J. Sweelssen, M.M. Koetse,  
P.W.M. Blom  
Origin of the efficiency improvement  
in all-polymer solar cells upon  
annealing.  
Appl. Phys. Lett.  
91, 073518

M.M. Mandoc, W. Veurman,  
L.J.A. Koster, B. de Boer,  
P.W.M. Blom  
Origin of the reduced fill factor  
and photocurrent in MDMO-PPV:  
PCNEPV all-polymer solar cells.  
Adv. Funct. Mater.  
17, 2167

B.K.C. Kjellander,  
C.W.T. Bulle-Lieuwma,  
L.J. van IJzendoorn, A.M. de Jong,  
J.W. Niemantsverdriet, D.J. Broer  
Quantification of liquid crystal  
concentrations in periodically  
stratified polymer-dispersed liquid  
crystal films by dynamic secondary  
ion mass spectrometry and  
multivariate statistical analyses  
J. Phys. Chem  
C 111 (29), 10965 -10971

F. Verbakel, S.C.J. Meskers,  
M. Cölle, M. Büchel, H.L. Gomes,  
R.A.J. Janssen, and  
D.M. de Leeuw  
Reproducible resistive switching  
in non-volatile organic memories  
Appl. Phys. Lett  
91, 192103/1-3

L.K.J. Vandamme, M. Coelle,  
D.M. de Leeuw, and F. Verbakel  
Resistive switching and noise in  
non-volatile organic memories  
Proc. SPIE  
6600, 66000B/1-10

F. Verbakel, S.C.J. Meskers,  
R.A.J. Janssen  
Surface modification of zinc oxide  
nanoparticles influences the  
electronic memory effects in  
ZnO-polystyrene diodes.  
J. Phys. Chem. C  
111, 10150

V. Marin, R. Hoogenboom,  
B.C. Moore, E. Holder, U.S. Schubert  
Synthesis and copper(I) complexa-  
tion of 3,6-di(2-pyridyl)pyridazine and  
2,2'-bipyridine ligands functionalized  
with a dangling iridium(III) complex  
Aust. J. Chem.  
60, 229-235

V. Marin, D. Wouters, S. Höpener,  
E. Holder, U.S. Schubert  
Synthesis and surface assembly  
of ruthenium bipyridine complexes  
Aust. J. Chem.  
60, 414-419

M.M. Mandoc, B. de Boer,  
G. Paasch, P.W.M. Blom  
Trap-limited electron transport in  
disordered semiconducting polymers.  
Phys. Rev. B  
75, 193202

*Filed patent applications*  
#532 F. Fahmi, L.J. Van IJzendoorn,  
J.M.J. den Toonder, M.W.J. Prins  
Microfluidic system based on  
actuator element

#546 + #530 J. Perelaer,  
K. Hermans, C.W.M. Bastiaansen,  
D.J. Broer, U.S. Schubert  
Process for preparing a polymeric  
relief structure

#529 M.-C. Hermant,  
L. Klumperman, C.E. Koning  
Process for the preparation of a  
conductive polymer composition

*Reported inventions*  
#529 M.-C. Hermant,  
L. Klumperman, C.E. Koning  
Process for the preparation of a  
conductive polymer composition

#437 S. Harkema, R. Kicken,  
B. Langeveld  
Fluorene copolymers in blue organic  
LEDs

#532 C.L. van Oosten,  
C.W.M. Bastiaansen, S.J. Picken,  
J.M.J. den Toonder, D.J. Broer  
Fluid manipulation in microchannels

#523 F. Verbakel, S. Meskers,  
R.A.J. Janssen, D. de Leeuw  
Aluminum oxide layers for resistive  
memory applications

#530 K. Hermans, I. Tomatsu,  
R.P. Sijbesma, C.W.M. Bastiaansen,  
D.J. Broer  
High aspect ratio photo-embossing

#532 C.L. van Oosten,  
C.W.M. Bastiaansen, D.J. Broer  
Preparation of polymer  
micro-actuators

#532 C.L. van Oosten, D. Nowak,  
C.W.M. Bastiaansen, D.J. Broer  
Sensors for smart packaging



*Sandra Hofmann: "Can DPI help solve the increasing problem of finding good people to fill our vacancies?"*

## Eco-friendly waterborne coatings

Waterborne coatings are coatings in which water is the main solvent or carrier. For environmental reasons they are preferred over solvent-based coatings. But are they just as good? And if not, what technological and economic hurdles have to be overcome to make them better? What is the role DPI can play in this field?

The use of waterborne coatings in car finishing applications has grown over the last few years, helped by new legislation in some European countries. It is encouraging that coating professionals who have learned how to use waterborne coatings do not want to go back to using solvent-based coatings. In industrial applications in OEM companies, where drying and curing conditions are easier to control, waterborne coatings have been used for a long time. And for more general purposes more and more waterborne products are being developed. The market is growing.

### Advantages

The main advantage of waterborne coatings over solvent-based coatings is their low level of volatile organic components (VOC), which in most cases translates into lower odor, improved working conditions and reduced fire hazards. "But you have to consider all aspects in which waterborne and solvent-based coatings differ from each other", says dr. Pieter Geurink, senior scientist at Akzo Nobel. "It is not just VOC levels and odor that are important, but also durability, gloss level, ease of application and drying behavior. If waterborne coatings have more advantages than disadvantages, they will ultimately be used. We saw the same thing with wall paints a long time ago. Latex overcame the disadvantages of solvent-based wall paints in terms of odor, drying speed and yellowing, and within a couple of years it was the wall paint of choice. There was no legislation involved in that. But if you look at other types of paint, for instance for doors and houses, the so-called 'trim paints', you need a higher quality level in gloss and general appearance, and this imposes restrictions on rheology and the open time of the paint. Professional painters are used to solvent-based paint. They know how to apply it and how fast it dries. The first generation of waterborne paints did not give the same results. After two minutes their viscosity became so high that brush marks would not flow out and the result was a moderate appearance."

"The crucial difference between waterborne and solvent-based coatings is that the binder, the material that causes pigment particles to adhere to one another, is dissolved in the latter case and dispersed in the former", explains professor Martin Cohen Stuart, head of the Colloid Chemistry department of Wageningen University (Netherlands). "A waterborne coating always has to undergo

a phase inversion, and that I would call a technological hurdle. Waterborne paints are dispersions that are meant to be stable as long as they are in the pot. That means that you have to add material that sits on the surface of the binder particles to keep them suspended in water. But as soon as the paint is applied and the water evaporates, this material has to go in order to get a nice and continuous polymer film. The rheology of concentrated dispersions is not completely understood and very difficult to control. There is still a lot of empirical knowledge. In particular if you want to be flexible in the choice of pigment, stability is an issue that has not yet been solved." Dr. Sandra Hofmann, Dow's technology development leader in Europe, adds: "Latex is a classical system where polymerization and film formation is pretty well understood. If you want the same process to happen for other raw materials, you either have to disperse them in a solvent that will aid film formation or, if you want to reduce the amount of solvent and replace it with water, you have to find new ways for doing that. You will typically have to work with lower-molecular-weight polymers and introduce some level of ionic modification to make the polymers 'disperse'. In the absence of organic solvent that route will impose challenges on film formation as well as on final film performance, such as hydrolytic stability. The big challenge is to find an applicable solution to overcome these issues and to develop products in waterborne form without compromising the customer's wishes. This has led to a push in the development of suitable crosslinking technology."

### Role of DPI

A combination of clever chemistry, good physical insight and application knowledge is needed to answer questions such as 'How do stabilizers and viscosity modifiers in a dispersion work?', 'How do we formulate such additives?' and 'What happens during film formation and drying?'. Cohen Stuart: "DPI is instrumental in bringing people from industry and academia together to define the real problems, exchange good information and discuss possible solutions. It is a good thing that DPI's Technology Area Coating Technology offers a platform where academics can bring good ideas to the table. These are then judged by industrial and academic researchers and if this judgment is positive it will lead to research projects. If DPI did not have this Technology Area, a substantial fraction of the research that is now being focused on coatings would not be done at all."



Coatings research at Akzo Nobel, Sassenheim (NL)

DPI's involvement in coating technology is very valuable, Geurink and Hofmann agree. Cohen Stuart's Colloid Science Group in Wageningen is world class and it is one of the few colloid science groups in the world, if not the only one, focusing on waterborne coatings (by contrast, the research groups focusing on latex form a large and highly organized community – but there is more to waterborne coatings than only latex). Other colloid science groups focus on mineral processing or medical applications. Geurink is glad that the issues surrounding waterborne coatings have proved intriguing and rewarding enough to make the Wageningen group focus its attention and knowledge on solving them – at a level unmatched by any other institution or organization in the world.

#### Wild ideas

Not all ideas can lead to actual projects. Budgets are not unlimited. Yet the three people discussing DPI's activities in the field are happy with the choices being made. Hofmann: "We see DPI, with its involvement in pre-competitive research in the area of waterborne coatings, as a key contributor to the development of fundamental knowledge on material properties. Not every industrial laboratory will have the equipment and expertise needed for this. DPI is pretty unique in bringing together a relevant chain of companies and research groups that covers everything from material synthesis to application testing. If, as part of a DPI project, we develop contacts with a university group whose equipment and expertise are of interest to us, these contacts might even evolve into a bilateral project. But that is not all: we also expect DPI researchers to come up with wild ideas, out-of-the-box thinking, novel approaches to the concept of eco-friendly coatings."

Cohen Stuart has a suggestion for making the choices even more deliberate and to the point: "To identify the area where ideas for a breakthrough are needed and to focus on that, DPI could organize a meeting with key players from industry and universities in a certain field prior to a call for proposals. The aim would be to discuss the important issues such as whether a breakthrough is really needed and what the necessary techniques and methods are to achieve it. Participants from industry can then explain what the problems are they are struggling with and the discussion partners from the universities can be inspired by this. They can sharpen their ideas, perhaps join forces and come up with better ideas." Hofmann supports this idea: "It would give us the opportunity to draw on knowledge institutions other than our typically preferred partners. DPI, with its unique setup in which academia and industry are combined, is perfectly positioned to provide a multi-angle view, with a number of research groups teaming up in order to resolve huge fundamental challenges and thus maximize the impact for industry."

Ten years of DPI and seven years of activities in the Coating Technology Area have been very valuable for the discussion partners from industry and these partners are happy that continuation is ensured for the near future. The network function is highly appreciated and DPI is a good hunting ground for talent. Hofmann is very satisfied with the quality of the DPI researchers Dow hires. "They have been more exposed to industry than their university-only colleagues. Maybe DPI can play a greater role in solving the increasing problem of finding good people to fill our vacancies."



**Martin Cohen Stuart:**  
*"A waterborne coating always has to undergo a phase inversion and that is a technological hurdle."*

**Pieter Geurink:** *"You have to consider all aspects in which waterborne and solvent-based coatings differ."*



Dirk Jan Voorn  
 Manoranjan Prusty  
 Shankara Narayanan Keelapandal  
 Sachin Jain

## Coming well-prepared

**One of the objectives that the Dutch Ministry of Economic Affairs had in mind in 1996 when it initiated Leading Technological Institutes (LTIs, one of which is DPI) was to make it easier for companies to hire well-trained scientific experts. The idea was that the close interaction between the LTI researchers and industry would promote this recruitment aspect.**

DPI celebrated its tenth anniversary in 2007, so it seems an appropriate time to evaluate whether this objective has been achieved. A good place to investigate this is BASF. The company joined DPI in 2007 but already has a number of former DPI PhD students under its wings. After getting his PhD from Eindhoven University of Technology (Netherlands) in the DPI Coating Technology Area, Dirk Jan Voorn was invited by BASF to apply for a job. With three of his BASF colleagues, Manoranjan Prusty, Shankara Narayanan Keelapandal and Sachin Jain, all originally from India, he discusses the role of DPI in their professional careers. All four of them worked on their theses in DPI projects and some of them are now involved as industry contacts in DPI projects of other PhD students.

### Eager

Voorn: "I met someone from BASF at a conference in the US and he asked me to send him my résumé. BASF had not been involved in my PhD project. Other companies had, but they were less eager and not so active in their recruiting efforts. Within two weeks everything was arranged and I had a job." Prusty adds: "They invited me for one day, I had six interviews and at the end of the day they offered me a contract."

Voorn looks back on his two years with BASF: "Working in Germany has its advantages, not only financially but also in terms of the position you have. In the Netherlands you are less valued as a graduated PhD. Here in Germany you have more responsibility. In the Netherlands the difference between employees with a PhD degree and employees with a Master's degree is not so big." Yet all four agree that the Netherlands is the better place to do PhD research. Not just because in Germany PhD students get paid

only for the educational work they do, but also because in the Netherlands PhD students have more freedom and more responsibilities in their projects. Keelapandal: "From day one in your PhD project you know that it is your problem and not your professor's. You sure do encounter lots of hurdles, but it is up to you to find ways around them. This makes you more confident in the future and that will help you in an industrial environment." Voorn adds: "A Dutch PhD graduate is more independent, has seen more of project management and can take responsibility faster than a German PhD graduate, who has been told by his or her supervisor what to do." All four agree that the Dutch PhD system has helped them to prepare for their jobs in industry. But has being a DPI PhD graduate helped them extra?

### Prepared

In DPI projects, PhD students have regular review meetings with their contacts from industry. Of course these interactions can vary in intensity from one company to another and from one person to another, but in general the four BASF employees are very positive about the input they received from industry in their research work. Were they better equipped for a job in industry than their university-only colleagues because of these contacts? Jain is sure of it. "At DPI we learned to approach people, to take the initiative instead of waiting for someone to come to you. I remember that my bosses at BASF were pleasantly surprised when I took an initiative only a few months after I had arrived here. But in Eindhoven this would have been the normal thing to do."

Their DPI projects prepared them, they agree, but there were also a lot of new skills to be learned. Working as an industrial researcher is different from being an academic researcher. Keelapandal: "The main difference is that a good idea is only a really good idea if it brings profit for the company. The question you need to answer is: Do the customers want to pay for it? And one of the first things you learn here is the value of your time to the company. How much does half a day's work cost? I simply didn't think about such things at the university." The way of thinking is the same, only the conditions are different when the money aspect is added. In DPI projects in universities the financial element is deliberately left out of the equation; bothering scientists with financials would be in direct conflict with the free-spirit way of thinking needed in fundamental research. "At BASF you have to be aware of the price of the materials and the methods you are working with. This holds a certain danger, of course: you could miss the solution to a problem by skipping

an analysis you deem too expensive”, Voorn adds. But not only money is an extra condition, speed is also important. A very accurate but slow measurement of viscosity may be preferred in an academic environment, but in production circumstances it will have to be replaced with a faster one. Innovations in industry have a ten-year horizon. In a university you can start from an idea and produce a result, a prototype to show that the principle works, in one year. But does it work in the application? That takes longer and decisions to stop or continue have to be made in the process. Voorn: “Believing in your idea, convincing others and pursuing an idea to the end, that kind of experiences you only get when you are really involved in a company and have the responsibilities that come with it. DPI cannot prepare you for that.”

Voorn has a suggestion for improving the interaction between industry and DPI PhD students. They are after all their potential future employees. “A meeting between industry people and PhD students intended for networking and not dedicated to a technical subject might help to get more interaction. Industry has the opportunity to talk to people involved in projects other than those in their own cluster and the students learn to speak the language and become aware of the industry problems outside their own field of expertise.”

In their new roles the four BASF employees now sit on the other side of the table when DPI projects are discussed. Voorn: “When we at BASF do not have the time to investigate all ideas, we are happy to let others do that. It does not have to result in a product, we will learn from it anyway. Industrial research is not only aimed at products, its goal is also to gain more insight. That is something I had to learn when I came to BASF. When I worked at the university I thought that we did the fundamental research and that industrial researchers worked on products. Now I know that industrial research can be fundamental as well. But you do not necessarily find the results in the outside literature.”

Sachin Jain works in the field of polymer nanocomposites, Shankara Narayanan Keelapandal is engaged in process development and scale-up for different polymers, Manoranjan Prusty is now involved in the field of polycondensates at BASF and Dirk Jan Voorn is in BASF involved in coatings for printing paper. 

*Manoranjan Prusty: “I had six interviews and at the end of the day they offered me a contract.”*

*Narayanan Keelapandal: “From day one in your PhD project you know that it is your problem and not your professor’s.”*



*Dirk Jan Voorn: “In Germany you get more responsibility as a PhD. In the Netherlands the difference between a Master’s graduate and a PhD graduate is smaller.”*

## Facts and figures

### Objectives

The Coating Technology research area is doing frontier research in the general field of organic coatings. The aim is to develop fundamental insights that will 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), preparing the coatings industry for future challenges. The research programme is divided into three subprogrammes.

### Renewable raw materials, formulation and powder coatings

- Investigating the feasibility of the use of sustainable, renewable resources for the development of alternative monomers and co-monomers for the production of coating resins, without compromising the final coating (film) properties.
- Gaining a fundamental understanding of the colloidal stability of waterborne coatings as a basis for increasing their shelf-life and the number of applications.
- With a view to extending the application field (wood, MDF, plastics) for powder coatings, finding innovative solutions to meet the stringent demands on the cure window with respect to both rheology (levelling) and reactivity (cure).

### Functional (smart) coatings

The objective is to develop new coatings with additional functional properties at the surface as well as in the bulk apart from protecting underlying layers and decorating effects, which are the functionalities normally associated with coatings. Preferably, these additional functional properties should be demonstrated using fewer sequential coating layers. 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. Furthermore, the programme aims to develop new testing methods for coatings, such as adhesion, gloss and scratch resistance, which correlate to meaningful physical parameters. Last but not least, a joint project with the M2I programme on understanding the mobility of water and charge

carriers under metal corrosion conditions started effectively in 2007.

### Partners industry

The Netherlands: Akzo Nobel, DSM, Océ Technologies, Shell; Germany: Bayer, Evonik Degussa; Switzerland: Dow Europe.

### Partners research

The Netherlands: the universities of Amsterdam, Wageningen, Eindhoven and Agro Technology and Food Innovations; South-Africa: the University of Stellenbosch; Germany: Forschungsinstitut für Pigmente und Lacke (FPL).

### Budget and organization

The total cost in 2007 amounted to € 2.1 million (budget € 1.6 million). The total number of FTEs allocated at the end of 2007 was 20, distributed over 25 researchers. The total expenditure on equipment, expensive consumables and special analysis time was € 400,000. In 2007 prof. Claus Eisenbach was actively engaged in the scientific development as Scientific Chairman, alongside the Programme Area Coordinator dr. John van Haare.



*Sachin Jain: "At DPI we learned to approach people, to take the initiative, not wait for someone to come to you."*

## Publications and inventions

The publication of 15 refereed papers (doubled output compared to 2006), in addition to a significant number of contributions to scientific symposia in the form of posters and presentations, reflects that the Technology Area considerably has improved its contribution to international science in this area. Three inventions were reported and two filed patents.

## Projects

- #292: Kinetics of adsorption and desorption of mixtures of polymers and surfactants
- #422: Low-temperature powder coating by encapsulated cross-linker
- #451: Bio-based building blocks for coating and toner resins
- #452: Dispersing pigments in waterborne paints
- #564: Colloidal interactions modified by associative thickeners in waterborne paint formulations; surface force experiments and Scheutjens-Fleer theory
- #565: Thiol-ene based 2-pack-in-1-pot waterborne coating
- #607: Polycarbonate powder coatings
- #657: Dyktiogenic polymer ions
- #423: Self-replenishing low-adherence coatings
- #494: Light-switchable coatings
- #556: Self-healing coatings based on nano-capsules in waterborne coatings
- #557: Coatings with layered silica based novel pigments and/or reinforcing fillers
- #570: Self-stratifying antimicrobial coatings
- #576: Incorporation of olefins in emulsion copolymers: towards super hydrophobic coatings
- #655: Fully reversible coating networks
- #419: Weathering and durability of industrial coatings
- #439: Correlation of molecular changes, physical parameters and product properties of selected coatings in early stages utilizing a novel testing/characterization approach
- #440: Durability of metal oxide / coating interfaces
- #600: Molecular aspects of scratch resistance
- #606: Real-time 3D imaging of microscopic dynamics during film formation

## Output

### Scientific publications

- V. Khatavkar, P.D. Anderson, H.E.H. Meijer  
Capillary spreading of a droplet in the partially wetting regime using a diffuse-interface model  
*J. Fluid Mech.* 572, 367-387
- S. Kisin, F. Scaltrio, P. Malanowski, P.G.Th. van der Varst, G. de With  
Chemical and structural changes at the ABS polymer-copper metal interface  
*Polymer Degradation and Stability* 92, 605-610
- B. Postmus, F. Leermakers, L. Koopal, M. Cohen Stuart  
Competitive adsorption of non-ionic surfactants and non-ionic polymer on silica.  
*Langmuir* 23, 5532
- D. Senatore  
Controlled release of micro-encapsulated cross-linker in powder coatings.  
*Polymeric Materials Science and Engineering Preprint* 97, 912
- V. Khatavkar, P.D. Anderson, P.C. Duineveld, H.E.H. Meijer  
Diffuse-Interface Modelling of Droplet Impact  
*J. Fluid Mech.*

B.A.J. Noordover, R. Duchateau, R.A.T.M. van Benthem, W. Ming and C.E. Koning  
Enhancing the functionality of biobased polyester coating resins through modification with citric acid  
*Biomacromolecules* 8, 3860-3870

J. Sprakel, N.A.M. Besseling, F.A.M. Leermakers, M.A. Cohen Stuart  
Equilibrium capillary forces with atomic force microscopy.  
*Phys. Rev. Lett.* 99, 104504

T. Dikic, S.J.F. Erich, W. Ming, H.P. Huinink, P.C. Thüne, R.A.T.M. van Benthem, G. de With  
Fluorine depth profiling by high resolution magnetic resonance imaging.  
*Polymer* 48, 4063

P. Geelen; B. Klumperman  
Intermediate Radical Termination in RAFT mediated polymerization – Identification of termination products  
*Macromolecules* 40, 3914-3920

J. Sprakel, N.A.M. Besseling, F.A.M. Leermakers, M.A. Cohen Stuart  
Micellization of telechelic associative polymers; self-consistent field theory and comparison with scaling concepts.  
*J. Phys. Chem. B* 111, 2903

B. Klumperman; J.B. McLeary; E.T.A. van den Dungen; G. Pound  
NMR spectroscopy in the optimization and evaluation of RAFT agents  
*Macromol. Symp* 248, 141-149

D.J. Voom, W. Ming, J. Laven, J. Meuldijk, G. de With, A.M. van Herk  
Plate-sphere hybrid dispersions: heterocoagulation kinetics and DLVO evaluation  
*Colloids Surf. A* 294, 236-246

N.K. Singha, A.L. German  
Pseudohalogens in atom transfer radical polymerization of methyl methacrylate  
*Journal of Applied Polymer Science* 103, 3857-3864

J. van Haveren, E.A. Oostveen, F. Micciché, B.A.J. Noordover, C.E. Koning, R.A.T.M. van Benthem, A.E. Frissen, J.G.J. Weijnen  
Resins and additives for powder coatings and alkyd paints based on renewable resources.  
*J. Coat. Technol. Res.* 4, 177

J. Sprakel, J. van der Gucht, M.A. Cohen Stuart, N.A.M. Besseling  
Rouse dynamics of colloids bound to polymer networks.  
*Phys. Rev. Lett.* 99, 208301

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

#451 B.A.J. Noordover, R. Duchateau, C.E. Koning, R.A.T.M. van Benthem, D. Haveman  
Polycarbonate and process for producing the same

*Reported inventions*  
#451 B.A.J. Noordover, R. Duchateau, C.E. Koning, R.A.T.M. van Benthem, D. Haveman  
Polycarbonate and process for producing the same

#451 + #607 B.A.J. Noordover, R. Duchateau, M.L.J. Frijns, W.J. van Meerendonk, C.E. Koning  
Renewable polycarbonates

#451 D.S. van Es, J. van Haveren, R. Koelewijn, B.A.J. Noordover  
Cross-linkers for powder coating systems

*Wilhelm Meyer: "I would definitely advise other small companies to join DPI."*

## Printing ink and more

Inkjet printing is without a doubt the preferred technology for applying polymers onto substrates. It generates hardly any material waste and if there is one technology that has been optimized for patterning, it is printing. There is a need to test new combinations of materials and substrates as well as printing conditions for this technology.

There is no stopping professor Ulrich Schubert, Scientific Chairman of the High-Throughput Experimentation Technology Area and Chairman of the Laboratory of Macromolecular Chemistry and Nanoscience at Eindhoven University of Technology (Netherlands) and the Laboratory of Organic and Macromolecular Chemistry at the Friedrich-Schiller-University Jena. "We started with inkjet printing of 'innocuous' polymers, by which I mean non-active polymers like polystyrene. When we had mastered the physics behind those we could start varying the material parameters. We are lucky to have Microdrop Technologies as a DPI member in this Technology Area. They provide us with tailor-made equipment, including the different printing heads we need."

Microdrop Technologies is a small company in Hamburg, Germany, an early spin-off of Philips, which concentrates on inkjet printing for industrial applications. Dipl.-Phys. Wilhelm Meyer is its Managing Director. "We try to adapt our technologies to different applications. We started with applications for low-viscosity materials for biotechnology applications, for instance transferring DNA solutions to a substrate, for analysis purposes. When professor Schubert contacted us in 2002 we became interested in using this technology to print functional polymers for plastic electronics." Microdrop Technologies has been a partner of DPI almost from the start of this Technology Area.

One of the later partners, at least in this Technology Area, is Océ Technologies. Dr. Rolf Koevoets is one of this company's research scientists. "Océ has a history in document and wide-format printing making use of toner and inkjet technology. Recently we have also been looking more and more into other applications of inkjet technology. That is why Océ recently opened an inkjet application centre at the High Tech Campus Eindhoven and joined the High-Throughput Experimentation (HTE) cluster of DPI."

### Libraries

Schubert continues: "When we knew how to print 'innocuous' polymers, we moved on to active polymers, light-emitting polymers for instance, and learned how to print combinations of them in test films with different thicknesses in various patterns on a number of different substrates. We wrote a very highly appreciated and much cited paper about that in 2004.

Then we moved on to print semiconducting nanoparticles with different sizes corresponding to different colours. We composed libraries of possible combinations."

A frequently recurring problem in the printing of polymers is the so-called coffee-drop effect. Instead of the polymer solution drying to form nice, even, homogeneous dots or films, the polymer material ends up in a ring around the edges with very little material in the centre. Schubert's group responded to this challenge and came up with one way of overcoming this problem: a polymer material that is in solution while being printed and turns into a gel as soon as it hits the heated substrate. Another of the group's achievements is that they are now able to print conducting lines with a width of only 40 microns at a low temperature. This is important since devices and their building blocks need to be smaller and smaller in the future. Conducting lines can be used, for instance, in antennas for radio frequency identification (RFID) tags, which will replace the current product barcodes, or in sensor applications. Schubert: "We are now very close to applications and the interest is growing. The workshop that we organized last year attracted no more than 170 people. It is now up to a company to take the technology and develop a product with it."

Meyer agrees with him. "Not only in research, but also in industry interest is growing. Through DPI, we are getting in touch with potential customers and with researchers who help us to improve our printers. Our involvement in DPI is starting to pay back." In the HTE Technology Area the whole chain is represented: not only the technology provider and the scientific community but also materials companies such as Dow, Evonik Degussa or Bayer, which can provide substrates with different surface properties and polymer solutions to print. This arrangement offers much more than a single research institute could do. A single institute could perhaps buy one machine and would not be able to vary so many parameters. Schubert: "The interaction is essential. Microdrop supplies us with ten different nozzles for printing, the materials suppliers are closely involved and very interested to motivate us to continue our work. We were able to get to this point, close to applications, while other organizations, for instance the National Institute of Standards and Technology in the US, had to give up."



*Rolf Koevoets: "We have the opportunity to use DPI's infrastructure and this is very valuable to Océ."*

It is not only the interaction with the DPI partners from different backgrounds that is important. Koevoets: "Even though we have access to a large analysis department and many test set-ups at Océ, there are techniques that we do not have in-house. We have the opportunity to use the infrastructure of DPI present in Schubert's group. We have for instance used the Microdrop equipment to test inks we developed. This is very valuable to Océ, as is the huge amount of knowledge that is present in DPI. It is a matter of finding the right projects, following the progress of these projects and seeing whether the developed technology is of interest to us. An example of a technique that is useful to us is using micro-waves or ultrasound instead of heating in the printing process."

### **Soft matter**

In the next few years, research will continue with printing polymers that are less stable than those used until now. The line widths of conductive polymers will continue to decrease. Printing in three dimensions in hard materials leading to a kind of rapid prototyping will be investigated, but soft materials will also receive due attention, for instance printing gels that can be crosslinked once they are on the substrate. One step further will be to print biological materials. Recently it was shown that not only proteins and enzymes can be printed, but even complete living cells can survive the printing process. Schubert enthusiastically pictures the future: "You can think of printing skin to heal burns instead of having to transplant complete large-area skin sections from another part of the body. In the US they even dream about printing complete organs and researchers have already constructed complete arteries from three-dimensional pictures."

In Jena I am now setting up a laboratory for printing soft matter and living cells, and investigating the interaction with our libraries of polymers. We now have Innovent on board, a knowledge institute with fifteen years of experience in the field of biomaterials. Before bringing a material into a human body you must test all the interactions. Innovent knows the materials and we know how to print them.”

An example of this interaction between polymers and living tissue in a body is a project of Microdrop. Meyer explains: “We have printed a uniform layer of polymers on the outside wall of metal stents, which are used to avoid restenosis in arteries. The polymer serves as a reservoir for a drug that can be released over time and rapidly reaches only the place where it is effective, namely the blood vessel wall. Printing is the method of choice because you can deposit

precisely the amount you want in the exact location where you want it. You can adapt the choice of drug and the amount to the individual patient.”

There is a market for such individualized products and production will not move to China. For Microdrop Technologies, a small company, it is definitely worth the effort and the money to be part of DPI. “I would definitely advise other small companies to join DPI to obtain access to a whole scientific community and to large chemical companies”, says Meyer.

A problem the cluster faces is that, because the printing of polymers is a new field, there are not many experienced people available and Schubert’s collaborators are sometimes headhunted away from his group. “You need a solid background in chemistry, physics and engineering in this field, and such people are hard to find and in high demand. It is a hot Technology Area.”



*Ulrich S. Schubert: “Inkjet printing is a hot technology area.”*

*Berend-Jan de Gans:  
"When you know  
people in industry they  
can draw your attention  
to vacant positions."*

**Berend-Jan de Gans**

## **Fast and efficient measurements**

The high-throughput experimentation approach is not just used for synthesis purposes; it is also a fast and efficient way of testing and measuring properties of combinations of materials, for instance polymer/solvent/additive combinations meant for inkjet printing.

Berend-Jan de Gans is a former DPI Post Doc. He studied chemistry and physics at the University of Utrecht and did a PhD project at the University of Twente (both in the Netherlands). The subject of his PhD project was magneto-rheology. Polymers entered his professional life during the two years that he worked at the Max Planck Institute for Polymer Research in Mainz, Germany. He gained his DPI experience in 2003 as a Post Doc in the group of professor Ulrich Schubert at Eindhoven University of Technology (Netherlands).

“We investigated whether it would be possible to print polymers with an inkjet printer. Mostly they will not print directly, but by varying additives and solvents we could show that some combinations were suitable for printing. We did not synthesize new polymers, but we quickly and efficiently (in a way similar to HTE synthesis) measured the properties of combinations of polymers, solvents and additives that did print. I concentrated on surface properties, for example, the surface tension of the printed materials.” The goal of this research was to find mechanisms that determine whether or not printing is possible and how the printed materials behave. “It turns out to be quite tricky. The familiar coffee-ring effect makes it almost impossible to print homogeneous structures, but we found ways to overcome it.”

In his daily work De Gans did not experience the influence of DPI. “Your work is the same whether it is financed by the university or by DPI. The good things of DPI are the project meetings, once every three months, first only in Eindhoven and later also in other places. I had direct contacts with the industrial DPI partners in the project. They contributed ideas to our work, but I noticed that it was hard for them to really commit themselves. Now that I am working in a company myself, I can understand that there is a delicate balance between the research a company wants to do itself and the research that can be shared with others.”

## Defoamers

Indirectly, De Gans' contacts with industry helped him get his present job in Evonik Degussa. “I applied for this job with help from people I had met in my DPI time. When you know people in industry they can draw your attention to vacant positions.”

De Gans now works for Evonik Degussa in the division that used to be Goldschmidt, a specialty chemicals company known for additives used in for instance cosmetics and coatings. “Some of our most important products are defoamers. Foam is a major concern in many applications. It can severely hinder the filling of a container or cause surface defects in coatings. Defoamers are complicated formulations containing both nanoparticles and polymers. Only a physical chemist can understand and formulate such products.”

Evonik is an industrial partner of DPI, but De Gans is not involved in any DPI projects at the moment. His main contact with DPI is the PhD student Jolke Perelaer, who continued his line of research in Schubert's group.

“In industry you have access to technologies universities do not know about. When I see or hear something that could be of interest in his project, I give him a call.”

Berend-Jan de Gans worked as a Post Doc on inkjet printing polymers at the Eindhoven University of Technology. He is now responsible for colloid and interface chemistry at Evonik Degussa.



## Facts and figures

### Objectives

High-throughput experimentation 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 will allow the design and preparation of tailor-made materials and devices with predetermined properties based on previously established structure-property relationships. The main focus will be on creating and applying full workflows, covering the design of experiments, automated and parallel synthesis, fast structural characterization, preparation of thin-film libraries, fast and efficient investigation of macroscopic polymer and material properties, formulation, up-scaling, combinatorial compounding, processing and complete data-handling, data-mining and modeling. DPI's unique combination of leading industries and academic partners provides an excellent basis for successful output. It also guarantees speed in the pre-competitive evaluation of the new (platform) technologies and rapid transfer into commercial R&D programmes of the industrial partners. At the same time, considerable efforts will be made to educate students and post-doctorate graduates in the use of HTE and CMR approaches in polymer and materials science.

### Subprogrammes

#### Synthesis, Catalysis & Formulation

The research in this sub-cluster focuses on the preparation of libraries of (co)polymers and formulations as a basis for the determination of structure-property relationships. The polymer synthesis within the cluster focuses on living and controlled polymerizations that allow the preparation of well-defined polymers with systematic structural variation. Besides fundamental research on the use of microwave irradiation, feasibility studies are performed on up-scaling microwave-assisted polymerization procedures. In addition to fast synthesis and formulation platforms, the incorporation of high-throughput screening techniques for e.g. molecular weight, polymerization kinetics and thermal and surface properties is investigated.

The current high-throughput experimentation workflow is used for the optimization of polymerization methods and the synthesis of libraries of (co)polymers based on 2-oxazolines, (meth)acrylates, styrenics and cyclic esters. In 2007, these focus areas were further expanded (in collaboration with the Polyolefin Technology Area) to include the synthesis of polyolefins, the emphasis being on the development of a complete high-throughput workflow including parallel synthesis and high-throughput screening using for example automated high-temperature size exclusion chromatography. The existing high-throughput workflow was further expanded to include capabilities for polymer water-uptake screening and polymer solubility screening. Therefore, the synthesis efforts were intensified in the direction of water-soluble polymers.

#### Thin-Film Library Preparation & Screening

This sub-cluster mainly focuses on gaining a detailed understanding of thin-film preparation technologies (mainly inkjet printing), on the application of these technologies, and on the screening of thin-film materials properties by automated atomic force microscopy and nano-indentation technologies. Fields of research are the processability of polymer inks (coatings and light-emitting materials) and homogeneous drop and film formation on different substrates (including polymeric ones). Application fields include the processing of light-emitting materials, surface patterning and the preparation of conductive tracks on polymeric substrates. In the area of AFM, the investigations (in collaboration with the Functional Polymer Systems Technology Area) cover photo-embossed relief structures. Now, combinations of inkjet printing and other structuring techniques, such as hot-embossing, are explored to further decrease the size of printed features.

#### Combinatorial Compounding

The programme of the combinatorial compounding sub-cluster is executed at the Deutsches Kunststoff Institut (DKI) in Darmstadt (Germany). The central objective of the programme is the development of a process, closely related to technical production processes, that facilitates the acceleration (by up to 100%) of the preparation, characterization and optimization of plastic formulations.

The combinatorial extrusion line used for this purpose 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 visualization systems. In addition, new screening facilities have been set up.

#### Materials Informatics & Modelling

This programme concerns data handling, database construction and the build-up of integrated knowledge capture systems for combinatorial materials and polymer research as well as experimental design, hard and soft modelling tools and tools for deriving quantitative structure-property relationships, supporting mainly the programmes on Synthesis, Catalysis and Formulation, Thin-Film Library Preparation & Screening and Combinatorial Compounding. A model is being developed for the screening of MALDI matrices to facilitate faster screening of molecular weights. In addition, activities for the installation of a cluster-wide inventory system as well as the first steps into an e-notebook system have been initiated.

#### Detailed Characterization Techniques

The sub-cluster on detailed characterization techniques focuses on the development of detailed characterization methodologies, mainly microscopic and chromatographic techniques, for specific applications. One aspect is the combination of different measurement techniques (high-resolution TEM and AFM in combination with SAXS/WAXS measurements) with the aim of characterizing multi-phase (amorphous/crystalline) or multi-component materials (rubber-reinforced polymers or nanocomposites) on macro, micro and nanoscales. A further focus of interest is the analysis of branched polymers by means of two-dimensional liquid chromatography. In 2007 unique results were achieved regarding the fractionation of high-molecular-weight branched polymers. This has significant implications, e.g. in the polyolefins field. Moreover, the development of tools and models for the nanoscale characterization of interfaces using AFM technology was continued. In combination with the Synthesis sub-cluster, new projects are being started to develop and evaluate high-throughput screening methods for polymer solubility, including phase transitions such as lower and upper critical solution temperatures, dispersion formation and micellization.



*Colloid and interface chemistry at Evonik Degussa, Düsseldorf (Germany)*

### Partners industry

The Netherlands: Accelrys, AstraZeneca, Avantium, Basell Polyolefins, Bayer MaterialScience, Chemspeed Technologies, Dow Benelux, Evonik Degussa, Hysitron, Microdrop Technologies, NTI-Europe, Océ Technologies, Ticona and Waters.

### Partners research

The Netherlands: Eindhoven University of Technology, University of Amsterdam and University of Twente;  
Germany: Deutsches Kunststoff Institut, Friedrich-Schiller-Universität Jena.

### Budget and organization

The total expenditure of the High-Throughput Experimentation Technology Area in 2007 amounted to € 3.18 million (budget 3.1 million). About € 1.03 million was spent on equipment. The remaining budget was allocated to 46 researchers (26 FTE). In 2007, prof. Ulrich S. Schubert was Scientific Chairman of the Technology Area and acted as interim Programme Area Coordinator.

### Publications and inventions

The research programme of the Technology Area generated two theses and 39 scientific publications (plus 1 book chapter and 15 proceedings/editorials/technical publications) in 2007, including contributions in high-ranking scientific journals such as *Advanced Materials*, *Advanced Functional Materials*, *Macromolecules* and *Soft Matter*. In addition, 4 scientific papers were published in collaboration with other Technology Areas of DPI. This collaboration resulted in 3 reported inventions and 1 filed patent applications.

### Projects

- #399: Automated analysis of thin films using atomic force microscope (AFM): Rapid preparation and screening of thin functional films and coatings
- #400: New thin-film and dot preparation techniques
- #401: Screening of polymerization catalyst activities and polymerization rates as a function of temperature
- #405: Development and application of new tools based on the AFM technology
- #447: Determination of residual metal catalysts, additives and stabilizers in polymer solutions, thin films and in the bulk within a high-throughput workflow
- #448: Automated parallel investigation (and preparation) of poorly soluble polymers, polyelectrolytes and strongly interacting polymers using high-throughput viscosimetry
- #449: Technical support for, and upgrading of, synthesizers/standard characterization
- #496: Correlation of optical data (IR and Raman) with physical properties of polymers and polymer materials
- #500: Development of integrated knowledge capture systems for combinatorial materials and polymer research
- #501: Fast and automated development and optimization of polymeric materials by combinatorial compounding and high-throughput screening (CC-HTS)
- #502: Combinatorial approaches to rational coating design: From polymerization kinetics via coating libraries to structure-property relationships and mathematical descriptors
- #508: Quantitative characterization of morphology and structure development of multi-component/ multi-phase polymers on the nanoscale
- #509: Comprehensive characterization of branched polymers
- #510: Advanced nanoscale characterization of interfaces
- #543: Polymer manufacturing using new approaches
- #546: Combinatorial discovery and optimization of photo-embossed polymeric bi-layers with dual functionalities
- #588: Optimization of polyoxymethylene (POM) additive recipes by combinatorial compounding for lower formaldehyde emission
- #589: High-throughput screening of functional materials in plastic electronics: optimizing ink-jet printing and electro-optical property pre-screening
- #611: From polymer synthesis to mechanical testing by high-throughput experimentation
- #612: High-throughput investigation of well-defined (co)polymers with lower critical solution temperature
- #613: Optimization of acrylonitrile/butadiene/styrene (ABS) and polycarbonate(PC)/ABS additive recipes by combinatorial compounding for UV stabilization
- #619: Development of polymer ontologies
- #620: Rapid prototyping and inkjet printing using polyurethane precursors
- #621: In-situ preparation of polymer nanoblends
- #622: Combinatorial screening of polymer solubility
- #645: High-throughput experimentation approaches to Ziegler-Natta-type catalytic olefin polymerizations

## Output

## Theses

E. Tekin  
Thin film libraries of functional polymers and materials prepared by inkjet printing.

C.A. Guerrero Sanchez  
Ionic systems in materials research; new materials and processes based on ionic polymerizations and/or ionic liquids

## Scientific publications

R. Hoogenboom, A. Nakahashi, G. Kickelbick, Y. Chujo, U.S. Schubert  
3-(2,2',6',2''-terpyridin-4'-yloxy)-propyl toluene-4-sulfonate  
*Acta Crystallogr. Sect. E* 63, o2311-o2313

H.M.L. Thijs, M.A.R. Meier, U.S. Schubert  
Application possibilities of preparative size exclusion chromatography to analytical problems in polymer science  
*e-Polym.* 46, 1-10

D. Founier, R. Hoogenboom, U.S. Schubert  
Clicking polymers: a straightforward approach to novel macromolecular architectures  
*Chem. Soc. Rev.* 36, 1369-1380

E. Tekin-Kazancioglu, E. Holder, D.A. Kozodaev, U.S. Schubert  
Controlled Pattern Formation of Poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) by Ink-Jet Printing  
*Adv. Funct. Mater.* 17, 277-284

I.Y. Phang, N. Aldred, A.S. Clare, G.J. Vancso  
Development of Effective Marine Antifouling Coatings. Studying Barnacle Cyprid Adhesion with Atomic Force Microscopy  
*NanoS* 1, 34 - 39

D.A.M. Egbe, E. Tekin-Kazancioglu, E. Birkner, A. Pivrikas, N.S. Sariciftci, U.S. Schubert  
Effect of styryl side groups on the photophysical properties and hole mobility of PPE-PPV systems  
*Macromolecules* 40, 7786-7794

J.M. Kranenburg, C.A. Tweedie, R. Hoogenboom, F.D. Wiesbrock, H.M.L. Thijs, C.E. Hendriks, K.J. Van Vliet, U.S. Schubert  
Elastic moduli for a diblock copoly (2-oxazoline) library obtained by high-throughput screening  
*J. Mater. Chem.* 17, 2713-2721

C.A. Fustin, H. Huang, R. Hoogenboom, F.D. Wiesbrock, A.M. Jonas, U.S. Schubert, J.F. Gohy  
Evaporation induced micellization of poly(2 oxazoline) multiblock copolymers on surfaces  
*Soft Matter* 3, 79-82

V. Marin, E. Holder, R. Hoogenboom, U.S. Schubert  
Functional ruthenium(II)- and iridium(III)-containing polymers for potential electro-optical applications,  
*Chem. Soc. Rev.* 36, 618-635

A.M.J. van den Berg, A.W.M. de Laat, P.J. Smith, J. Perelaer, U.S. Schubert  
Geometric control of inkjet printed features using a gelating polymer  
*J. Mater. Chem.* 17, 677-683

M.A.R. Meier, R. Hoogenboom, U.S. Schubert  
High-Throughput Screening in Combinatorial Material Research (book chapter)  
Wiley-VCH, Editors: K. Matyjaszewski, Y. Gnanou, L. Leibler  
3, 1967-999

T. Erdmenger, C. Häscher, R. Hoogenboom, U.S. Schubert  
Homogeneous tritylation of cellulose in 1-butyl-3-methylimidazolium chloride  
*Macromol. Chem. Phys.* 7, 440-445

E. Tekin-Kazancioglu, P.J. Smith, S. Höppener, A.M.J. van den Berg, A.S. Susha, A.L. Rogach, J. Feldmann, U.S. Schubert  
Inkjet printing of luminescent CdTe nanocrystal/polymer composites  
*Adv. Funct. Mater.* 17, 23-28

A.M.J. van den Berg, P.J. Smith, J. Perelaer, W. Schrof, S. Koltzenburg, U.S. Schubert  
Inkjet printing of polyurethane colloidal suspensions  
*Soft Matter* 3, 238-243

R. Hoogenboom, F.D. Wiesbrock, M.A.M. Leenen, M. van der Loop, S.F.G.M. van Nispen, U.S. Schubert  
Kinetic investigations on microwave-assisted statistical terpolymerizations of 2-oxazoline monomers  
*Aust. J. Chem.* 60, 656-661

C.A. Guerrero Sanchez, T. Lara-Ceniceros, E. Jimenez-Regalado, M. Rasa, U.S. Schubert  
Magnetorheological fluids based on ionic liquids  
*Adv. Mater.* 19, 1740-1747

C.A. Fustin, N. Lefevre, R. Hoogenboom, U.S. Schubert, J.F.M.W. Gohy  
Micellization of poly(2-oxazoline)-based quasi-diblock copolymers on surfaces  
*Macromol. Chem. Phys.* 208, 2026-2031

C.A. Guerrero Sanchez, M. Lobert, R. Hoogenboom, U.S. Schubert  
Microwave-assisted homogeneous polymerizations in water-soluble ionic liquids: an alternative and green approach for polymer syntheses  
*Macromol. Rapid Commun.* 28, 456-464

D. Wouters, W. van Camp, J. Desvergne, F.E. du Prez, U.S. Schubert  
Morphological transition during the thermal deprotection of poly(isobornyl)-*b*-poly(1-ethoxyethyl acrylate),  
*Soft Matter* 3, 1537-1541

C.M. Chiper, M.A.R. Meier, J.M. Kranenburg, U.S. Schubert  
New insights into nickel(II), iron(II) and cobalt(II) bis-complex based metallo-supramolecular polymers  
*Macromol. Chem. Phys.* 208, 679-689

A. Winter, U.S. Schubert  
New polyester-based terpyridine-macroligands and their blue iron (II) complexes  
*Macromol. Chem. Phys.* 208, 1956-1964

R. Hoogenboom, H.M.L. Thijs, M.W.M. Fijten, B.M. van Lankvelt, U.S. Schubert  
One-pot synthesis of 2-phenyl-2-oxazoline-containing quasi-diblock copoly(2-oxazoline)s under microwave irradiation  
*J. Polym. Sci. Part A: Polym. Chem.* 45, 416-422

C.R. Becer, C. Haensch, S. Hoepfener, U.S. Schubert  
Patterned Polymer Brushes Grafted from Bromine-Functionalized, Chemically Active Surface Templates  
*Small* 3, 220-225

M.A.R. Meier, J.O. Metzger, U.S. Schubert  
Plant oil renewable resources as green alternatives in polymer science  
*Chem. Soc. Rev.* 36, 1788-1802

N. Adams, U.S. Schubert  
Poly(2-oxazolines) in biological and biomedical application context  
*Adv. Drug Delivery Review* 59, 1504-1520

B.J. de Gans, S. Höppener, U.S. Schubert  
Polymer relief microstructures by inkjet etching  
*J. Mater. Chem.* 17, 3045-3050

I.Y. Phang; T. Liu; W.-D. Zhang, H. Schönherr, G.J. Vancso  
Probing buried carbon nanotubes within polymer-nanotube composite matrices by atomic force microscopy  
*Eur. Polym. J.* 43, 4136 - 4142

A. Winter, D.A.M. Egbe, U.S. Schubert  
Rigid  $\pi$ -conjugated mono-, bis- and tris(2,2',6',2''-terpyridines)  
*Org. Lett.* 9, 2345-2348

R.M. Paulus, T. Erdmenger, C.R. Becer, R. Hoogenboom, U.S. Schubert  
Scale up of microwave-assisted polymerizations in continuous-flow mode: cationic ring-opening polymerization of 2-ethyl-2-oxazoline  
*Macromol. Rapid Commun* 28, 484-491

J.M. Kranenburg, M. van Duin, U.S. Schubert  
Screening of EPDM cure states using Depth-Sensing Indentation  
*Macromol. Chem. Phys.* 208, 915-923

M.A.R. Meier, N. Adams, U.S. Schubert  
Statistical approach to understand MALDI-TOFM matrices: discovery and evaluation of new maldi matrices  
*Anal. Chem.* 79, 863-869

R. Hoogenboom, M.A.M. Leenen, H. Huang, C.A. Fustin, P. Guillet, J.F. Gohy, U.S. Schubert  
Synthesis and aqueous micellization of amphiphilic tetrablock ter- and quarterpoly (2-oxazoline)s  
*Macromolecules* 40, 2837-2843

M.W.M. Fijten, J.M. Kranenburg, H.M.L. Thijs, R.M. Paulus, B.M. van Lankvelt, K. Hult, C. Sprecher, D. Thielen, C.A. Tweedie, R. Hoogenboom, K.J. Van Vliet, U.S. Schubert  
Synthesis and structure-property relationships of random and block copolymers: a direct comparison for copoly(2-oxazoline)s  
*Macromolecules* 40, 5879-5886

R. Hoogenboom, H.M.L. Thijs, M.W.M. Fijten, U.S. Schubert  
Synthesis, characterization and cross-linking of a library of statistical copolymers based on 2'-soy alkyl'-2-oxazoline and 2-ethyl-2-oxazoline,  
*J. Polym. Sci., Part A: Polym. Chem.* 45, 5371-5379

M. Rasa, M.A.R. Meier, U.S. Schubert  
Transport of guest molecules by unimolecular micelles evidenced in analytical ultracentrifugation experiment  
*Macromol. Rapid Commun.* 28, 1429-1433

D. Founier, R. Hoogenboom, H.M.L. Thijs, R.M. Paulus, U.S. Schubert  
Tunable pH- and temperature-sensitive copolymer libraries by reversible addition-fragmentation chain transfer (RAFT) copolymerizations of methacrylates  
*Macromolecules* 40, 915-920

T.J. Joncheray, K.M. Denoncourt, M.A.R. Meier, U.S. Schubert, R.S. Durán  
Two-dimensional self-assembly of linear poly(ethylene oxide)-*b*-poly( $\epsilon$ -caprolactone) copolymers at the air-water interface  
*Langmuir* 23, 2423-2429

H.M.L. Thijs, C.R. Becer, D. Founier, C.A. Guerrero Sanchez, R. Hoogenboom, U.S. Schubert  
Water-uptake of hydrophilic polymers determined by thermal gravimetric analyzer with a controlled humidity chamber  
*J. Mater. Chem.* 17, 4864-4871

C.R. Becer, R. Hoogenboom, D. Founier, U.S. Schubert, Cu(II) mediated atp of mma by using a novel tetradentate amine ligand with oligo(ethylene glycol) pendant groups  
*Macromol. Rapid Commun.* 28, 1161-1166

R. Hoogenboom, U.S. Schubert  
Microwave-assisted polymer synthesis: recent developments in a rapidly expanding field of research  
*Macromol. Rapid Commun.* 38, 368-386

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

*Reported inventions*  
#502 J.T. Delaney, P.J. Smith, U.S. Schubert  
Preparation of conductive lines on polymer substrates

#502 J.T. Delaney, U.S. Schubert  
Macroporous hydrogels for tissue engineering

#501 M. Moneke, F. Becker, J. Barth  
Fast and automated development of polymeric materials

## The royal route to sustainability

**Natural polymers can be an inspiration to make polymers with properties tailored to an application. Moreover, by synthesizing them researchers might gain a better understanding of how they work. Nature as an example will play a role in achieving a more sustainable society. DPI is happy to be able to continue working along these lines.**

Dr. Gerard Robijn is a senior scientist working with Friesland Foods, a multinational company that develops, produces and sells nutritional and high-quality dairy products, fruit-based drinks and ingredients. Friesland Foods is one of the latest DPI partners. Robijn explains what he hopes to gain from the cooperation: "Food is a very complex mixture of categories of ingredients and many of these ingredients are natural polymers. In food research a lot of aspects play a role. It is not only taste and composition, it is also the structure of food and for that polymers are important. For some markets our products must contain as many calories as possible, for others as few as possible, but preferably without affecting taste and mouth feel. We cannot simply modify polymers and put them in food. It is a long and difficult route to comply with regulations. But from these modifications we can learn. If we modify a molecule and it has better properties than the one we used before, we can go back to nature and see if we can find it there."

Of course, Friesland Foods also cooperates with the Top Institute Food and Nutrition (TIFN) in Wageningen (Netherlands). Robijn: "In DPI we hope to learn from a field of science that is dealing with better-defined systems that are studied in more molecular detail than is usual in the more phenomenological way of working in food research."

### Synthesis

Dr. Norbert Windhab has been involved in biophysical chemistry throughout his professional life, which includes careers at Hoechst and Evonik Degussa. At Evonik Degussa he currently represents Strategic Projects in the business line Pharma Polymers at Evonik Industries' Röhm GMBH in Darmstadt. Robijn's remark about modifying polymers triggers him. "Looking at polymers and trying to understand them is not enough. You need to synthesize them to really understand the catalysts and

the processes. Analysis and synthesis are complementary approaches. By pursuing them both we can accelerate research in both fields." Windhab is very enthusiastic about his involvement in DPI. "Even from the discussions about the proposals I was already able to derive information that was useful for my own work. A network covering the complete value chain from research to market and from banks and investors to academia is not something you will easily find outside of DPI."

Windhab is not put off by the complexity of food that Robijn pictures. Complexity appeals to him. He thinks that it would be a good idea if academic researchers, rather than using the 'tamed' systems in which they change only one parameter in their research, changed to systems with more relevance to this industry. "There are cases where researchers have been working on the same molecules for generations. Experienced scientists never change two things at the same time in an experiment. They first use their new tools with the boring examples. In DPI the industrial partners can push them to use these tools with industrially relevant examples. That is my motivation for being active in DPI." Robijn agrees: "We have to take a bigger step in complexity to fill the gap between the model systems and the real-life ones. Only then will innovation be possible."

*Norbert Windhab:  
"Industrial partners in  
DPI can push academia  
to use more relevant  
systems in their  
projects."*



In this respect both Windhab and Robijn think that it can be very inspiring and motivating if contacts between industry and academia are intensified. Universities should focus on satisfying their scientific curiosity and industry can teach them where the real problems are and which directions to take. Professors should take their students to industrial laboratories more often. The need to bridge the gap between academia and industry is more urgent than ever, now that industrial research and the sheer robustness of the big industrial chemical companies are vanishing. And it is encouraging to see that research results are still operational even if the companies involved no longer exist.

### Interaction

The properties of biomaterials are determined not only by their chemical composition but also by physical parameters. Interaction between physicists and chemists is therefore vital – so vital that there can hardly be too much of it. “You never know beforehand which combination of persons will be fruitful”, says Robijn. “We recently spoke to researchers who investigated galactic systems with terahertz spectroscopy. When they explained that they used this method to identify compounds millions of light years away and how they did this, we discussed the possibilities of the technique for our company and eventually agreed that it could definitely be used as an economically feasible detection system in some of our factories. You cannot know when synergy arises, so you will have to talk to others. DPI offers a very effective platform for this.” And as Windhab mentions, the world of molecular science is such that most of its proponents get along quite well together.

Ir. Richard van den Hof, interim Chairman of the Technology Area of Bio-Inspired Polymers, illustrates the role DPI plays in this respect. “In the call for proposals we found two proposals that were very similar and asked the researchers who submitted these to combine the two. At first they said it could not be done, because their intentions were different, but when we insisted they came up with one new and better proposal. Now they love to work together.” In the same spirit DPI as a research institute seeks cooperation with other knowledge institutes and organizations such as TIFN, the medical and pharmaceutical top institutes and FOM, the Dutch Foundation for Fundamental Research on Matter. The industrial DPI partners that were originally only active in synthetic polymers are shifting their attention to these fields as well. This is because health is an important subject and polymers can play a role

in the development of better food, effective medicines and innovative implants. Van den Hof: “Organizations such as FOM think too much in physical terms, we think too much in chemical terms, so we have to do this together, to integrate the disciplines and their way of working. It used to be the industrial engineers who did this.”

“DPI should not confine itself to Europe when looking for excellent knowledge institutes. Scouting around the globe for local initiatives and top experts and convincing them to work together on a certain topic can really speed up innovation. You should not stop at a border. After all, the product market is also global.” Robijn stresses more than once during the discussion that he would like DPI to adopt a more international approach.

A number of bio-based trends in the world will have an effect on bio-based polymer research. Testing new materials without using animals, going from organic solvents to water-based solutions, using less water and less energy, using renewable rather than fossil resources but without affecting other markets, such as the food market... the royal route to a sustainable society is technology. The best way to go that route is not by duplicating efforts but by joining forces.

“In comparison with nature, we do not have millions of years to change things”, says Robijn. “We really have to be creative to make big steps.”

*Gerard Robijn: “We hope to learn more about complex systems such as food from a field of well-defined systems.”*



*Jules Harings: "It is very inspiring and motivating to see that there may be a useful application of our work on the horizon."*

Jules Harings

## How a spider spins

In the Bio-Inspired Polymers Technology Area, nature is the inspiration for new materials. One such inspiration is the process by which spiders spin their silk at room temperature, which ultimately results in a fibre with a unique combination of properties. It has long been a dream to mimic this process and use it to spin fibres from aliphatic polyamides. This concept has been a driving force for professor Sanjay Rastogi and his PhD student Jules Harings, as it has been for many others in the field. Rastogi and Harings aim to investigate hydrogen bonding in the presence of water and ions, which plays an important role in the natural spinning process of silk.

Jules Harings started his DPI project three years ago. He recalls how spider silk is formed: "In a spider's silk gland, hydrogen bonding of the silk peptides is shielded, preventing crystallization in the aqueous solution. Secondary interactions, such as ionic and hydrogen bonding, are important parameters in the self-assembly of the peptides. In the specific drag flow a liquid crystalline phase develops through which these peptides tend to orient themselves, leading to the desired properties. That is what I am looking for in our project: how to influence the self-assembling of synthetic polymers by influencing the hydrogen bonding. We start from relatively simple synthetic polyamides, not from sophisticated biological poly-peptides as some others in the field do."

Professor Sanjay Rastogi tells how the project Harings is engaged in was defined. "At DSM people found that it is possible to dissolve hydrogen-bonded materials such as nylon in superheated water. DSM established the fact, patented it and there it stopped for them, but we wanted to understand the mechanism. Molecular understanding, based on advanced experimental techniques, is essential to make any further progress in this well studied subject. Though considerable efforts have been made to develop oriented polyamide fibres, the use of superheated water in the presence of ions is an unexplored area. This also provides the possibility to introduce biological concepts for synthetic polymers."

### Superheated water

The project has been under way for some time now. Following successful initial experiments on a small scale, Rastogi and Harings have built a new device for spinning. This device makes it possible to heat a solution to the superheated state and cool it down again in a controlled way. In this device Harings dissolves nylon in superheated water in the presence of ions that prevent crystallization. He then removes the ions sufficiently fast to establish hydrogen bonding and to freeze the desired structure.

As was to be expected, several chemical companies have shown considerable interest in this project. Among them are DSM, BASF, Dow and Teijin Aramid. Harings is happy about this: "In general, working in DPI projects, bridging academia and industry, is inspiring and motivating. Especially as people from industry follow your work with potential applications in mind. For me personally it is also good to build a network of contacts in industry which will continue

to be useful after I finish my project. I have not yet decided what I will do after that. The fundamental research I am doing now is still very appealing, but I will keep my options open". "Maybe he will start his own company," a smiling Rastogi adds. "DPI projects are very attractive to young people because of the connection with industry. Therefore PhD positions on DPI projects tend to be taken up first."

Jules Harings started his PhD project at Eindhoven University of Technology (Netherlands) in 2005. He is studying the shielding of hydrogen bonding in peptides by ions and the subsequent crystallization in fibres when the ions are removed.

Professor Sanjay Rastogi has been involved in DPI's Bio-Inspired Polymers Technology Area since the beginning of 2004. He is currently working mainly at Loughborough University in Leicestershire in the United Kingdom and has a part-time position at Eindhoven University of Technology.

TU/e technische universiteit eindhoven

*Sanjay Rastogi: "DPI projects are very attractive to young people because of the connection with industry."*



## Facts and figures

### Objectives

The goal of the programme is to develop advanced bio-inspired polymeric materials and methodologies for existing and new applications. The development of these materials is inspired by natural polymeric structures and nature's principles (such as self-assembly and biocatalysis). These polymers can be produced from natural or synthetic resources and by using (chemo)enzymatic and microbial catalysis. The structure-property relationships of the novel materials are to be studied in order to elucidate why they exhibit these unique properties. The scale of the synthesis is to be developed to such an extent that tangible amounts of materials will become available for testing. The aim is to demonstrate scale-up potentials as well.

### Partners industry

Dow Benelux, DSM, Océ Technologies, Agrotechnology & Food Innovations, Evonik Degussa, Friesland Foods

### Partners research

The Netherlands: the universities of Eindhoven, Maastricht and Wageningen, PTG Eindhoven, Agrotechnology and Food Innovations.

United Kingdom: the universities of Leeds and Loughborough. Germany: Max Planck Institut and Friedrich-Schiller-Universität Jena.

### Budget and organization

The total cost in 2007 was € 0.7 million (budget € 1.2 million). The total number of FTEs allocated at the end of 2007 was 8, distributed over 13 researchers. In 2007 ir. Richard van den Hof acted as Scientific Chairman and as interim Programme Area Coordinator.

### Publications and inventions

In 2007 the first scientific article was published in this Technology Area. Furthermore there was one reported invention, which was made jointly with the Performance Polymers Technology Area.

### Projects

- #587: Crossing the border between synthetic and natural polymers: Keratins as cheap feedstock for novel self-organizing oligomers and polymers
- #599: Interaction of superheated water with hydrogen bonding semi-crystalline polymers: a computational approach
- #602: Collagen-inspired self-organizing materials
- #603: Strengthening/shielding of hydrogen bonding by physical processes in the presence of salts and water
- #604: Biomimetic polymers for the encapsulation of functional entities
- #608: High molecular weight aliphatic polyesters by enzymatic polymerization for medical applications
- #609: Advanced materials on the basis of cellulose via novel reaction processes
- #610: Molecular engineering with self-assembled peptides/Mimicking nano-structured natural materials following a modular approach

### Output

*Scientific publications*  
Jie Yin, Sanjay Rastogi, Ann E. Terry, Crisan Popescu  
Self-organization of Oligopeptides Obtained on Dissolution of Feather Keratins in Superheated Water  
*Biomacromolecules*  
8, 800-806

*Reported inventions*  
#603 + #460 J.A.W. Harings, Y. Deshmukh, E. Vinken, S. Rastogi  
Polyamide with reduced crystallinity

## Filling the gap

**Polymer electronic devices are typically multi-layer devices in which the materials that are used largely determine the performance. Prototypes of such devices are usually made in a batch-wise process, such as spin coating. To actually produce devices in a high-volume, high-yield process other processing techniques such as inkjet printing and screen printing are needed. DPI's Large-Area Thin-Film Electronics (LATFE) Technology Area aims to fill the gap between laboratory-scale and industrial deposition techniques and, moreover, to improve the reliability and the yield of device production.**

Materials companies produce materials. Device designers and device manufacturers realize devices by depositing and patterning layers of these materials. Which deposition method is optimal for which device depends on the desired operation characteristics of the device. Decisions on the deposition method can only be made if the advantages and disadvantages of all possible deposition methods are well known. Patterning, stack integrity and yield are just a few of the process parameters that are important.

### *LATFE Kick-off meeting*

Large-area deposition techniques are investigated in the LATFE Technology Area. The first projects have been granted in this latest of DPI's Technology Areas, but there is also room for research into new disruptive device architectures that allow more robust processing and improved yields. Early March 2008 there was a kick-off meeting for this new Technology Area, where project leaders of projects that have already been granted presented their plans.

### **Vapour barrier**

One of the present challenges in polymer-based electronic devices, such as flexible Organic Light-Emitting Diodes (OLEDs) and flexible solar cells, is their limited lifetime due to their sensitivity to water vapour and oxygen. Therefore packaged polymer electronic devices contain barrier layers.

The state-of-the-art solution in moisture and oxygen diffusion barrier technology is a multilayer system based on alternating inorganic layers (the effective barriers) and organic layers. This approach is rather empirical and the role of the organic layer is not yet understood.





### LATFE Kick-off meeting

The DPI project is therefore approaching the issue of barrier technologies for flexible devices by means of a new model system in which both the inorganic and the organic layer chemistry, porosity and surface morphology can independently be tuned to investigate their effect on overall barrier performance. The inorganic-organic multilayer system will be deposited by means of a hybrid approach via two vacuum deposition techniques: plasma-enhanced Chemical Vapour Deposition (CVD) for the inorganic layer and initiated CVD for the organic layer, implemented in the same chamber which is presently under construction.

Project leader dr. Mariadriana Creatore of the Eindhoven University of Technology in the Netherlands: "The goal of this project is to shed light on the issues related to the moisture and oxygen barrier technology that are still unresolved: porosity and pinhole presence control by means of a systematic approach to the role of the inorganic and organic layers."

### Shorts

Another challenge to take up is the prevention of electrical shorts in OLEDs for solid-state lighting. Shorts have dramatic consequences since large surfaces will become inactive if there is only one short. Contaminations may cause such problems. But solving shorts is not simply a matter of locating the contaminations and preventing them: not all contaminations result in shorts and not all shorts occur early in the lifetime of the device. A method to determine the probability of a certain contamination resulting in a short can help here. Professor Klaus Meerholz of the University of Cologne in Germany has defined a project to this end. Meerholz: "We study the behaviour of shorts before they occur, using such methods as local photocurrent mapping, electroluminescence, and surface-plasmon imaging. Comparison of this behaviour with suspicious-looking locations should give us indications of possible shorts. Afterwards, we disintegrate the devices and investigate the shorted area by scanning-electron

microscopy. Once we understand the short formation process, we can come up with chemical and physical measures to prevent shorts from happening.”

### Robust

State-of-the-art Polymer Light Emitting Diodes (PLEDs) consist of one active layer in which charge carriers (electrons and holes) move and through their recombination emit light. This layer is usually very thin (60 to 80 nm) in order to reduce the operating voltage and thus increase the power efficiency of the PLED. For thicker layers the low mobility of the charge carriers in conjugated polymers requires a high voltage to obtain the current and light output as required by the applications. However, a disadvantage of using such thin layers is that it also increases the probability of shorts. Devices with two or three active layers can remedy this shortcoming, but if they are not designed carefully the additional layers might also lead to additional voltage losses. This can then be counteracted by doping the layers. In the group of professor Paul Blom at the University of Groningen these doped multilayer PLEDs will be investigated. “We want to unravel the mechanism of doping and by modelling the device make it more robust. Our hope is also that with these doped layers we can also get rid of the reactive metals that are now used as electrodes.”

### Morphology

As opposed to display pixels with a diameter of 100 microns, lighting applications require deposition of light-emitting polymers on large surfaces; areas of a few square meters are no exception. Instead of inkjet printing, techniques such as dip-coating and die-coating are being considered. In die-coating a moving metal blade distributes a thin liquid film on the surface to be coated. It is a highly attractive option because it incurs significantly less waste of material compared to spin-coating and it can be used with flexible substrates processed in a reel-to-reel fashion. In professor Anton Darhuber's group at Eindhoven University of Technology the deposition process and the subsequent drying process will be studied. “We need to identify the process window, for example with respect to speed, gap clearances and substrate surface composition, in which die-coating gives suitable results. A prototype die-coater is being built at the moment. Numerical simulations and process modelling will facilitate the identification of optimal process conditions. Evaporative phenomena such as the coffee-stain-effect

tend to degrade the layer homogeneity. It is our goal to control and eliminate them in a material-independent way, that is, without introducing chemical additives but rather by adapting the drying process.”

### Materials

The materials that perform best in laboratory devices do not necessarily do so in mass produced devices, where they have to be deposited on large areas. The organic semiconductor with the highest mobility of the charge carriers and the best stability in air, TIPS-PEN (tri-isopropyl-silyl-ethynyl pentacene), owes these good properties to the alignment of the molecules during crystallization in single-crystal-like material. However, defects such as polycrystalline regions, orientation variability, voids and cracks often occur in this solvent-based process.

In a joint project between Eindhoven University of Technology and Queen Mary University in London it will be investigated whether a blend of TIPS-PEN with self-organizing polymers will indeed improve the molecular alignment properties and stability without influencing the mobility of the charge carriers.

“It will be an interplay of thermo-dynamics of phase separation and the kinetics of film formation and the drying process after the deposition. The final quality of the layers produced with the improved process will be verified by measuring the characteristics of arrays of organic field effect transistors containing these layers. Of course it is important that they can be produced in a reproducible way”, says professor Dick Broer of Eindhoven University of Technology.

These projects all take the polymer electronic devices or the materials they are made of as starting points and look into suitable robust deposition techniques. There is also another side to start from. Can existing printing techniques be adapted to the materials, the thickness of the layers, the processing speed and the desired homogeneity of the layers? Are there any disruptive technologies and wild ideas about that? Manufacturers of photographic printers are looking for new markets, so maybe they can fill the gap between materials providers and device makers? Or is the printing industry unable to take the lead, and does it have to wait for demanding and hopefully successful applications. One thing is certain: DPI will play an important role in the field.

## Facts and figures

### Objectives

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

### 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 realize the transition from lab scale to industrial scale and reliably processed devices. Although lab-scale devices perform extremely well, mass production is still far away because industrial processes and fundamental knowledge about large-area material deposition are lacking.

### Disruptive device architectures

The objective is to develop disruptive device architectures for more reliable and easier production of large area solid-state lighting. Current device architectures require very thin films (about 100 nm) having less than 2% thickness deviation. These architectures are placing very strict demands on the processing and production of devices, and this is currently resulting in poor yields. New device architectures allowing more robust processing and production and improved yields without affecting device performance (efficiency, homogeneity of light output) would be very welcome.

### Partners industry

The Netherlands: Philips, OTB and TNO (Holst Centre).

### Partners research

The Netherlands: the universities of Groningen and Eindhoven. Germany: University of Cologne. United Kingdom: Queen Mary University of London.

### Budget and Organization

Total expenditure in 2007 was € 292,000 (budget € 910,000). The total number of FTEs allocated at the end of 2007 was 1 (3 researchers), because research proposals were granted in 2007 and applicants were recruiting skilled researchers. Total expenditure on equipment, expensive consumables and special analysis time was € 214,000. In 2007 Programme Area Coordinator dr. John van Haare was actively engaged in setting up the Technology Area and granting projects after thorough industrial evaluation and peer review. A Scientific Chairman has not been appointed yet.

### Publications and inventions

Since the LATFE Technology Area was still in the start-up phase, hardly any contributions to scientific symposia in the form of posters and presentations were possible. The granting of excellent projects will certainly generate a take-off in publications in 2008. In March 2008 the Technology Area organized a public kick-off meeting to attract broader attention from industries and academia for the LATFE research programme. New projects were staffed at the end of 2007.

### Projects

- #618: Stacked Polymer Light-Emitting Diodes
- #640: Engineering the morphology of organic (semi)conductor layers
- #663: Initiated chemical vapour deposition of polymer interlayers for ultra-high moisture diffusion barrier systems
- #665: Composite  $\pi$ - $\pi$  stacked organic semiconductors: materials and processing towards large area electronics

*John van Haare and Dietrich Haarer during kick-off meeting Large Area Thin-Film Electronics*



# Gateway to the future

Chemical companies have closed their central research laboratories and scaled down their long-term, high-risk but high-potential research. Analytical technologies require expensive equipment and experienced teams of people to use them. University groups cannot afford to keep this competence in the air on their own. DPI and in particular the Corporate Research Technology Area is needed more than ever to provide a gateway to the future of the polymer application field.

*Claus Eisenbach: "Now that central laboratories in the big companies have gone, DPI becomes increasingly important for them."*

Professor Claus Eisenbach, director of the Forschungsinstitut für Pigmente und Lacke (FPL) in Stuttgart, is Scientific Chairman of DPI's Coating Technology Area. Like all other Technology Area chairmen he is a member of the programme committee of the Corporate Research Technology Area. "Big chemical companies used to have what they called a central research laboratory, where research projects not directly aimed at a particular business unit were carried out. Among these were the synthesis of novel materials, the development of characterization and visualization techniques, advanced computer modelling methods, and studies into the fundamental relationships between structure and properties of polymers. Now that these central laboratories have gone, big chemical companies will more and more turn to universities and knowledge institutes for long-term research. DPI will become increasingly important for them."

#### Science-intensive

Professor Dietrich Haarer, recently retired from the University of Bayreuth in Germany and Chairman of the Functional Polymer Systems Technology Area, adds: "It is good that DPI has a place where very science-intensive experimental research such as crystal structure studies and topology studies is being done and where electron microscopy is practised and perfected for use in polymer science. The instrumentation involved in such work is generally too extensive and too expensive for a single university group to maintain. In addition, it requires teams consisting of four or five experienced workers to prepare the samples and operate the equipment, which is also a difficult task for one university group. And for the other Technology Areas at DPI it is essential that there is a central place where research for the benefit of all is being done."

Europe is a leader in the global chemical industry. DPI contributes to maintaining this position by providing an international platform for discussion between universities and industry. This is unrivalled in the rest of the world. Most European chemical companies are represented in DPI. "A German chemical company such as Bayer and a Swiss company such as Ciba choose to discuss their issues not in Germany or Switzerland but in the platform provided by DPI because of its long-standing tradition of excellent connections between universities and industry", says Haarer. "What I also like very much is the close contact and good cooperation between

physicists and chemists at DPI. In industrial companies one of the two disciplines usually dominates, but here at DPI it is almost a fifty-fifty distribution, at least in the areas I am familiar with."

#### Well-trained

Not only have big chemical companies closed down or considerably reduced their central research facilities, some of them have also changed their product portfolio and their research targets. DPI needs to refocus the programme in the Corporate Research Area to align it with industry interests. Both Haarer and Eisenbach hope that these companies, once they have sorted out their own problems related to the changes in their portfolios, will be a little bit clearer about what they expect from DPI in this field. And there is the aspect of time. When companies are focused on business-related research, their time horizons are typically two or three years, a period that obviously is too short for many technologies. Exploring a new technology takes two or three PhD projects. Such traditions are needed to maintain Europe's leading position in the chemical world in the long run. Universities have become the constant factor and industry will need them for their ability to maintain science in a consistent manner over the years.

*Dietrich Haarer: "As a source of well-trained polymer chemists and physicists DPI is well worth the 'little' money industry spends in it."*



Eisenbach: "Companies may expect to be able to buy all the research results they need from other sources." But even when a company wants to buy research results with the intention of turning them into innovative commercial use, they will also need their own research people to be able to judge their real value. And they will need researchers for further development efforts to turn these results into commercial successes. In other words, more than ever before industry needs DPI for its precompetitive long-term projects, but DPI has an equally strong need for industrial participation to provide guidance and direction. "And industry also needs DPI as a source of well-trained polymer chemists and physicists", adds Haarer. "This may even be more important than the actual project results and is well worth the little money industry spends on DPI."

#### Unique

DPI offers a unique platform for discussing and executing high-risk, high-potential projects in new research fields. There will certainly be new long-term projects in the corporate area (in the Functional Polymers Area these will result

from the shift from devices to life science that some companies are going through, and in the coatings area they will be driven by the increased use of renewable feedstock). After all, in the long run the risky projects will be the ones where the main progress will be made.

Modelling of mechanical behaviour and life time prediction of amorphous polymers under loading conditions as is being done in the group of professor Han Meijer at Eindhoven University of Technology (Netherlands) has already provided very useful knowledge that can directly be implemented in industry. Real life is more complicated than models but a solid basis was provided to expand into more complex processes such as injection moulding, into more complex materials such as semi-crystalline materials, and into making the connection with the molecular explanation of the phenomena observed and modelled. The latter, multi-scale modelling and molecular dynamics, is being done in the group of professor Thijs Michels also at Eindhoven University of Technology. In 2007 new projects covering these items were started.



## Facts and figures

### Objectives

The objective of the Corporate Research Programme is to initiate and support enabling science and conceptual new science, of interest to all partners of DPI because of its long-term potential impact.

This programme is primarily science-driven with a vision on industrial future needs and opportunities. It operates at the forefront of scientific knowledge and capabilities of polymer science. Three sub-clusters are appointed

### Enabling Science

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

### New Science

New concepts in polymer chemistry and polymer physics in view of long-term future needs of sustainability, durability and bio-related polymer systems.

### Partners industry

There is no industrial partnership in this area so far. All Technology Areas are represented by their Scientific Chairmen.

### Partners research

The Netherlands: the universities of Amsterdam and Eindhoven, NWO. Germany: Deutsches Kunststoff Institut, Leibniz-Institut für Polymerforschung.

### Budget and organization

The total cost in 2007 was € 1.5 million (budget € 1.9 million). € 0.3 million was spent on equipment. A total of 13 FTEs were allocated, distributed over 28 researchers. In 2007 ir. Richard van den Hof chaired the Corporate Research Area and acted as interim Programme Area Coordinator.

### Publications and inventions

In 2007 a total number of 14 scientific publications appeared, including 3 theses. Moreover, there were 2 reported inventions and 1 filed patent application in the Corporate Research Area.

### Projects

- #511: Nanostructure and chain mobility in polymers studied with solid-state NMR
- #596: Chemically improved polysaccharides – Detailed structure-property relationships
- #597: Ultra performance polymer separation
- #598: DUBBLE, development of (and general support for projects needing) advanced X-ray analysis
- #601: Synthesis of well-defined branched architectures for method development in polymer characterization
- #615: 3-D tomographic reconstruction of local morphology and properties of polymer systems with nanometric resolutions by means of TEM and AFM
- #643: Development of high-temperature two-dimensional liquid chromatography for the characterization of polyolefins (CR+PO#642)
- #446: Structured fluids & rheology in processing
- #487: Deformation, damage and failure: deformation mechanisms below the continuum scale
- #578: Determining mechanical properties without the need for mechanical testing
- #414: Self-assembling, monodisperse polymers forming ultrastrong fibers and materials for medical and technical purposes
- #488: Biocatalytic polymerization in supercritical CO<sub>2</sub>
- #475: Bioactive scaffolds for tissue engineering of cardiovascular substitutes
- #429: High-resolution (energy and lateral) analysis of polymer materials by cryo-transmission electron microscopy based electron energy loss spectroscopy (> cont. #615)
- #398: Intervertebral disc prosthesis
- #381: Enzymatic catalysis in the preparation of block copolymers

*Tim Mulder: "DPI is very successful at achieving synergy by bringing people into contact with each other. It is through DPI that I came into contact with all the people who are relevant to my project."*

Tim Mulder

## Modelling reality

Polymer chemistry dictates much of what is going on at DPI. It is important to know how a material is made, but it is just as important to know why it behaves the way it does. Models play a very important role in this field.

During the four years that Tim Mulder worked in the Corporate Research technology area he tried to unravel the mechanical behaviour of amorphous glassy polymers. Mulder: "Some polymers are brittle, some are ductile and some can be either brittle or ductile, depending on their history. We tried to understand this behaviour at the molecular level with the ultimate goal of being able to develop new materials with excellent properties. Experiments in this field are very expensive and have so far failed to bring the desired insight, so we used molecular and rheological modelling. However, modelling also has its limitations, which are related to the extremely wide ranges of length and time scales that are important to polymer behaviour. With the help of an algorithm that Professor Doros Theodorou of the University of Athens developed ten years ago, and with methods such as coarse graining and scale jumping, we were able to greatly improve upon earlier simulations of commonly used polymers such as polystyrene and we could make a step towards understanding the mechanical behaviour of glassy polymers."

Professor Theodorou has been working in this field for a long time and was made aware of DPI via contacts he had at DSM and at the Eindhoven University of Technology (Netherlands). Theodorou: "What I appreciate most about DPI is that it is a very creative and lively polymer research community comprising both industrial and academic researchers. It is an excellent source of inspiration for new research programmes and provides opportunities for very vigorous scientific interaction. I submitted two proposals and both were granted. In my home country there is nothing comparable to DPI. As far as I know, the possibilities for close interaction between industry and academia that DPI offers are unique in the world."

### Multi-scale

Even in the Corporate Research technology area, where members are mostly of academic origin, the influence of industrial people is important. Theodorou is very positive about it: "There have been people who, looking at the work that we do, were able to find ways in which this work could be useful for solving their very practical materials design and optimization problems. That is something I could not do myself. I'm quite impressed by the knowledge, judgement and resourcefulness of these people." In the academic world molecular models tell you everything about processes taking place at length scales of tens of nanometres and time scales of microseconds. The challenge for Theodorou is to bridge the gap to the industrial world and

predict what happens at time scales of hours and length scales of metres. Multi-scale modelling it is called and according to Theodorou it is made possible not only by the advances in computer hardware but certainly also because new insights and algorithms have been developed. In his current DPI project he is investigating how cavities emerge in rubbery polymers subjected to tensile stress. Mulder defended his thesis earlier this year and now works for Océ-Technologies, the Dutch printer and copier company, in a completely different field: image processing. Yet the experience he has gained with rheological models helps him to choose useful strategies for tackling image processing problems. "By analyzing and manipulating images we attempt to obtain optimal results in terms of print quality and image productivity, given the hardware limitations of a printer, or we correct or mask errors in printers. A well-known example is the appearance of white lines when you use the fast print mode of a standard inkjet printer. But is not only the technical experience of DPI that I use in my new job. I have also experienced the value of a good competence network. DPI is very successful, via a multitude of ways, at achieving synergy by bringing the right people into contact with each other. It is through DPI that I came into contact with all the people who are relevant to my project." Tim Mulder studied the behaviour of polymer glasses and its relationship with polymer properties in his PhD project at Eindhoven University of Technology in the Netherlands. He now works at Océ-Technologies and investigates strategies to tackle image processing problems.

Professor Doros Theodorou did his PhD project at MIT, was Professor of Chemical Engineering at the University of California, Berkeley (USA), and is now Professor at the National Technical University of Athens (Greece). He has two DPI projects related to modelling of materials and is very interested in DPI [klinkt vreemd; misschien eerder: is very interested in the possibilities offered by DPI].



**Doros Theodorou:**  
*"What I appreciate most about DPI is that it is a very creative and lively polymer research community."*



**Output***Theses*

M. de Geus  
Enzymatic Catalysis in the Synthesis of New Polymer Architectures and Materials

E. Boelen  
Novel radiopaque biomaterials for spinal surgery

R.P.M. Janssen  
Quantitative prediction of polymer failure

*Scientific publications*

P.J.A. Janssen, P.D. Anderson  
Boundary-integral method for drop deformation between parallel plates, *Phys. Fluids* 19(4), 043602

E.A. Tocha, J. Song, H. Schönherr, G.J. Vancso  
Calibration of Friction Force Signals in Atomic Force Microscopy in Liquid Media

*Langmuir* 23, 7078 – 7082

Theodora Spyriouni, Christos Tzoumanekas, Doros N. Theodorou, Florian Mueller-Plathe, and Giuseppe Milano  
Coarse-Grained and Reverse-Mapped United-Atom Simulations of Long-Chain Atactic Polystyrene Melts: Structure, Thermodynamic Properties, Chain Conformation, and Entanglements  
*Macromolecules* 40, 3876-3885

Doros N. Theodorou  
Hierarchical modelling of polymeric materials  
*Chemical Engineering Science* 62, 5697-5714

Tim Mulder, Jing Li, Alexey V. Lyulin, M.A.J. Michels  
Monte Carlo simulation of uniaxial deformation of polyethylene-like polymer glass: role of constraints and deformation protocol  
*Macromolecular Theory & Simulation* 16, 348-358

Y. Song, H.H. Weekamp, M. Kamphuis, Z. Zhang, I. Vermes, A.A. Poot, D.W. Grijpma, J. Feijen  
Porous tubular scaffolds based on flexible and elastic TMC (co)polymers  
*Tissue Engineering* 13(7): 1745

Ramona A. Orza, Pieter C.M.M. Magusin, Victor M. Litvinov, Martin van Duin, M.A.J. Michels  
Solid state H NMR study on chemical crosslinks, chain entanglements and network heterogeneity in peroxide-cured EPDM rubbers  
*Macromolecules* 40, 8999

J. Song, J.F.L. Duval, M.A.C. Cohen-Stuart, H. Hillborg, U. Gunst, H.F. Arlinghaus, G.J. Vancso  
Surface Ionization State and Nanoscale Chemical Composition of UV-Irradiated Poly(dimethylsiloxane) Probed by Chemical Force Microscopy, Force Titration, and Electrokinetic Measurements  
*Langmuir* 23, 5430 – 5438

P. Forcen, L. Oriol, C. Sanchez, R. Alcalá, S. Hvilsted, K. Jankova, J. Loos  
Synthesis, characterization and photoinduction of optical anisotropy in liquid crystalline diblock azo-copolymers,  
*J. Polym. Sci., Part A: Polym. Chem.* 45(10), 1899-1910

Alexey V. Lyulin, M.A.J. Michels  
Timescales and mechanisms of relaxation in the energy landscape of polymer glass under deformation: Direct atomistic modelling  
*Physical Review Letters* 99, 085504

Alexey V. Lyulin, M.A.J. Michels  
Timescales and mechanisms of relaxation in the energy landscape of polymer glass under deformation: Direct atomistic modelling  
*Virtual Journal of Biological Physics Research* 14, 5

*Filed patent applications*  
#414 A.A. Martens, M.W.T. Werten, G. Eggink, M.A. Cohen Stuart, F.A. de Wolf  
Multi-block copolymers

*Reported inventions*  
#414 A.A. Martens, M.W.T. Werten, G. Eggink, M.A. Cohen Stuart, F.A. de Wolf  
Multi-block copolymers

#475 Balguid, A. Mol, M.H. van Marion, C.V.C. Bouten, F.P.T. Baaijens  
Electrospinning of nano-fibre scaffolds

**High-throughput experimentation in polyolefins research at the University of Naples Federico II (I)**

