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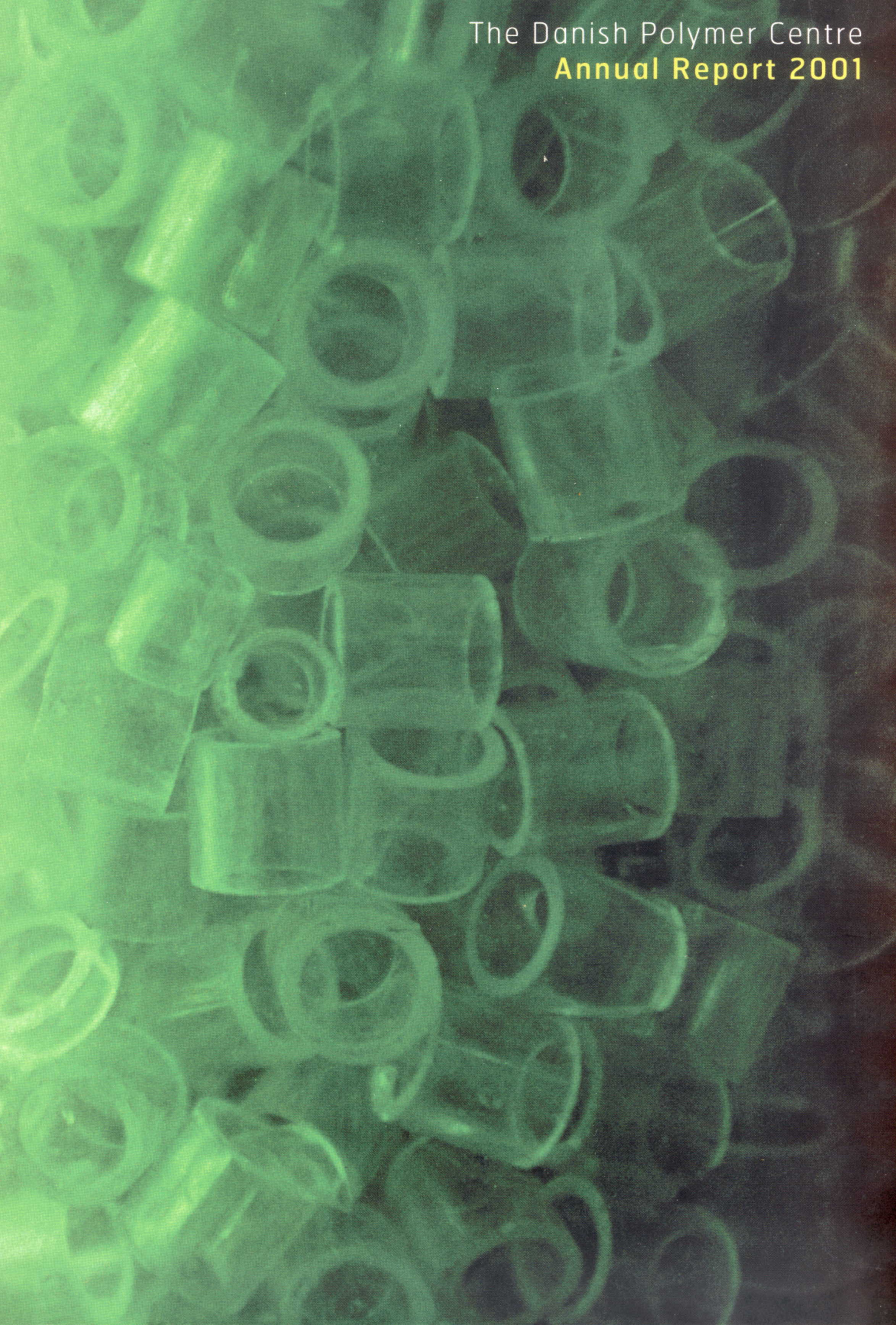
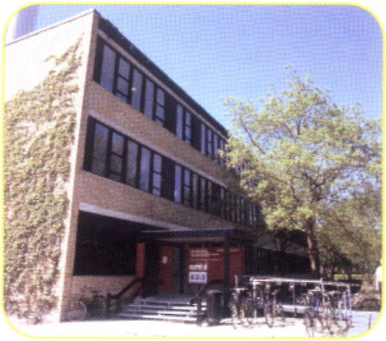
The Danish Polymer Centre
Annual Report 2001





Annual Report 2001

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Table of contents:

1 INTRODUCTION

Background

The Danish Polymer Centre was established in October 1999 following a recommendation for a national materials research strategy in Denmark. The purpose of the centre is to provide a strong unit for research, education and industrial cooperation within polymer engineering and science in support of the Danish polymer industry.

Instrumental in the establishment of the Centre was a donation from Aage and Johanne Louis-Hansen's Fund of a research professorship to the Centre, in addition to a special grant from the Danish Technical Research Council.

The centre is a collaboration between the Risø National Laboratory and the Technical University of Denmark (DTU). At the DTU the Department of Chemical Engineering and the Department of Manufacturing Engineering and Management participate in the centre. From 2001 the Polymer Department at Risø coordinates the activities at Risø

Entrance to the new laboratories in building 423, DTU established in 2001.

Thermogravimetric analysis of polymer sample in the new laboratories at DTU.

From the outset it was considered important with common laboratories to obtain the full effect of the collaboration between the two departments at the DTU and Risø National Laboratory. In 2001 new laboratories for polymer research and education were established at the DTU campus in Lyngby as shown in the pictures on this page. In addition to well equipped laboratories at Risø which will be expanded in 2002 and 2003, these facilities provide a common ground for polymer chemists, polymer physicists, chemical engineers and mechanical engineers from the two institutions.

The Annual Report for 2001 represents therefore the first report from a period in which the new facilities have been utilized to full advantage.

Summary of 2001

Polymer centre staff.

The research is concentrated within 4 specific areas. A motivation for these areas and a general description of the research is given in section 2. In addition, the section describes a number of selected projects that have led to remarkable results in 2001. These contributions are in no way exhaustive of the research results obtained in the year but are intended to given an appreciation of the Centre activities.

The complete list of scientific results in section 5 reveals 66 publications in international journals with peer review in 2001. Titles of 7 Ph.D, 8 Masters and 6 B.Sc. theses are found in section 3. A description of industrial cooperation is found in section 4.

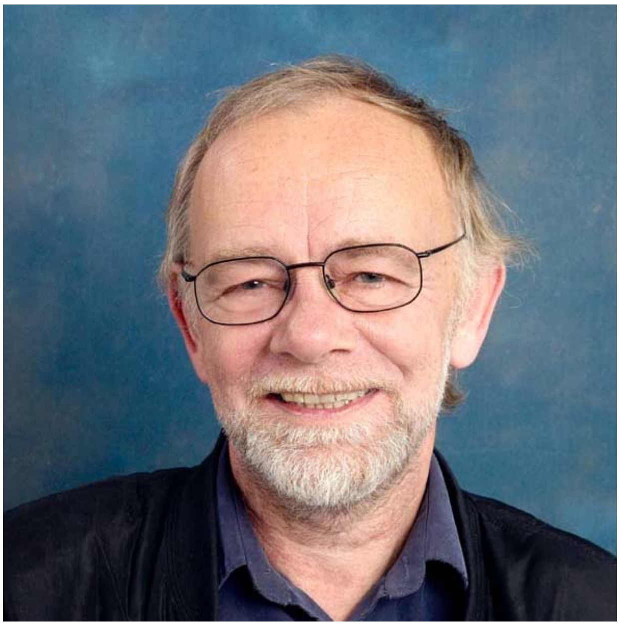
It is worth mentioning that staff members in the Polymer centre in 2001 contributed to the filing of 3 patent applications and participated in the commercialisation of 4 previously filed patents.

The turnover of commercial contracts amounted to approximately 3.2 million DKK in 2001 with more than 15 national and international enterprises.

Centre Management

From the start of the Centre its director has been Ib Johannsen. In December 2001 he decided to accept a position at The Carlsberg Laboratories. Ib Johannsen's contributions to the establishment and running of the centre and to the construction of the new facilities are strongly acknowledged among his colleagues and we wish to thank him for his indefatigable efforts in making the Centre a success.

In 2002 DTU will operate under new statutes and therefore a revision of The Polymer Centre's legal foundation was needed. The Managements of DTU and Risø and the Board of the Polymer Centre have initiated this work with the expectation that a new agreement can be signed during the summer of 2002.
With professor Klaus Bechgaard acting as director in the interim period, a new Centre director will be appointed following the installation of new statutes for the Centre.



Acting director, professor Klaus Bechgaard.

2 RESEARCH

The development and processing into useful objects of new materials has long been recognized as one of the key factors that determine historical progress. This is evident even from the way we categorize historical periods by the materials employed (stone, bronze, iron). Transitions from one material age to the next mark periods of major changes. In fact it may be argued that we live in the polymer age today. Certainly western Europe has witnessed an increase in the consumption of polymers by more than 20 percent over the last 5 years, to a total consumption of almost half the world wide production of 80 million ton of polymers per year[1].

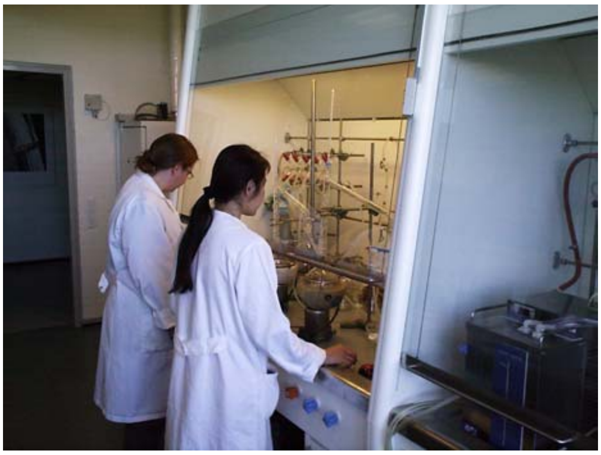
New polymer materials

Part of the reason for the enormous growth in the application of polymers is the almost unlimited variation in properties that may be obtained with polymer materials. Thus the synthesis of new polymers is one of the designated key research areas in the centre. Special emphasis is currently on the synthesis of polymers with very controlled structure. This involves controlled molecular weight, branching structure or the insertion of special functional units. The synthesis of block copolymers with carefully controlled blocks is another general area of intense current interest.

Controlled radical polymerization is a relatively new method with the promise of becoming attractive from an industrial viewpoint. Atom transfer radical polymerization has been used with success for the synthesis of a variety of block copolymers. Examples include amphiphilic bloc copolymers as explained further in 2.1 and functional block copolymers with a host of properties including fully or partly fluorinated polymers as is further explained in 2.2.

Section 2.3 describes a rather unique polymer that has been synthesized. It is a polymer molecule with a functional group inserted in the backbone capable of measuring the tension in the backbone. This polymer is synthesized with the aim of being able to shed light on the molecular mechanism behind the important relation between macroscopic stress and strain in polymeric materials.

A pilot scale facility for the synthesis of kg quantities of well defined polymers is under construction.



Facilities for polymer synthesis.

Polymer networks and blends

Crosslinking of polymer systems is a classical way of changing material properties by the formation of networks. Likewise complex morphologies can be obtained and controlled by clever molecular design. Drastic changes in physical properties (barrier, electrical, optical) may be obtained by additives even of nano scale particles.

Scattering methods are widely used to understand the structure of complex networks and blends. Frequently the systems are molecularly self-assembling at the nanometre scale as is the case with linear ABA tri-block copolymers as explained in 2.4.

The ability to act as flexible barrier materials is the basis for the abundant useage of polymers in the packaging industry. In fact, nearly half the world wide production of polymers is used for packaging[1]. The measurement and correlation of barrier properties such as diffusion coefficients in polymers are illucidated in 2.5.

Polymer networks form the basic material for the development of a new type of soft actuators. Significant progress has been made towards the

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[1] Association of plastics manufacturers in Europe (www.apme.org)

construction of a new type of soft actuators. Based on polymer networks, the actuators described in section 2.6 perform in a manner resembling natural sceletal muscles.

Surface properties of materials are clearly important in most products. It is therefore natural that surface modification and characterization is a major activity at the centre. By way of an example it is described in 2.7 how the modification of a polymer surface to prevent protein adsorption has been successfully achieved.

Structure development in polymer melts

Most polymer products are created by forming polymer melts into the desired shapes. In this process the long chain molecules become oriented and stretched. Upon rapid cooling of the product, this orientation is often frozen into the final product. In addition, crystallization may take place, often linked to the induced orientation of the molecules. The net result is that final polymer products generally have strong internal molecular orientation, which may be a disadvantage as it may be responsible for loss of long term geometrical stability by warpage of the product. In other situations, such as fibre spinning, the orientation may be an advantage since the resulting strain hardening of the melt imparts stability into the spinning process. The strain hardening of polymer melts may be measured in the filament stretching rheometer for melts described further in 2.8. This rheometer is expected to bring new insight into molecular orientation and stress-strain relations for polymer melts.

Advanced process engineering

Recent years have witnessed an increasing interest in the processing of products with nanometre scale structures. Indeed polymers are now used to produce structures that previously could only be created, if at all, in metal or silicon. Possible applications of microinjection moulding to influence the surface character of a product include the production of advanced lenses, holograms for credit card making and structured surfaces for biological and medical purposes. Researchers at the centre have been able to replicate the complex nanostructure fibrillar collagen which is widely used to support anchorage dependent cells in culture. In this work the minimum length scales that can be reproduced by injection moulding have been explored as explained in 2.9.

Computer aided design of polymer processing operations is vastly superior to trial and error methods. However, the challenges are large because the stress-strain relation of polymer melts are complex functions of molecular weight, temperature, pressure and molecular orientation. To complicate matters, the instantaneous molecular orientation is itself a function of the deformation history of a given material element. One way of to deal with this complex situation is to use a numerical method in which a polymer processing operation is modelled as a transient process starting from a known equilibrium state. This method, now widely used at the centre, is illustrated in 2.10 in the modelling of a prototype blowmoulding process. The question addressed is to obtain an understanding of how material burst in blowmoulding is related to material and process parameters.

Micro injection moulding machine.

2.1 Synthesis of Amphiphilic Block Copolymers by Controlled/”Living” Radical Polymerization

Oxide types of block copolymers have since their introduction in the early 1950's been widely used in industrial applications of aqueous systems. These block copolymer systems provide a large variation in combination possibilities, which makes them attractive in a wide range of applications ranging from medical and pharmaceutics products to photographic and plastics applications. During the last decade controlled/living radical polymerization has developed into a good alternative to living ionic polymerizations. In the Danish Polymer Centre we are both working with polymerization of new polymer systems, and with advanced chemical and physical characterization. In the following we will focus on the polymerization parts, using "controlled/living" radical polymerization.

Controlled/"living" radical polymerization is a relatively new method that has several advantages in comparison to living ionic polymerizations such as lower demand for the solvent purity. Another special aspect is that water can be used as solvent. Also a broad range of monomers with functional groups can be polymerized by controlled/”living” radical polymerization including hydroxy groups and carboxylic acids. This reduces the number of synthesis steps by at least two (protection and deprotection). However, since it is a radical process termination reactions can not be totally omitted and hence it is not a true living polymerization. Still, it is possible to obtain (co)polymers with narrow molecular weight distributions and controlled architecture by controlled/”living” radical polymerization. These advantages makes controlled/”living” radical polymerization more interesting from an industrial viewpoint.

We have been working with controlled/”living” radical poly-merization in the form of atom transfer radical polymerization (ATRP), including amphiphilic block copolymers from poly-(ethylene glycol) (PEG). ATRP is based on an equilibrium between active polymer radicals (P_n*) and dormant halogen terminated polymers (P_n-Br) which is shifted towards the dormant halogen terminated polymers (see Figure 1), ensuring a low concentration of active polymer radicals. The equilibrium is mediated by a transition metal halogen complex for example CuBr/2,2'-bipyridine, where the active radical is formed by a one atom transfer oxidation process of the halogen from the dormant polymer to the transition metal halogen complex. The active radical can then either propagate by addition to monomer (M), terminate by reaction with another radical or it can react with the deactivator (Cu(II)Br_2/2,2’-bipyridine).

During the last few years we have studied the synthesis of amphiphilic ABA triblock copolymers by ATRP in aqueous media. The amphiphilic block copolymers are synthesized by polymerizing either sodium 4-vinylbenzoate (NaVBA) or oligo(propylene oxide) methacrylate (OPOMA) from bifunctional PEG10,000 and PEG16,000 macroinitiators. These novel block copolymers have either a pH-stimuli response or a temperature-stimuli response depending on the choice of monomer.

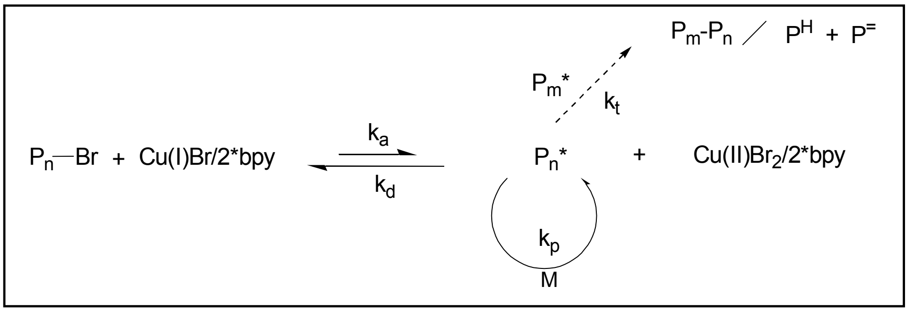


Figure 1 Reaction scheme for atom transfer radical polymerization (ATRP).

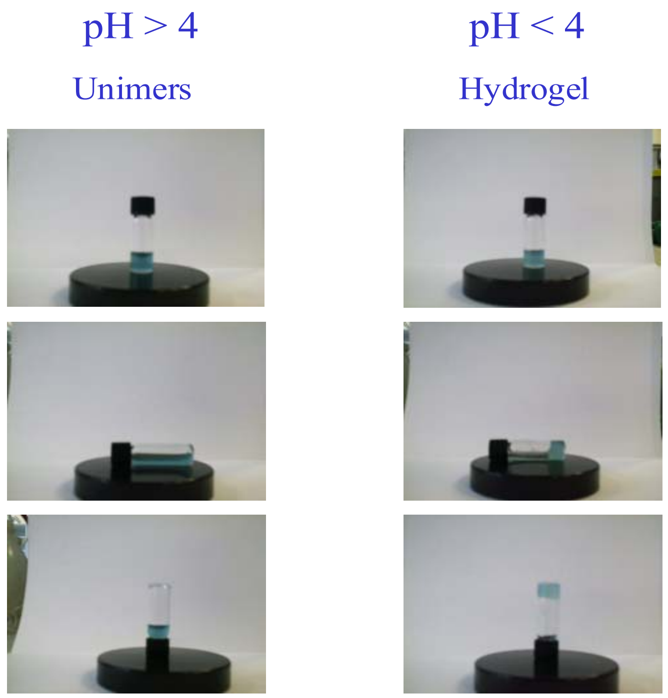


Figure 3 Solubility behavior of P(NaVBA)-block-PEG10k-block-P(NaVBA) (4.8 w-%) in water as function of pH (By ^{1}H NMR the molecular weight of the P(NaVBA) block was found to be 4300)

In Figure 2 is given a sketch of the solubility behavior of P(NaVBA)-*block*-PEG-*block*-P(NaVBA) in water as a function of pH and the concentration, as revealed from scattering experiments. At high pH (>4) the polymers are soluble in water whereas at low pH (<4) the poly(NaVBA) blocks become protonated giving the water insoluble poly(4-vinylbenzoic acid) (PVBA) blocks. The solubility of the PEG is independent of pH and therefore either pH reversible micelles or hydrogels can be formed depending on the polymer concentration. When micelles are formed the hydrophobic PVBA blocks form the core while the hydrophilic PEG blocks are looped in the corona.

When a hydrogel is formed, the PVBA domains constitute the knots in a network structure as illustrated in Figure 2. Figure 3 shows the solubility behavior for P(NaVBA)-*b*-PEG10k-*b*-P(NaVBA) (4.8 w-%) in water. It is observed from this Figure, that a solution is formed at high pH (the polymer solution flows when the sample vial is turned) and a hydrogel is formed at low pH (the hydrogel stays at the bottom of the sample vaial when it is turned).

Further information: Jens Høg Truelsen, Jørgen Kops, Walter Batsberg, Kell Mortensen

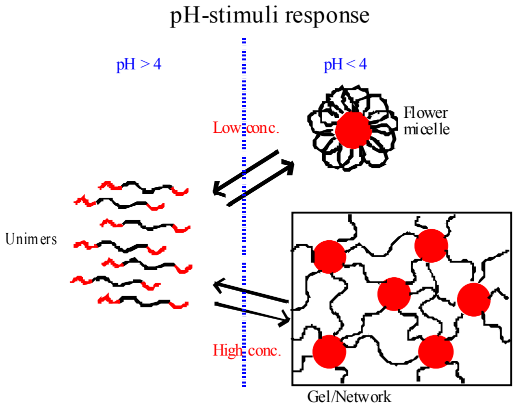


Figure 2. Solubility behavior of **P(NaVBA)-*block*-PEG-*block*-P(NaVBA)** as a function of pH and concentration.

2.2 Functional Block Copolymers

Functional polymers with well-defined structures and compositions are normally prepared by living anionic or cationic polymerization techniques. Such techniques require very high purity of the involved chemicals and total exclusion of moisture and oxygen. Handling and charging reagents thus often require sophisticated techniques. Moreover, the arsenal of monomers susceptible to these polymerization techniques are limited and especially hampered by most substituents on the monomers. Functional or reactive substituents are attractive or necessary in order to produce functional block copolymers.

In our hands the term *functional block copolymer* is ambitious. Accordingly we give a short description of our different use of the term functional. We can think of block copolymers where one block contains functional substituents that can afford further reaction after the polymerization and isolation of the polymer materials. That material serves as a scaffold or a template polymer. Another way of thinking is a polymer containing certain parts or moieties that can respond to external stimuli e.g. light or an electrical field causing an exploitable change in properties. Some polymer materials would locally either temporarily or permanently change refractive index when exposed to coherent laser light, a property that can be exploited for storing optical information. Response to an electrical field is already exploited in the light emitting diodes. Another example on influence of voltage is the induced dimensional changes as the basic principle for the action of polymer actuators. Thirdly, differences in hydrophilicity or ionophility between different blocks would strongly affect compatibility with other materials or surfaces in general. Such differences appear as potential tools for significant changes of surface affinities and energies and thus significant changes of materials characteristics should be possible just by applying thin block copolymer films. Finally it should be mentioned that combinations of the described different features of block copolymer functionality can possibly be made through the correct polymer design.

We have primarily focussed on the new radical polymerization techniques that can now be performed under controlled conditions that almost have the living polymerization characteristics. The most valuable merits of these new thechniques are the controlled polymer chain growth with low polydispersities and the preservation of the chain end reactivity, ideally enabling synthesis of block copolymers. Furthermore, they require relatively simple equipment that can easily be adopted in other laboratories also in industrial production.

Block Copolymers with Fluorostyrenes

Fully or partly fluorinated polymers are a class of materials that attract significant attention due to high thermal stability, oil and water repellency, and good resistance to chemical and physical treatments.

2,3,4,5,6-Pentafluorostyrene (FS) was polymerised by Atom Transfer Radical Polymerization (ATRP) at 110 °C using 1-phenylethyl bromide as the initiator and the catalytic system Cu(I)Br/2,2'-dipyri-dine. 96% conversion can be achieved in 100 min. and the polymerization appears to perform in a controlled manner. This high rate assumingly reflects the electron-withdrawing character of the fluorines on the phenyl ring. Furthermore, the molecular weight increases linearly with monomer conversion. Finally, the determined molecular weights fit the theoretical values with relative low polydispersities ($M_w/M_n < 1.2$). The Br-terminated poly(2,3,4,5,6-pentafluorostyrene) (PFS) thus prepared can function as a macroinitiator for synthesis of polystyrene (PS) containing block copolymers with relatively narrow polydispersities. FS block copolymers can likewise be pre-pared from a similar PS macroinitiator. FS homo- and block copolymers gain higher thermal stability compared to PS; the extent of the thermal stability reflects the relative size of the FS block. T_g of FS homo- and block copolymers with styrene depend on the molecular weight up to approximately 16,000 where a final value at around 101 °C is reached. Although the solubility

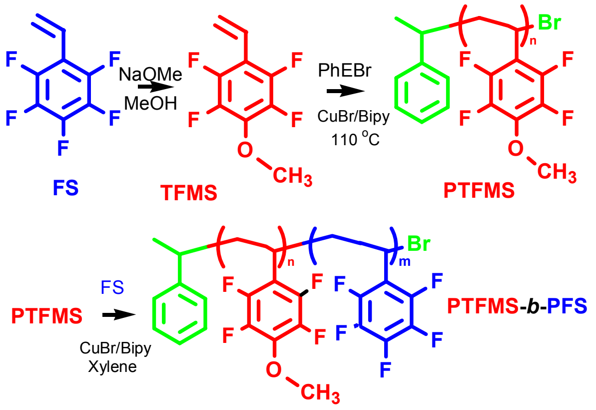


Fig. 1 Preparation of TFMS and ATRP protocol

FS-containing polymers, especially the homopolymer, is much smaller than that of PS, the materials can still be handled as solutions. Especially fluorobenzene is a good solvent for the PFS with somehow reduced solubility for the block copolymers and PS itself.

Solutions of homo- as well as block copolymers are expected viable for creation of new low energy, low friction, or higher thermal resistance surfaces cast or spin coated on other polymer surfaces. These types of investigations are under way and the subject of further investigations.

In a continuation of this work other fluorinated styrenes such as 4-methoxy-2,3,5,6-tetrafluorostyrene (TFMS) have been prepared and polymerized under ATRP conditions (Figure 1). Block copolymers with 2,3,4,5,6-pentafluorostyrene (PTFMS-*b*-PFS) have also been prepared. Again both types of macroinitiators were employed with success. Optimization of the hydrolysis of the methoxy groups is underway. This opens up new ways to functionalize these highly fluorinated block copolymers, since the resulting 4-hydroxy-2,3,5,6-tetrafluorostyrene sites are expected to easily undergo alkylations via the Williamson ether synthesis approach. Different alkylation schemes, e.g. insertion of fluoroalkanes, will be undertaken in the future.

Block Copolymers with Hydroxystyrene

We have for several years developed a number of polymer materials embedding azobenzene moieties in side chains that has proved "successful" for optical storage of information (Figure 2) especially by applying polarization holography. Block copoly(4-hydroxystyrene) is one material type that has never been investigated. The hydroxy handle on PS is attractive due to the versatility of possible reactions e.g. by Willliamson ether synthesis or esterification either with acid chlorides or by DCC coupling. The monomer, 4-hydroxy-styrene, does not exist due to tautomerism so the template approach utilizing protected 4-hydroxystyrene is necessary. 4-Acetoxystyrene has previously been copolymerised with styrene by ATRP and subsequently deprotected by hydrolysis. However, great care is needed in the deprotection step to avoid crosslinking leading to untractable, useless materials. In our hands this appeared unavoidable with the molecular weights we are targeting. Consequently, we looked for other possibilities and chose living anionic polymerisation of 4-*tert.*-butoxystyrene. Styrene and 4-*tert.*-butoxystyrene are monomers that both successfully undergo anionic polymerization retaining the living character thus preparation of well-defined block copolymers is possible.

Procedures for the preparation of di- and triblock copolymers with different compositions have been developed. Furthermore, an analytical method by use of ^{1}H NMR allowing for accurate determination of compositions has been developed. Effective removal of the protective *tert.*-butoxy group and subsequent alkylations on the resulting hydroxy sites with azobenzenes with different alkyl spacers ($-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-(CH_2)_{10}-$) and with different terminal substituents on azobenzene ($-CN$, $-F$, $-CF_3$) have been performed. Molecular weight characteristics have been established, structural characterization have been performed as well as phase characterizations by thermal and optical methods.

Fig. 2 Medical records optically stored in an optical "chip" on a smart-medical insurance-card

One attractive feature is that the expected phase separation principally would result in small, isolated liquid crystalline domains that do not scatter light. Provided no light scatter exits, relatively thick films (~100 μm) could be used for volume holography where all three dimensions the materials can be exploited. Volume holography allows hologrammes on top of each other (3-dimensional) and thereby increases the capacity of the material by the number of stacked hologrammes as compared to a thin film material (2-dimensional).

Further information: Søren Hvilsted and Katja Jankova

2.3 Nanosensors for Molecular Tension in Polymers

The widespread use of polymeric materials such as plastics, rubbers and fibers is dependent upon a range of favourable mechanical properties. In particular the relation between macroscopic stress and strain is of key importance in many situations. While a number of methods exist to determine this constitutive relation at the macroscopic level, the molecular origin of macroscopic stress is more difficult to probe by experimental means. However in order to tailor new materials with improved mechanical properties, understanding of the molecular origin of stress and strain is of paramount importance. This project is aimed at the development of sensitive molecular sensors to measure mechanical tension at the molecular level.

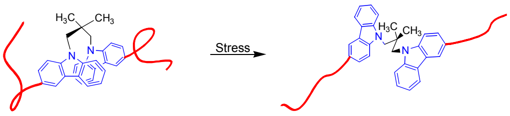


Figure 1. The sensor unit (blue) in the polymerbackbone (red)

On a molecular scale, momentum is primarily transferred through the polymer backbone. Hence a sensor unit should be part of the backbone in order to elucidate on the transfer of mechanical tension through the material. When a polymeric material is stressed the individual chains undergo a structural change, to a varying degree, which the sensor unit must responds to with a change in its spectroscopic properties (in this case fluorescence). A range of different sensor principles may be recognised. Among these we have focused on molecules that may form an intramolecular excimer. This sensor principle is depicted in figure 1.

The sensor unit consists of two carbazole units (in blue) linked by a propylene bridge (black). When the sensor unit is illuminated and one of the carbazole units gets excited, two things can happen depending on the position of the other carbazole unit. In the stressed state the carbazole units are isolated and normal carbazole (monomer) fluorescence will be observed. However in the relaxed state the aromatic units interact and an excimer (*exci*ted di*mer*) will be formed, which has a different set of fluorescence properties. In this way the fluorescence of the material can be related to the mechanical state of the polymer chains.

To insure that the sensor molecule has sufficient freedom to change its structure (from relaxed to stressed state) we have focused on elastomers as the polymeric material of choice. Ideally the sensor unit should be placed in the middle of the polymer chain and all polymer chains in the sample should be of equal size. This can be accomplished through living anionic polymerisation that also allows the preparation of block-co-polymers, such as polystyrene-polyisoprene-polystyrene tri-blocks. These tri-blocks tend to phase separate and thermoplastic elastomers may be formed, where the styrene domains serve as physical (not chemical) bonds of the polyisoprene. The synthesis of a polymer with a sensor unit in the backbone is shown in figure 2.

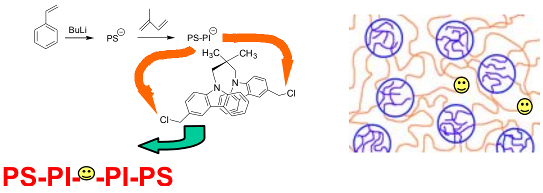


Figure 2. Left: The sensor molecule couples two polystyrene-polyisoprene di-blocks (PS-PI) and a polymer tri-block is formed with the sensor unit (smiley) in the middle. Right: The morphology of the material is shown. The styrene (blue) domains serve as physical bonds for the polyisoprene chains (orange). The sensor molecules (smiley) are in the middle of the polyisoprene chains.

First styrene is polymerised, isoprene is added and a polystyrene-polyisoprene di-block is obtained. The anions are powerful nucleophiles and react readily with the sensor molecule as a benzylic chloride, forming a tri-block with the sensor unit in the middle.

One of the great features of these thermoplastic elastomers is that they are soluble in a range of solvents (chloroform, THF etc.). Thus by letting the solvent evaporate from a solution of the prepared polymer, a transparent film is formed.

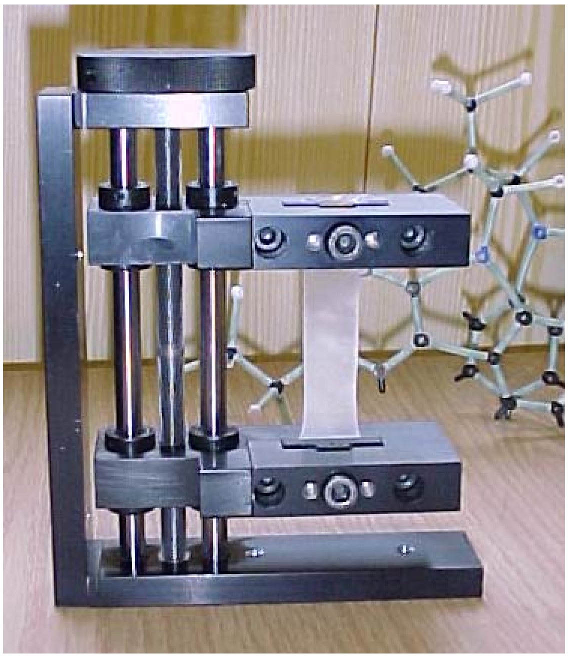


Figure 3. Straining device.

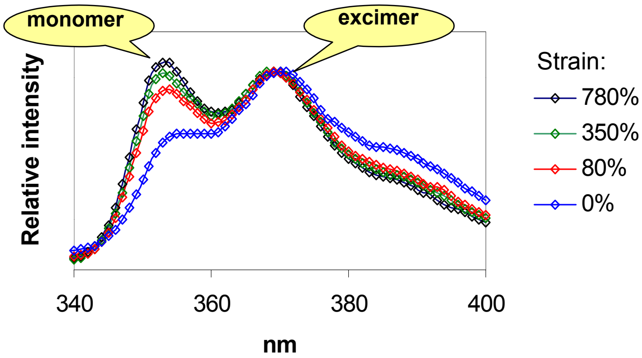


Figure 4. The fluorescence spectra of sensor molecule changes upon straining of bulk material.

When the film is strained, using a home made device (figure 3), the fluorescence spectrum changes as shown on figure 4. The excimer (relaxed state) emits around 369 nm and the monomer (stressed state) emits around 354 nm.

Looking at the normalised spectra it is obvious that the relative intensity of monomer fluorescence increases with increasing strain. This we interpret as molecular change similar to the one shown in figure 1 is taking place.

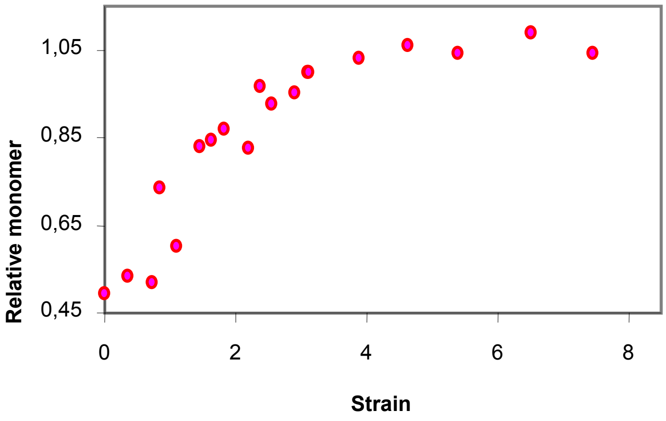


Figure 5. The relative monomer fluorescence intensity increases with strain.

In figure 5 the relative monomer intensity is plotted as a function of strain defined here as relative increase in overall length. When strain is applied the monomer intensity increases until the material is strained around 350% where a maximum is reached. The initial increase of the data point is related to the sensor molecule. The more favourable the relaxed structure is, compared to the stressed structure, the greater strain is needed in order to force the sensor molecule into an other conformation. Thus by careful design of the sensor molecule it should be possible to extend this methodology to (in principle) all kinds of polymer based materials.

To summarise; we have successfully developed a new concept for investigating mechanical properties for polymeric materials at the molecular level. Work is in progress to correlate these findings with current theory on the subject.

Further information:
Holger Spanggaard, Mikkel Jørgensen, Kristoffer Almdal and Jørgen Kops

2.4 Shear Controlled Morphology of Block Copolymer Gels

Molecular self-assembling of nanometre scaled aggregates and ordered mesophases have been extensively studied in recent years. Both block copolymer melts and block copolymers molecules suspended in selective solvents provide the basis for such structures as resulting from incompatibility between the various units within the material. Linear ABA triblock copolymers made up of two 'A'-blocks surrounding a 'B'-block form typically independent core-corona structured micellar aggregates when mixed with a solvent selective for the A-blocks.

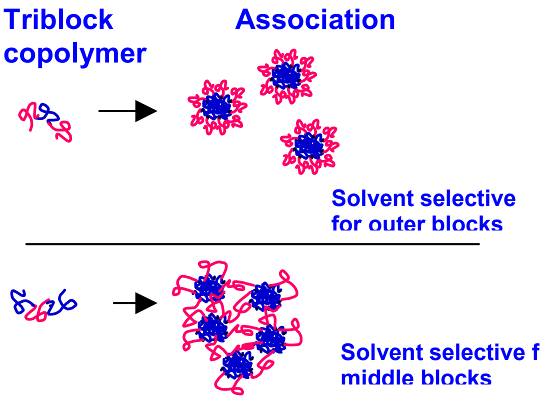


Fig. 1 Schematic illustration of triblock copolymer association into induvidual micelles and micellar networks

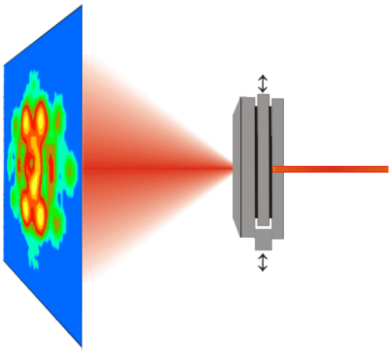


Fig. 2 Schematic illustration of the experimental setup for *in situ* scattering and rheology

The micelle formation is caused by thermodynamically driven reduction in enthalpic energy by avoiding direct contact between the B-polymer and the solvent. Different characteristics can be expected in systems of triblock copolymers mixed in solvents selective for the middle block. The middle-blocks of those polymers form either loops, starting and ending within the same core, or bridges between different micelles, thereby resulting in a network of interconnected micellar cores. These properties are illustrated in fig.1. Examples of such systems are organic suspensions of PS-PEB-PS, shortly abbreviated SEBS. The polymer abbreviations refer to PS for polystyrene and PEB for poly(ethylene butylene). Such micellar networks make the basis of thermoplastic elastomers with attractive materials properties. At temperatures above the glass transition, they typically have relative low viscous mechanical properties that allow easy processing, while at ambient temperature the material is solid-like with highly elastic characteristics.

Original scattering studies on SEBS gels showed that the ambient temperature organization of the spherical micellar PS-cores is typically liquid-like. Extended structural studies performed at temperatures above the glass transition temperature of polystyrene showed, however, a change in line-width, indicating slow build up of some highly correlated micellar organization. The structure observed at ambient temperature does therefore not represent a thermodynamical stable phase, but mimics rather a frozen state of the materials characteristics given by the temperature from where it was originally mixed and quenched.

It is well known that shear and strain can have dramatic effect on the texture of ordered block copolymer systems, including the possibility of forming monodomain crystalline structures. We have studied the correlated mechanical and structural relationship of SEBS polymers (Kraton-G1650) dispersend in the high-temperature oil, Fina A360, using a Rheometrics RSA-2 instrument modified for *in situ* measurements of small-angle neutron scattering and rheology (fig.2).

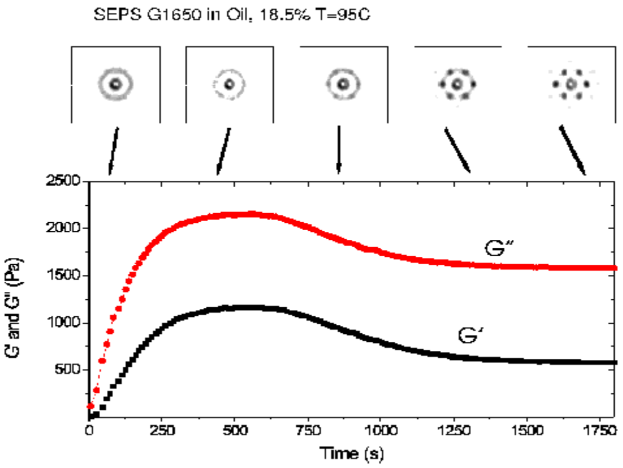


Fig. 3 Time evolution of scattering patterns and (G',G") shear moduli as obtained simultaneously

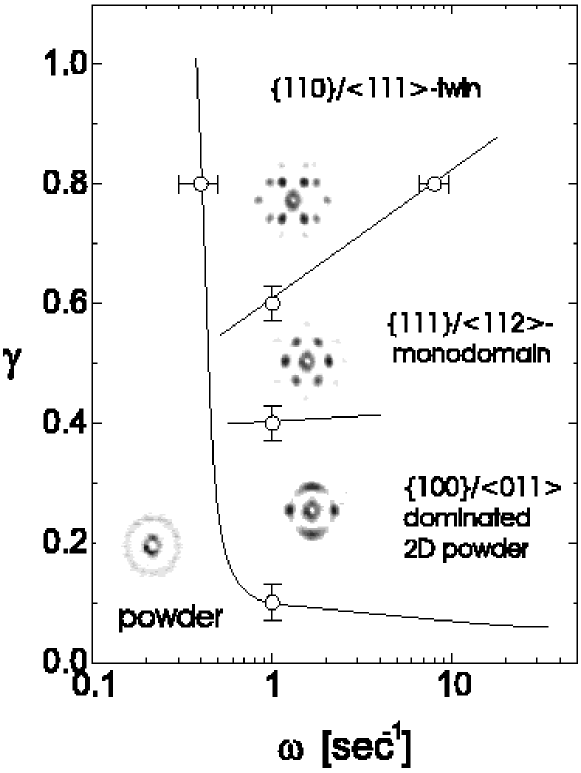


Fig. 4. phase diagram showing the texture developing for different shear amplitude and frequency.

An example of the time evolution of the texturing obtained during large amplitude oscillatory shear is given in details in fig.3, showing both the evolution of the complex rheological data, G' and G", and the time-dependent scattering patterns. Both moduli increase strongly within the first 5 minutes of the experiment.

The scattering patterns shows within the same time range a narrowing of the Debye-Scherrer scattering ring, reflecting the slow build up of an ordered micellar structure. During the following 5-10 minutes G' and G" go through a broad maximum. Simultaneously with the start of decrease in elastic moduli, texture starts to appear in the scattering patterns, revealing stress relaxation due to slip along given crystallographic orientations. After about 15 minutes of shear, a six-fold symmetric pattern emerges, and the moduli approach a steady state level.

The texture can in fact be controlled in great details by appropriate choice of shear amplitude γ and shear frequency ω. This is summarized in a the (γ,ω)-diagram given in fig.4.

The obtained results show that the formation of the bcc mono- and twin-morphology is constrained to a relative small (γ,ω)-window. The measurements prove that the creation of mono- or twin-morphology is restricted to the frequency range for which the loss modulus G" approach the storage modulus G'. This coincidence of high degree of orientational order and high loss modulus reflect major slip along well-defined crystallographic orientations.

Further information**:**
Kell Mortensen, Kristofer Almdal.

2.5 Diffusion in Polymers

Soft barrier materials

Polymeric materials are uniquely suited for applications where a combination of flexibility and barrier properties are required. A host of specific examples may be found in the medical field, where soft polymers completely dominate as material for storage and transportation of biological fluids. The abundant use of polymers in the packaging and handling of foods and beverages are other examples. In such situations the polymer is found in the rubbery state, in which it is capable of undergoing large reversible elastic deformations.

Flexible pipes for offshore applications

A particularly challenging application for polymers acting as soft barrier materials are as liner materials in flexible pipes for off-shore applications an illustration of which is shown in Figure 1.

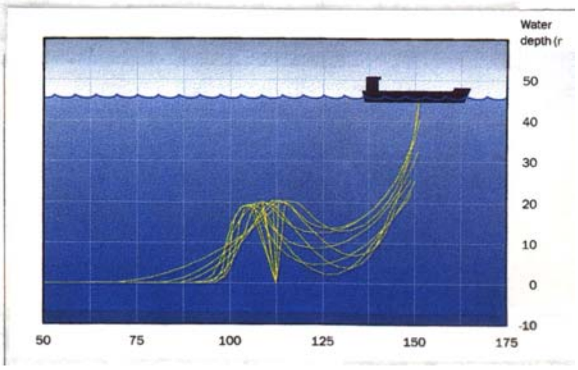


Figure 1: Flexible pipes are used in the off-shore industry for the transportation of oil and gas from wells to ships.

The flexible pipe consists of an inner and an outer polymer liner supported by several layers of coiled metal wires. The outer liner is intended to protect the pipe from external environment, while the inner liner contains the application fluids to within the pipe. However flexible polymers are not completely impermeable to the diffusion of gasses. Sour gasses such as carbon dioxide and hydrogen sulfide in connection with water may be detrimental to the metal supports in the pipes. The polymer centre has developed methods for the measurement and prediction of the permeability of polymers to gasses at total pressures up to 600 bars.

A model for the solubility and diffusion of gasses in polymers is therefore important for the prediction of the expected life-time for flexible pipes.

High pressure balance

The permeability of polymers of a gas such as methane is the product of the solubility of methane in the polymer and the diffusivity of methane in the polymer. The solubility determines the amount of methane dissolved in the polymer in equilibrium with a given partial pressure of methane in the surrounding gas. The diffusivity determines the rate at which dissolved methane moves from region of high concentration to regions of low concentration in the polymer. The two properties may be determined with a high pressure balance.
Sample experimental data are shown in Figure 2. A well defined test specimen of high density polyethylene has been placed on the high pressure balance in a chamber. Prior to the start of the experiment, the chamber has been evacuated for sufficiently long time that the sample has been effectively degassed. Then at time $t = 0$, the chamber is filled with methane at a fixed pressure in this case 150 bar. The weight of the sample (corrected for buoyancy) is then recorded as function of time as shown in Figure 2, top. Plotted as function of square root of time, the weight increases initially linearly with the square root of time. This is to be expected from a typical Fickean diffusion process. Then at large times, the weight tends towards an asymptotic value as dissolved amount of methane in the specimen approaches equilibrium with the 150 bar gas phase. At the bottom of Figure 2 the reverse process is shown. Here the chamber is evacuated showing the diffusion of methane out of the specimen. The two figures are in this situation mirror images of one

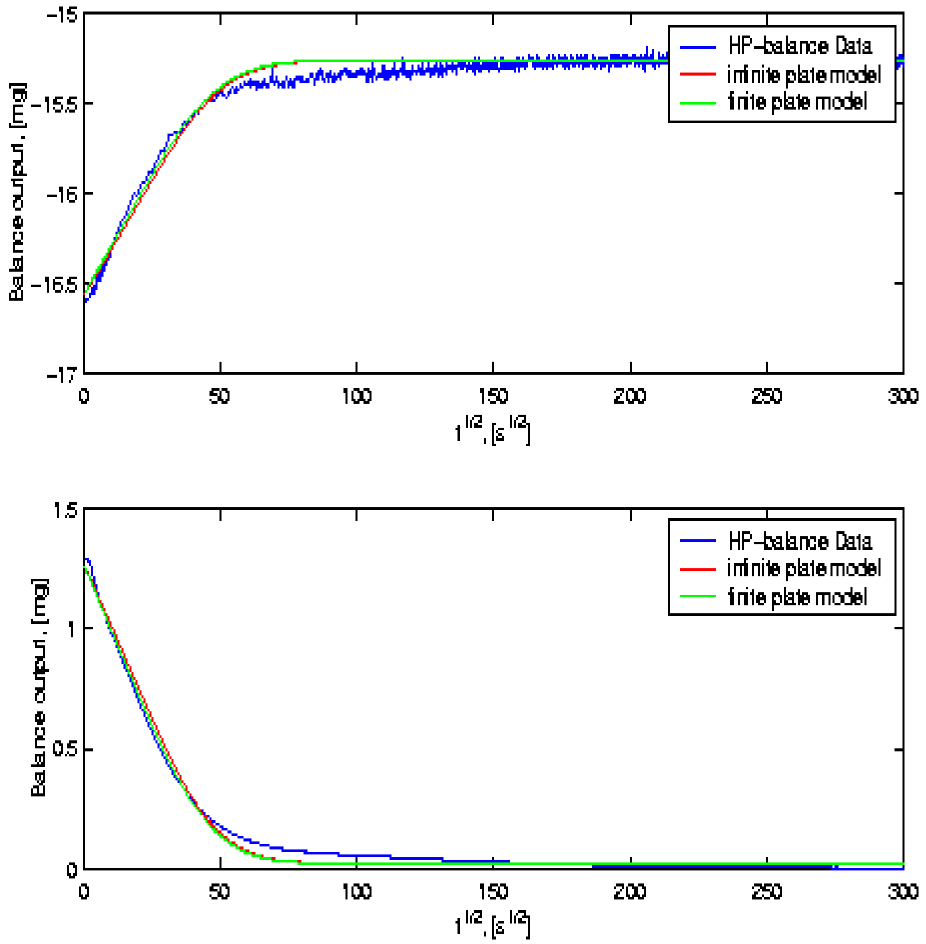


Figure 2. Top: The weight of a polyethylene sample suddenly exposed methane at time t = 0. The data show an initial process linear in the square root of time indicative of a Fickean diffusion process and an eventual approach to equilibrium given by the solubility. Bottom: The reverse experiment in which the the surrounding chamber is evacuated at time t = 0.

another. The resulting diffusion coefficients are shown below as function of inverse temperature.

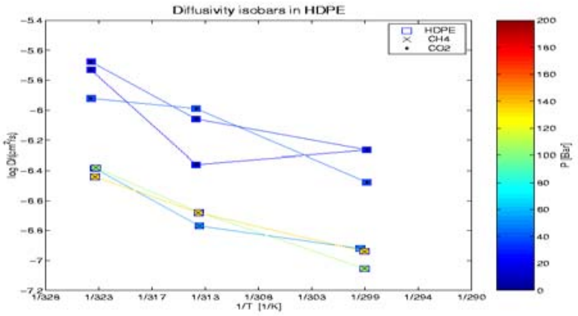


Figure 3: Diffusion coefficients of methane and carbon-dioxide in high density polyethylene as function of inverse temperature and pressures up to 150 bar.

Permeability.

The product of solubility and diffusivity is the permeability. In Figure 3 measured permeabilities of selected polymers are shown as function of inverse temperature at several pressures. The permeabilities include values obtained as product of solubility and diffusivity as well as data obtained in separate experiments.

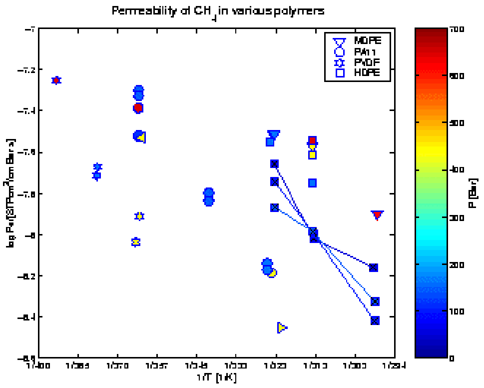


Figure 4: Permeability of polymers to methane.

Further information: Peter Szabo and Ole Hassager

2.6 Polymer Actuators

The aim is to develop a new type of soft actuators that can perform in a manner resembling natural skeletal muscles. Based on a feasibility study carried out in 1996 by Danfoss A/S and Risø, the ARTMUS project started in 1998 with funding from the THOR programme. The four-year project period was completed with a technology demonstration at Risø in January 2002.

The ARTMUS project

The ARTMUS project was one of the initiatives in the "Technology by Highly Oriented Research (THOR)" programme. This programme was funded through the Danish Research Agency, and the two other partners in the ARTMUS project were from DTU and Danfoss A/S. From the outset an ambitious goal was set up - to develop a polymer actuator capable of lifting 100 g over one cm in a tenth of a second. The actuator should be capable of being accurately electrically controlled, expanding or contracting linearly and be adaptable to low-cost manufacturing. During the project, 5 postdocs, 1 Ph.D. and many permanent staff members participated. The project resulted in several publications and three patents.

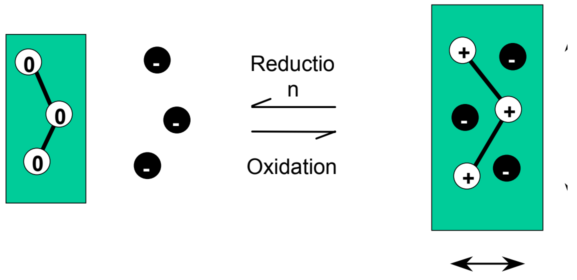
Polymer actuators perform in a manner that is quite different from other actuator technologies. Their action is smooth and noiseless, their performance is similar to that of natural muscles, and they are soft and flexible. In this way they resemble skeletal muscles, and polymer actuators are often nicknamed "artificial muscles". Such actuators will have a large potential in bio mimetic devices, and especially in applications where the flexibility of a moving system goes together with the need for accurate control of the motion - such as in robotics, advanced consumer products, toys, and medico-devices.

In the feasibility study, two actuation principles were identified as the most likely candidates to fulfil the goals set up for the ARTMUS project. One principle is based on the electrostatic compression of a soft elastomer (dielectric elastomer actuator - DEA) and the other is based on volume change of a conducting polymer during redox cycling. These two technologies were studied and optimised in parallel during most of the project period, but based on the results achieved, the DEA technology was selected for the final demonstration. In this demonstration it was proven that the dielectric elastomer actuator now is developed to a stage where its performance is equivalent to or better than the goals initially set out for the ARTMUS project. The two actuator principles and their relative merits are outlined below.

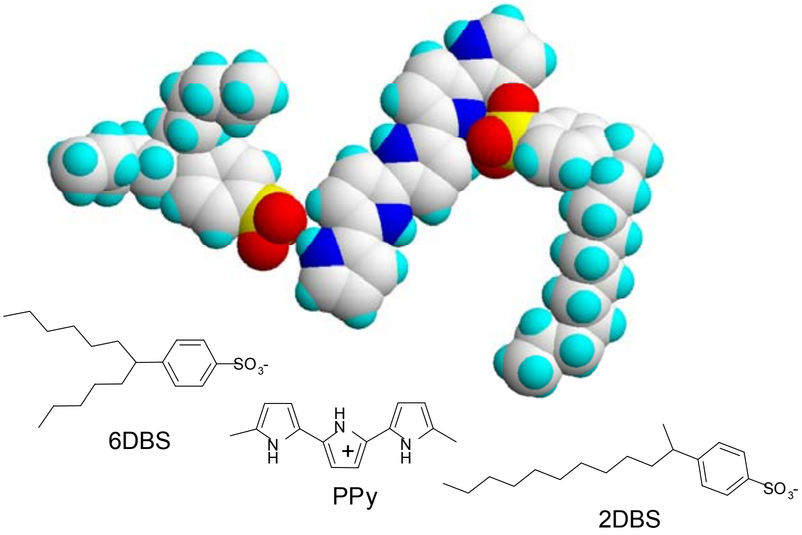
Conducting polymer actuators

Conjugated polymers are characterised by their ability to acquire electronic conductivity when they are suitably doped, and by their ability to be reversibly oxidised or reduced. Some of these polymers also change their volume when they are cycled between their oxidised and neutral forms. As the polymer is conducting, this redox cycling can be conveniently carried out with the electro active polymer as one of the electrodes in an electrochemical cell. At the start of the ARTMUS project this principle was already utilised in micro actuators and the challenge was to scale up this principle so it could be used in cm size devices lifting several grams.

It was soon realised that the volume expansion reported for conducting polymers at the time the project started (a few percent) had to be improved substantially if conducting polymer should be the active component in useful polymer actuators. In order to be able to operate the actuators with an



Box 1. Conducting polymers can be reversibly oxidised and reduced. By this process charges are created on the polymer backbone and these charges are compensated by ions migrating in from the surrounding electrolyte.The additional volume of the ions and the electrostatic interactions between charges on the polymer may lead to swelling of the polymer. In some cases the ions are followed by solvent molecules which amplifies the volume change.



Box 2. Poly pyrrole (PPy) is one of the conjugated polymers showing an appreciable conductivity in the oxidised ("doped") state. The positive charges on the polymer is balanced by anions. If large amphiphilic anions as e.g. dodecyl benzene sulfonate (DBS) are incorporated during synthesis, an unusually stable polymer complex is obtained. On the picture DBS (common dishwashing detergent) is shown in two of its isomeric forms. Note that the dopants constitute more than half of the weight of this polymer complex.

aqueous electrolyte and still obtain a good lifetime, the development was focused on poly pyrrole doped with anionic detergent molecules. These are one of the few types of conducting polymers that are long-time stable in contact with air and water.

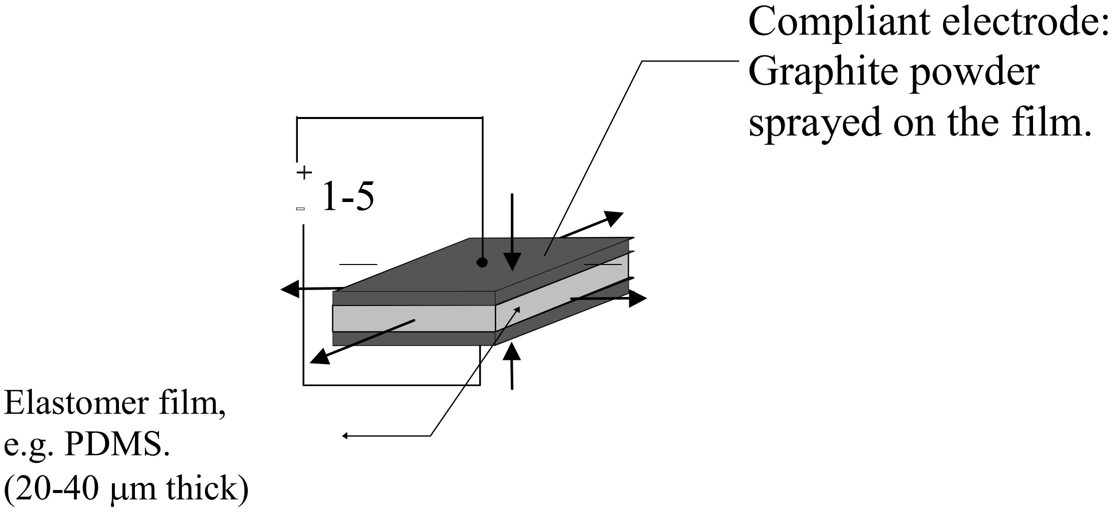
A systematic investigation of the effect of the size of the dopant and an optimisation of the synthesis conditions lead to the identification of a material, poly pyrrole doped with octyl benzene sulfonate that showed a reversible expansion of nearly six percent. A further optimisation of the design of the actuator using the compliant electrodes described below, lead to a polymer device capable of a linear expansion of 12 %. Devices were constructed that were able to lift 200 g, but the response time of conducting polymer actuators of this size is of the order of tens of seconds, and we were not able to increase the speed much, as it is limited by the rate at which ions can diffuse in and out of the polymer.

Besides the effort on optimisation of the mechanical response of conducting polymer actuators, a thermodynamic description of the actuation mechanism has been established and proven experimentally. According to this model two effects cause the mechanical response: an "intrinsic" expansion due to changes in polymer conformation and an "osmotic" expansion due to influx of solvent molecules driven by the difference in concentration of small ions in the polymer and the electrolyte. In systems that show the best actuator performance, these effects are of the same magnitude.

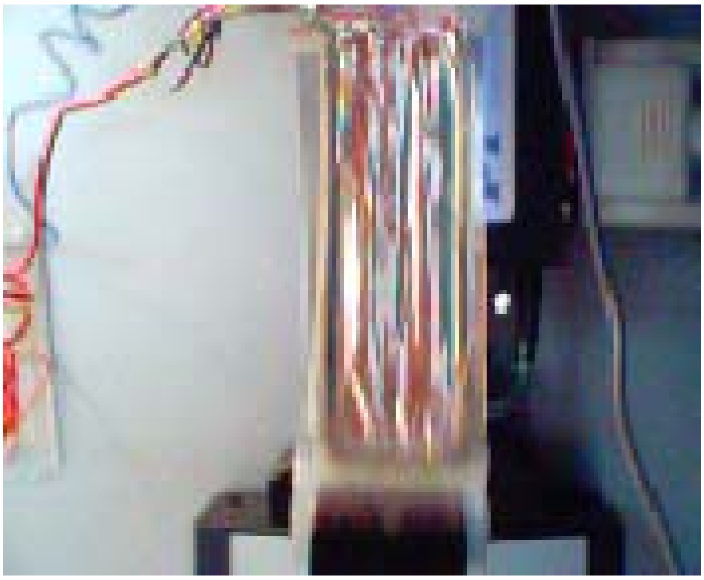
Dielectric elastomer actuators

Dielectric elastomer actuators (DEA) show impressive expansions when activated at high voltages. A response of 300% expansion in area has been reported. The technology is probably the most attractive polymer based actuator technology for robotic applications. In its process of evolution, the technology is at a stage where we expect to see prototypes for special applications and advanced demonstration models in broader application areas.

The DEA is electric field driven: it is the applied electric field that causes dimensional changes in the actuator - no mass transport in and out of the actuator takes place and to a good approximation, the actuator volume is constant during operation. The actuators are integrated structures combining an elastic film with two electrodes. See box 3. The elastomer material itself may not necessarily possess an electroactive response. This differentiates DEA from other classes of polymer actuators, e.g. the conducting polymer actuators.



Box 3. Basic design for a dielectric elastomer actuator: an elastomer film is sandwiched between two compliant electrodes. When charged, the electrodes attract each other, squeezing the elastomer in the film plane. A high voltage is needed to compress the film. Typical values for the driving voltage are kilovolts but the currents are very small – typically micro Amperes.



Strengths: Higher energy density than any other electric field powered actuator technique (e.g. piezoelectric or electric motor). Noiseless. Operates at temperatures between –20 and 150 deg. C. Driven with electronics that allow for reuse of at least 50% of the stored electric energy, efficiencies up to 80% can be obtained. In principle scalable between mm sized actuators and actuators capable of lifting tons. Materials costs are very low.

Drawbacks: High voltage is needed to drive actuators, although only micro amps current will run. Raw costs for a 5V to 5 kV amplifier is more than 3$.

Box 4. Dielectric elastomer actuator performance.

Extension: Depends on materials – 15 % for PDMS with Smart Compliant Electrodes (SCE).
Up to 170 % for stretched VHB tape (VHB™ 4910 acrylate elastomer tape from 3M™).

Stress: 0.15 (SCE) -0.5 MPa (VHB)

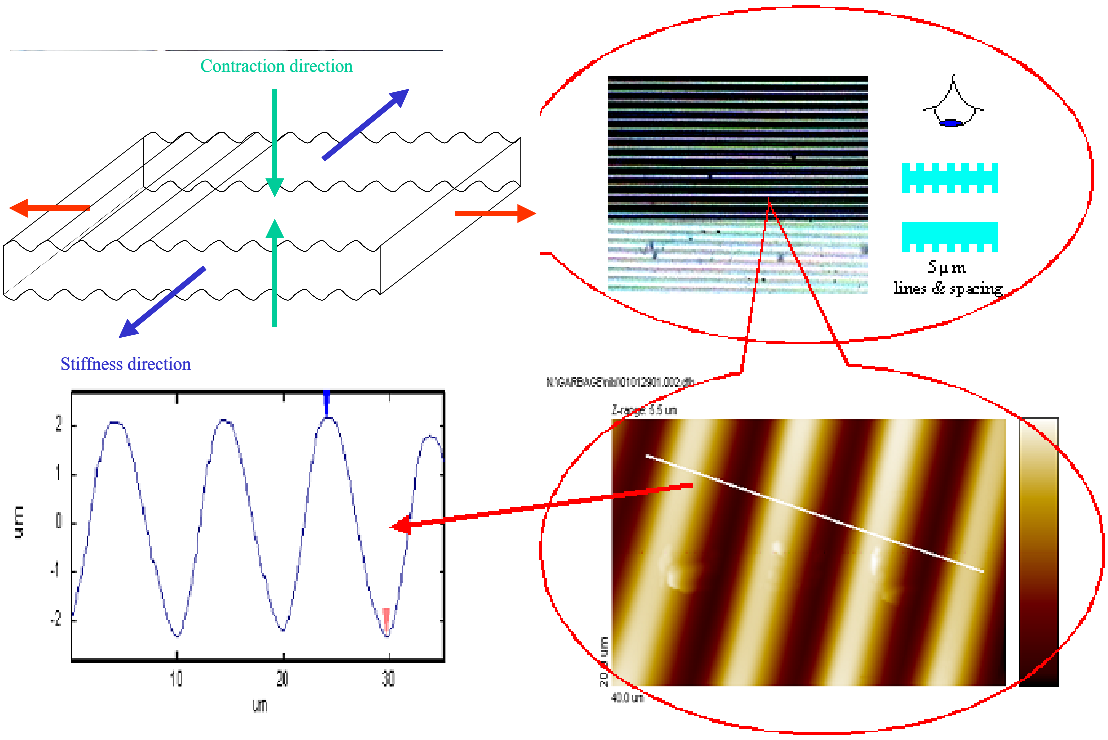
Speed (full stroke): 0.1(SCE) –10 s (VHB)

Efficiency: 10% (SCE)-60% (VHB)

Power/energy density: Very high

Power supply: High voltage (1-5 kV)

Best actuator results obtained: a) an 8 cm long actuator weighing 2 g lifts 400 g over 4 cm in seconds b) a 5 cm long actuator with “smart compliant electrodes lifts 50 g up and down over 0.3 cm at a 15 Hz repetition period. Cycled 100.000 times.



Box 5. Smart compliant electrode. A corrugation is imprinted in the polymer film and a thin silver layer is deposited on top of the corrugation. The electrode is compliant in one direction and stiff in the other. This transforms all of the electrical induced compressive stress into extensional stress in the compliance direction. Danfoss A/S patented the invention.

Though electroactivity is not a vital property for the base elastomer in a DEA, its "passive" mechanical and electrical properties influence the response of the DEA strongly. Hence much attention has been given to the characterisation of these properties for the elastomers used and to developing the theory for how they influence actuator performance. This knowledge is used to optimise actuator design and develop materials with optimised properties.

One other important outcome of the project is the development of a new class of dielectric elastomer actuators based on "smart" compliant electrodes. These actuators only expand 15%, but they can be produced in a process apt for industrial up scaling. Box 5 describes the details.

At the completion of the ARTMUS project we can conclude that this type of collaboration between industry and academia can be very fruitful and lead to technological innovations as well as to scientific discoveries. The goals that were set up for the project are fulfilled, and patents now cover central technologies. We are presently in the process of refining the scientific results obtained during the project so a better and deeper understanding of the underlying polymer chemistry and physics can support future developments in this field.

Further information:

Peter Sommer Larsen, Keld West

2.7 Making Polymers Biocompatible by Surface Modification and Characterisation

Introduction

A biocompatible material is defined as any substance (other than a drug), synthetic or natural, that can be used as a system or part of a system that treats, augments, or replaces any tissue, organ, or function of the body. Many existing polymer materials have favourable physical properties that afford high precision processing, however, in most cases their surfaces do not have desirable biocompatible properties. Surface modification with chemical entities that can either mimic natural biological interfaces or are inert to adverse interactions (such as those that lead to bacterial adhesion) is necessary if materials are to be biocompatible.

Surface modification plays an important role in both our research activities and our collaboration with industry. The types of modification include,

- Wet chemical methods for grafting of hydrophilic, functional polymers.
- Plasma surface modification to create reactive functional groups.
- Langmuir-Blodget (LB) films.
- Synthesis of new biocompatible polymers.

We meet our goals by integrating research on surface technologies with an understanding of the biological interactions with artificial materials. Figure 1 is an outline of the approach to surface modification and characterisation that we hope will ultimately lead to the development of better materials in medicine and biotechnology.

Advanced Characterisation of Surfaces.

Polymer surfaces are intrinsically complicated and require sophisticated analysis to determine their properties. The parameters which influence the way polymer surfaces behave include; specific chemical functionality, distribution of surface chemistry, orientation of chemical groups, surface texture, functionality, distribution of surface chemistry, modulus of elasticity, surface mobility, contamination, and surface energy. Multi-technique analysis is of paramount importance to unravelling the detailed information necessary to answer as many questions as possible about polymer surface properties. This will assist in the guided design of polymer surfaces with superior performance properties. In that regard the DCP is well equipped with a state-of-the-art surface analysis laboratory with instruments that include;

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

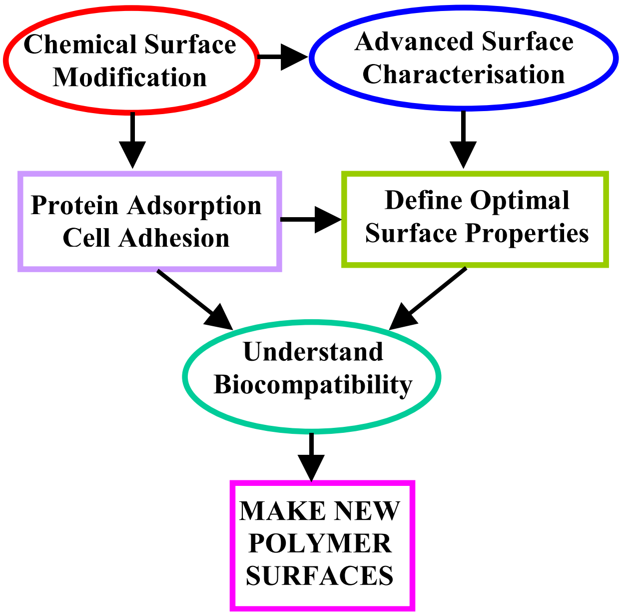


Figure 1: Overview of the approach at the DPC towards developing biocompatible materials by surface modification and characterisation.

ToF-SIMS is generally regarding as the most sensitive of all the chemical surface analysis techniques. The sampling depth is of the order of 10 to 20 Å. Two important instrumental features have been incorporated into SIMS instruments in recent years to greatly enhance the power of the technique. These include the use of time-of-flight (ToF) analysers and chemical state imaging (imaging-SIMS). In addition, the high transmission of ToF analysers provides sensitivity in the parts per billion range (ppb), and since ToF in theory has the unlimited mass range SIMS can facilitate detection of polymers with quite high molecular weights (10,000). Figure 2 highlights the features of ToF-SIMS and shows the Ion-Tof TOF-SIMS IV instrument.

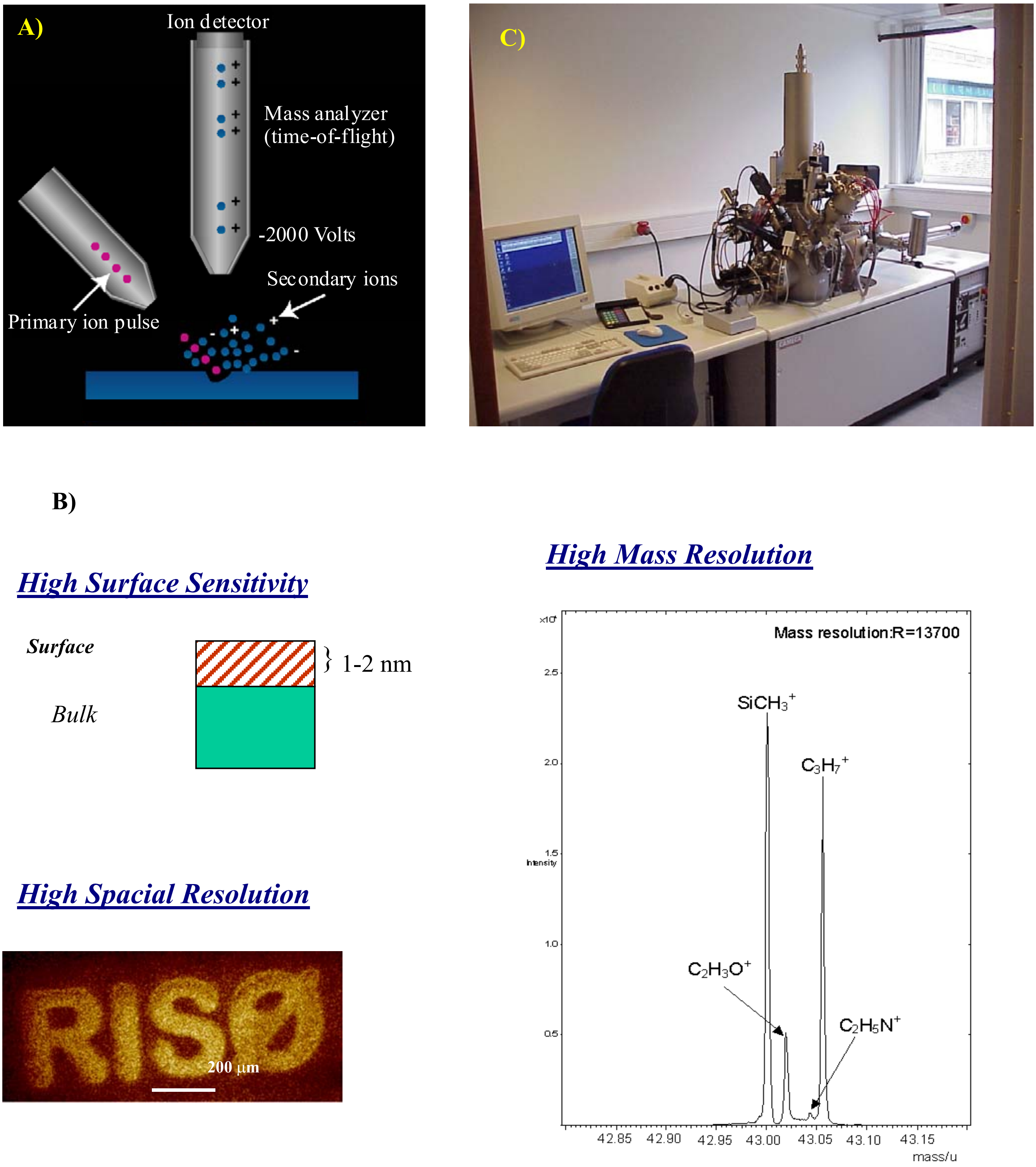


Figure 2: (A) ToF-SIMS is a highly surface sensitive technique in which an ion beam impinges on the surface resulting in ablation of surface material, which is extracted and mass analysed. (B) By use of a very bright liquid ion metal source (Ga^+) the primary ion dose is kept low and extreme sensitivity (1-2nm) is achieved. In the imaging mode mass spectra are acquired as the beam is rastered across the surface resulting in 2D chemical mapping. And, by use of a ToF analyser high mass resolution, and thus specific chemical information, is obtained. (C) The instrument is a TOF-SIMS IV (Ion-Tof GmbH, Münster, Germany).

X-Ray Photoelectron Spectroscopy (XPS).
XPS is routinely used for chemical analyses of polymer surfaces to obtain information about the chemical composition and structure of a surface. It identifies all elements (except hydrogen and helium) present in the outer 100 Å of the surface (detection limits ca. 0.1 atomic percent), and can determine the bonding state (molecular environment) and/or oxidation state for most atoms.

Atomic Force Microscopy (AFM).
AFM provides micrometer to nanometer scale information of surface topography, surface texture and surface modulus. In addition, in the force-mode it is possible to probe a wide range of intermolecular forces on surfaces including short-range forces such as H-bonding and longer range interactions such as van der Waals and electrostatic forces.

Contact Angles (CAs).
Measurements of contact angles are used to probe the surface energy, hydrophilicity, hydrophobicity and surface heterogeneity.

Ellipsometry.
An optical technique that measures the change in state of monochromatic polarised laser light after reflection from a surface when a thin film is present. The change in phase and amplitude of the reflected light are measured and used to calculate the refractive index and thickness of the thin film. A thickness resolution of 0.01nm or better is possible.

Fourier transform infrared (FTIR).
A technique that measures the absorption of various infrared light wavelengths by the polymer materials The infrared absorption bands identify specific molecular components and structures. In ATR and DRIFT modes the method is made more surface sensitive with a probe depth of several μm.

Confocal Raman Microscopy.
A technique used for the non-destructive characterisation, identification, mapping and imaging of polymers, polymer blends and depth profiling. The Raman effect arises when the incident light excites molecules in the sample, which subsequently scatter the light inelastically resulting from the molecule changing its molecular motions. The energy difference between the incident light and the Raman scattered light is equal to the energy involved in changing the molecule's vibrational state. This energy difference is called the Raman shift. Several different Raman shifted signals will often be observed; each being associated with different vibrational or rotational motions of molecules in the sample. The particular molecule and it's environment will determine what Raman signals will be observed. The technique is often used as a complement to FTIR.

Confocal scanning laser microscopy (CSLM).
An optical sectioning technique producing images free from out-of-focus blur. It is a light microscopy technique that employs visible wavelength lasers as light sources and confocal apertures or 'pinholes' in the detection path. It can generate completely in-focus 2D and 3D images of samples. In addition it can provide localisation of single multiple fluorescent labels in 3D space within a single sample.

Case Study: Preventing Protein adsorption and Cell Adhesion.
Preventing non-specific adsorption of proteins and cells remains a significant challenge in developing a ‘truly’ biocompatible material. Proteins spontaneously stick to surfaces, then cells adhere to the proteins by recognising peptide sequences of the protein. Most biological media contain many proteins, therefore the type of proteins that adsorb to the surface has a dramatic effect on biocompatibility since not all of the proteins have desirable properties. Preventing non-specific protein adsorption is thus a major challenge.

The first aim is to modify polymer surfaces with molecules capable of preventing protein adsorption. Poly(ethylene glycol) (PEG) has proved very successful at reducing protein adsorption however to be totally repellent to proteins the surface modification protocol needs to be optimised. A combination of wet-chemical modification to attach linear PEG chains to polymer surfaces and sensitive surface analysis has proved invaluable for such optimal modifications. We chose to modify poly(ethylene terephthalate) (PET) with linear PEG followed by XPS and ToF-SIMS analysis. In theory, linear PEG chains attached to a surface should prevent protein adsorption when the graft density and chain length are optimised, however, this is not a trivial exercise when attempting to modify polymer surfaces. Proteins are of the order nanometers in size, so preventing them from adsorbing means that the surface properties need to be controlled on a nanometer scale. We achieve this by modifying the PET to create reactive carboxyl groups onto which we graft a high Mw polyamine, and then finally the PEG. The polyamine ensures that the initial reactive group density is high enough so that the PEG will have a high graft density.

XPS is used to obtain chemical structure information. Table 1 summarises the elemental composition for a series of samples from XPS and is used to assist in interpreting the success of the modification, and Figure 3A shows the corresponding high resolution analysis of the carbon region, which provides chemical state information. Clearly there is a substantial difference in the structure of the surfaces after the various modification protocols. The spectrum shown is of a surface with a very high level of PEG coverage.

Sample	**% C**	**% O**	**% N**
PET	70.8	29.2	0.0
PET-COOH-PA	69.7	22.7	**7.6**
PET-COOH-PA-PEG	65.6	32.7	1.7

Table 1. XPS elemental composition for the surface modification of PET with a protein resistant layer of PEG.

ToF-SIMS analysis is used to support the XPS analysis for the surface modification. Mass spectra of the surface provide more structural information than XPS results. Figure 3B shows a typical ToF-SIMS spectrum (positive ions, mass range 0-100 Da) for the PEG surface described above. The most intense ions are from the fragmentation of the PEG background, as outlined in the spectrum and support the XPS results in confirming the that the surface has a high degree of PEG coverage, necessary for protein repulsion. Protein adsorption to this surface was not observed by XPS and ToF-SIMS after subsequent testing with β-lactoglobulin, a major protein found in milk. In addition, no mammalian cell adhesion is observed when the PEG surface is exposed to a cell suspension containing serum proteins.

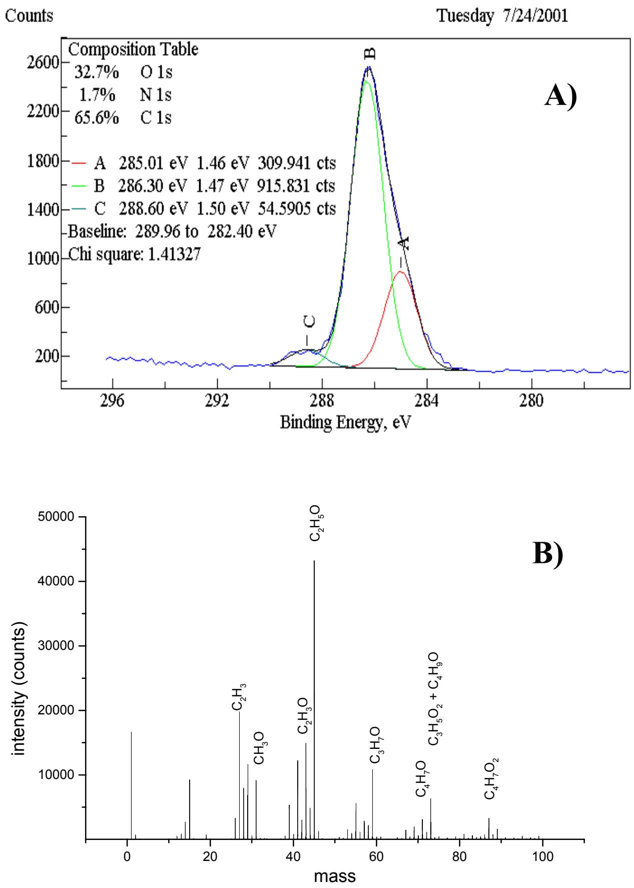


Figure 3. Surface Analysis of a 'non-fouling' PEG coating. (A) High resolution C 1s spectrum showing different oxidation states of carbon for the PEG surface. (B) Corresponding positive-ion ToF-SIMS spectrum showing fragment ions from the PEG backbone.

Thus, the combination of XPS and ToF-SIMS is very powerful for the chemical analysis of polymers after surface modification, and greatly enhances the ability of researchers, whether it be understanding biocompatibility or other applications, to optimise and develop new materials.

Further information
Peter Kingshott

2.8 Measuring Extensional Viscosity for Polymer Melts

In many polymer processing operations the polymer molecules experience a significant amount of orientation and chain stretching. These effects can sometimes be of benefit to the product, for example in a polymer fiber, where alignment of the molecules in the axial direction gives favorable characteristics for the finished product. On the other hand, the effect sometimes gives undesirable effects for the product, for example thermal form instability that may result in warpage of the product. Chain stretching and orientation also has a significant effect on the processing of the final product. Often processing is limited by sample breaks that are induced by the rheology of the polymer. Thus, knowledge of the chain orientation and stretch is of interest for not only scientists who are interested in polymer dynamics, but also for product engineers.

The conventional way of measuring the rheology of a given material is by using a shear rheometer. This method is very good at inducing chain orientation in the sample, and a large amount of data in this area has insured very reliable models of chain orientation and its effect on rheology. However, because of the rotational nature of the shear flow, the chains are given a chance to relax before a significant amount of chain stretching has occurred. Even at very high deformation rates only a limited amount of chain stretching is observed. Hence, shear rheology is not usable for probing chain stretch. As a result, a very limited amount of data is available for the understanding of chain stretch. The consequence of this lack of data is poor models available for estimating the effects of chain stretching on rheology and as a result, poor model predictions of processes at high deformation rates.

Still, there have been attempts on creating measuring apparatuses for generating the necessary flow for chain stretching. The most common instrument is the Meissner rheometer where ideal extensional flow is achieved by stretching a sample between four conveyer belts and estimating rheological relevant properties by relating forces and deformation rates. The problem with this approach is however, that only the overall deformation rate can be set. As the stretching of the filament becomes unstable very fast, local instabilities can not be controlled and filament breakup usually occurs before the chains become fully extended. This problem is even more severe as instabilities evolve very fast when the chains become extended. Another technique used for the measurement is the ‘Filament Stretching Rheometer’ (FSR). In this approach, the sample is simply placed between two parallel discs, the discs are separated at a given rate, and forces are measured on one of the discs.

Figure 1. The filament stretching rheometer.

As the flow in the beginning of the experiment defines where the instability takes place, the diameter of the filament at this place is measured during the entire experiment, ensuring an exact measure of the deformation at all times. In addition, regulating the separation rate of the two discs can control this deformation. Until today, the FSR has only been used at room temperature. The reason is that high temperature experiments gives problems of temperature gradients in the setup, measurement of deformation is difficult in an oven and polymer melts does not stick very well to the end-plates.

At the Danish Polymer Centre we have constructed a filament stretching rheometer capable of measuring extensional viscosity at high temperatures. We have solved the problems regarding temperature gradients by using several temperature controls. To further reduce temperature gradients inside the oven, we have built the oven in copper, which is a good heat conductor.

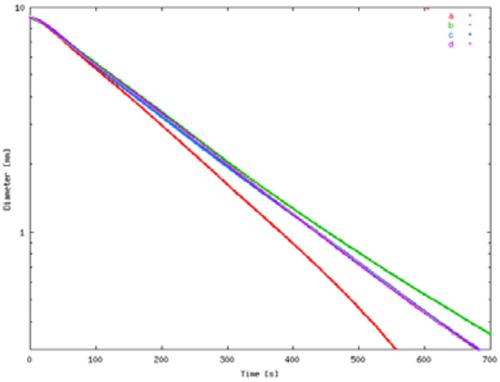


Figure 2. Convergence in diameter, after two experiments, development in filament diameter in the transient experiment becomes close to exponential.

Another problem in doing experiments on polymer melts is controlling the deformation rate. To obtain usable data, the rate must be constant during the entire transient experiment. We use a 'Master curve' approach proposed by Orr and Sridhar (1999), that relates the distance between the end-plates and the radius. Using this approach the development in radius converges towards the desired profile, and three experiments is usually required before a satisfactory development is obtained. In figure 2 we show how the radius converges towards the desired exponential decay.

The last major problem in doing filament stretching experiments is getting the filament to stick to the end plates. By choosing polymer melts, and take care in applying the sample to the end plates, we have overcome this limitation. However, we note that some polymer systems might not be measurable in the filament stretching rheometer without either gluing the sample to the end plates or use some kind of mechanical grips.

Measurements done on the rheometer have been compared with measurements done on a Meissner type rheometer (Rheomtrics polymer Melt Elongational rheometer RME). In figure 3 we plot experiments done on a low-density polyethylene, experiments are performed at strain rates 1.0s^{-1} and 0.01s^{-1}. The plot has been non-dimensionalized by plotting the transient Trouton ratio as function of Hencky strain. The Trouton ratio is the transient extensional viscosity normalized with the zero shear viscosity and Hencky strain is a measure of deformation.

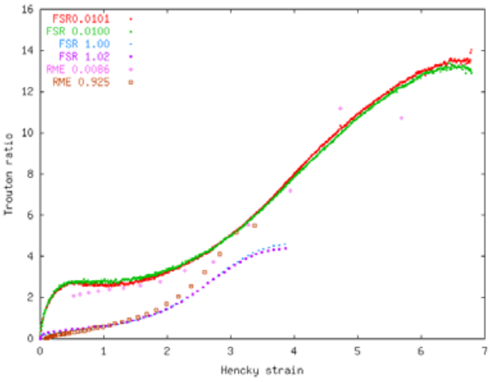


Figure 3. Trouton ratio as function of Hencky strain at strain rates 1.0s^{-1} and 0.01s^{-1}, performed on our Filament stretching rheometer (FSR) and a Meissner type rheometer (RME).

Considering the difficulties in doing these kinds of mechanical measurements, the agreement between the two methods is remarkably good. At the same time we note the ability of the filament stretching rheometer to measure at larger deformations and obtain a plateau in the Trouton ratio. The measurements represent in our opinion the first reliable stationary extensional viscosity for a polymer melt.

Further information: Anders Bach and Ole Hassager.

2.9 Biomimetic Polymer Nanostructures by Injection Moulding

Recent years have shown an ever increasing interest in polymer surfaces possessing well-defined topographical nanometer scale structures. Their current and projected applications include mass storage (Compact Disc / Digital Versatile Disc), nanolithography (sub-100 nm structuring of electronic and optical devices), diffractive optics (authentication and integrated optical processing), and biochemistry (sensing, separation, and catalysis). An upcoming use of such nanostructures is biomedical materials for cell culturing and tissue engineering purposes, which is a major target of our work.

All of these very different applications have as a prerequisite the ability to fabricate polymer nanostructures with high accuracy, good reproducibility, in high numbers, and at low cost. Large scale replication of potentially precious "master" nanostructures into polymer surfaces is the most obvious solution to these requirements. This is already demonstrated for mass storage applications (CD/DVD) using injection molding and diffractive optics (verification and decorative holograms) produced by hot embossing. Printing of such structures by soft lithography methodologies provides a recent and interesting addition to the other two main methodologies. Most exploration of the limits of reproduction has focused on the hot embossing process. It has been demonstrated that 10 nm wide pillar structures may be formed by embossing a hot (hard) original structure into a thin film of Acrylic (poly(methylmethacrylate)).

Relatively little work exploring the ultimate limits for nanostructuring a broader range of plastics (thermoplastic polymers) to provide added functionality has been presented so far. This is particularly true for the industrially very important injection molding process. The main advantages of injection molding in comparison to hot embossing include its 10-1000 fold shorter production cycle time (typically a few seconds instead of minutes or hours), its ability to shape an object as well as topographically structure its surface in a single process, and its allowance for simultaneous surface structuring of all object faces. We have explored the minimum length scales that can be reproduced by injection molding.

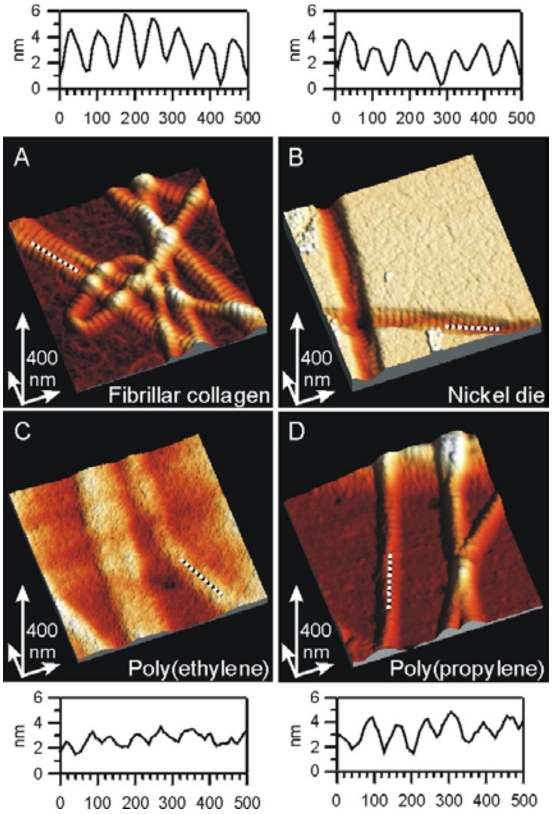


Figure 1. AFM topography micrographs of (A) a fibrillar collagen coated silicon wafer, (B) a nickel die negative of the fibrillar collagen, and injection molded replicas in (C) poly(ethylene) and (D) poly(propylene). Height profiles along fibril ridges (marked by a dashed line in each micrograph) show that both repeat spacing and striation amplitude is conserved during the replication steps, except for poly(ethylene). The axis arrows correspond to 400 nm in the lateral and vertical directions.

Nature makes extensive use of nanometric structural elements with length scales from angstroms to micrometers. It is of considerable fundamental as well as biotechnological interest to mimic such structures outside living organisms for *in-vitro* (i.e. outside the body) culturing purposes. A key cell biological issue is to explore the relative contributions of surface topography versus surface chemistry to cellular responses. We have targeted the accurate replication of the topologically complex nanostructure *fibrillar collagen* which is widely used for biomedical devices and is known to effectively support anchorage-dependent cells in culture.

We have extracted collagen from cows or pigs and re-assembled fibrillar collagen in the laboratory. It consists of a network of narrow fibrils with diameters ranging from 100-300 nanometers (nm) and possessing a striped structure with a spacing between the stripes of 69-70 nm. The height amplitude of the striation is only 3-4 nm. Such structures are too small to be observed by normal optical microscopy. We use an Atomic Force Microscope (AFM), which is basically a minituarized grammophone, to reveal the surface topography of the fibrillar collagen. Figure 1a shows a three-dimensional projection of the fibrillar collagen coating sedimented onto an atomically flat silicon substrate.

The original biological structures must be transferred into its inverted structure made from a hard material in order to be used as a die for injection molding. We have taken the approach of commercial CD/DVD production and used electroformed nickel for our die fabrication. The entire process is outlined in Figure 2. The fibrillar collagen is coated by a 100 nm thick layer of sputtered nickel metal to produce an electrically conducting film with a high replication fidelity at the surface. The nickel film is subsequently used as base layer for galvanic plating of nickel up to a thickness of 0.3 mm to provide mechanical strength during the injection molding process. The entire die formation process takes less than one hour. Atomic Force Microscopy of the nickel die formed (see Figure 1B) reveals that both the fibrillar structure and the very fine stripe structure of the collagen is transferred into the nickel die.

A range of thermoplastic polymers was tested for their ability to replicate the negative fibrillar collagen networks of the nickel die. These included poly(ethylene), poly(propylene), copolymer of cyclic and linear olefins (COC), poly(methylmethacrylate) as well as the biodegradable polymers poly(L-lactic acid) and poly(caprolactone). Biodegradable polymers are particularly interesting for implants as they may eventually degrade and be replaced by new in-growing tissue. Typical injection molding cycle times, taken as the time between ejection of subsequent replicas, were in the range of 30-45 seconds for all polymers used. Poly(ethylene) replicas showed unsatisfactory replication quality. Individual fibrils of the networks were poorly defined and they did not possess any defined cross-striation structure (Figure 1C). In contrast, all the other thermoplastic polymers produced highly accurate replicas of the original collagen network with fibrils displaying a clear cross-striation structure. A typical AFM micrograph of the surface of a poly(propylene) replica is displayed in Figure 2D.

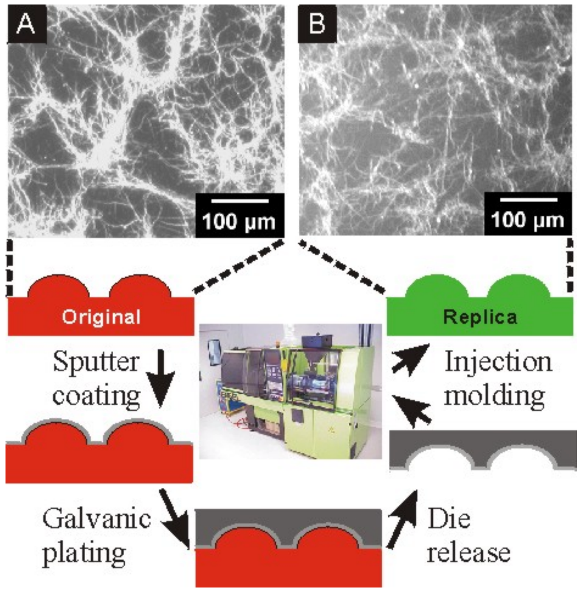


Figure 2. Schematic of the fabrication method from biological original to injection molded replica. Dark field microscopy shows the complexity of (A) the collagen networks and its faithful replication into (B) poly(propylene).

In conclusion injection molding is shown to be a viable process for the structuring of polymer surfaces with features in the 30 nm range present on collagen fibrils as well as for reproducing the topography of the sedimented fibrillar network with great accuracy. Process cycle times of less than 30 seconds compare favorably with embossing schemes and may easily be reduced for industrial production purposes. Higher replication fidelities are currently limited by our ability to make dies with sufficiently accurate surface details. This limitation might be overcome by turning to sputter coatings with smaller grains. We are currently pursuing this approach based on the existing extensive knowledge on ultra-fine electron microscopy coatings. Polymer replication of 10 nm wide grains in the die surface points to a plausible ultimate resolution close to one nanometer of the thermoplastic polymers tested. The fabricated polymer replicas mimicking the topography of fibrillar collagen with great accuracy are currently being compared to natural fibrillar collagen coatings in cell culture experiments.

Further informations: Niels B. Larsen, Nikolaj Gadegaard, Stephan Mosler

2.10 Material Burst in Inflation Processes - Thermoforming and Blowmoulding

The production process blow-moulding is used to produce different kinds of bottles in plastic. The final stage in this process is the inflation of some kind of (extruded or injection moulded) cylinder outward against the wall of the mould. This creates the final shape of the product. The inflation is performed by applying a gas pressure into the core of the cylinder, which press the plastic cylinder outward. The production of plastic part in the thermoforming process is analogue to blow-moulding. The normal products in thermoforming are different forms of packing. It is produced by inflating of a flat (and thin) plate with gas pressure on the top of the plate, down into a mould. During the inflation, in both thermoforming and blow-moulding, the plastic may burst. The occurrence of this burst, or break, puts a limit on the possibility to produce a specified product at some, or all, processing conditions. Here the purpose is to investigate and understand the burst with both experiments and numerical calculations (i.e. theory).

During the inflation the plastic is molten, as it normally solidifies when it reaches the colder mould. Hence, the material burst or break is occurring in the molten state of the inflation. Therefore, to understand the break it is necessary to understand the dynamic behaviour of the molten plastic during the inflation. This requires a description of the tension or stress build-up locally in the material as it deforms, i.e. the constitutive equation. Further a numerical method is needed in order to calculate how the plastic deforms during inflation.
As a model system I have considered the experimental inflation of a molten thin plastic plate into a circular cylinder and compared it with numerical modelling of the same process, as seen in Fig.1.

To model of the stress build-up in the material, e.g. the Constitutive Equation, the Molecular Stress Function (MSF) model, developed by M.H. Wagner, is used. This is a new and very promising model to describe stress versus the deformation in molten plastic. Though, the development of Constitutive Equations for plastic melt is still in the developing stages. The MSF model is based on the so-called reptation theory, where the polymer chains in the plastic moves inside a 'tube'. The orientation of the 'tube' then follows the deformation of the plastic. This is an idea originally introduced by the Nobel Prize laureate Pierre-Gilles DeGennes.

The experimental inflation into a circular cylinder has been performed using an inflation device similar to a thermoforming process, Fig.2, where a square plate (2.0mm thick) of different plastics (HDPE, LLDPE.) was clamped between a Teflon coated aluminium cylinder and a Teflon coated aluminium plate. The whole system is held at the same temperature (within 1°C). By applying air through small holes in the aluminium plate the molten plastic plate can deform into the circular cylinder. The internal diameter of the circular cylinder is 62mm. Fibre optic sensors mounted down through the cylinder monitor the position of the top of the inflating plate (Z) and the pressure difference across the plate (ΔP) is measured by a pressure transducer.

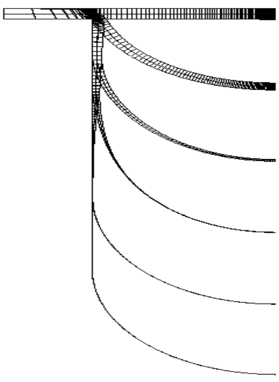


Fig 1: The numerical calculation of the inflation of the plastic plate.

Figure 2: The inflation equipment

The pressure (ΔP) used to inflate the plate is shown as a function of the top of the inflated plate (Z) in Fig.3 and Fig.4 for the inflation of the HDPE and the LLDPE melt respectively. The inflation times ranges from 0.08s to 14s. The corresponding numerical simulations of the inflation are shown in the same figures. Here, the L-MSF Constitutive Equation is used. This is a special model developed specific for plastics consisting of linear polymers. The L-MSF model used to describe the deformation of the LLDPE melt (Figure 4) allowed the maximal possible relative hardening of the plastic due to the deformation, where the HDPE (Fig.3) was described as less relative hardening.

The results show that the experimental inflation can be modelled accurately using the L-MSF Constitutive Equation and it is able to predict the burst or break of the plate (i.e. the sudden drop in the pressure) in reasonable agreement with the experimental data. The used numerical method is a general (three dimensional) Finite Element Method. Therefore it can be applied to a variety of analogous thermoforming and Blow-moulding problems.

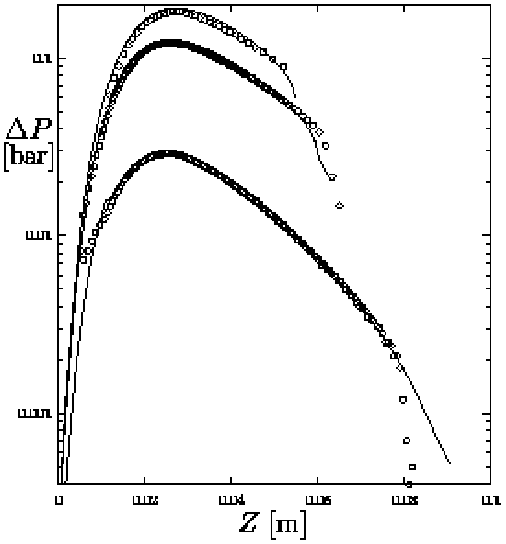


Fig. 3: The pressure difference over the HDPE plate at 140°C (○) as a function of the position of the membrane top (Z). The lines are the merically calculated pressures.

There are the following key observations. First, there is no material break at low inflation rates. This is due to the fact that molten plastic behave viscous at slow deformation and elastic at fast deformations. A pure viscous inflation is always stable and therefore the viscous behaviour or the molten plastic stabilizes the membrane at slow deformations. Second, at fast deformations or inflations, which normally are relevant for processing, the material always breaks. Note, finally that a plastic with the largest relative hardening can be inflated into largest total volume. Here the top of the inflated plate, Z, represents the total volume.

The same phenomena have been observed numerically for plastic consisting of branched polymers. This is normally a material as LDPE, often used in the Thermoforming process. Though, plastics consisting of branched polymers can be inflated into much larger volumes (e.g. Z values) than polymer melts consisting of linear polymers.

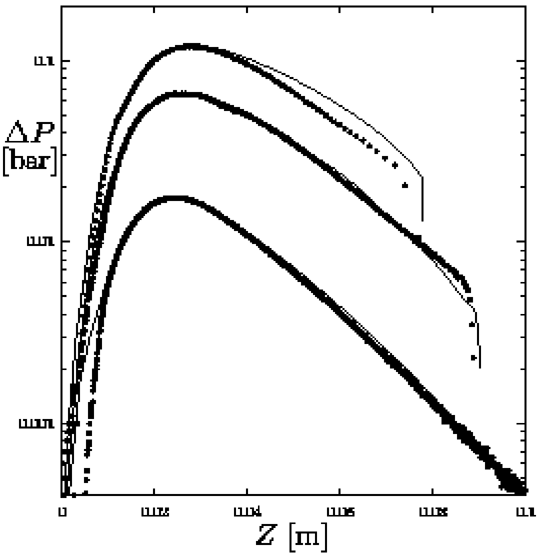


Figure 4: The pressure difference over the LLDPE plate at 120°C (●) as a function of the position of the membrane

Further information: Henrik Koblitz Rasmussen

3 EDUCATION

The Centre is strongly committed to the education of highly qualified candidates in polymer science and engineering. This is based on a belief that the most efficient form of technology transfer is through people. In fact, it has been argued[1] that the major beneficial effect of government sponsored research, arises from the knowledge carried to the society by highly qualified candidates graduated from the universities.

DTU Courses

The Batchelor of Science (B.Sc.) program at the DTU is a three and a half year program, while the Master of Science (M.Sc.) is a five year program. The two programs are parallel with separate entrance requirements. Also the curriculum and thesis requirements are specific for the two educations. The M.Sc. program has a much higher degree of flexibilty than the B.Sc. program. The polymer courses are organized within the two departments as follows:

Department of Chemical Engineering:

- 28212 Polymer chemistry (34)
- 28213 Polymer technology (27)
- 28315 Colloid and surface science (12)
- 28414 Rheology (8)

Department of Manufacturing Engineering and Management:

- 42230 Polymer processes[2]
- 42232 Design of plastic products (16)
- 42234 Experimental plastics technology (5)
- 42935 Injection moulding (19)
- 42946 Extrusion processes and special processes (8)
- 42947 Thermoforming (3)
- 42949 Simulation of injection moulding (6)

The numbers in parentheses indicate the student participants in fall 2001 or spring 2002.

The courses with 9 as the third digit are designeded for the B.Sc. polymer education in mechanical engineering, but they may be followed by all students.

Classroom instruction of B.Sc. students.

International Master of Polymer Engineering and Science

In 2001 we have taken the first step at establishing an M.Sc. program in Polymer Engineering and Science. Integrated within the existing polymer education, the program is targeted at students that have a B.Sc. degree from their home university. The education is of two years duration. Within this period the students can be associated with a Danish company at least for the duration of the thesis project.

The program will be administrated by the DTU. Stipends will be available for a limited number of students, partly sponsered by the Government and partly by the companies involved.

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[1] Materialeforskning – Oplæg til en national strategi, Forskningsministeriet, København, DK

[2] Not given 2001.

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Johansen, J.; Jørgensen, B., Rhinosleep. Advisor T. Lindemark.

Laursen, J.-H.; Overgaard, K., Development of tests for pressure sensitive adhesives. Advisor M.E. Vigild, collaboration with Coloplast A/S.

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M. Sc. theses

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4 COLLABORATION WITH INDUSTRY

An efficient transfer of research based knowledge to industry is of major importance in performing well in the international competition. Since the establishment, the Danish Polymer Centre has regarded the cooperation with the industry as an important part of its activities and has continuously been expanding its sphere of activities.

The Polymer Centre has assisted industry with valuable information and expertise, which otherwise could be difficult and expensive for the companies to attain, especially for small- and medium sized ones.

Centre Contracts

The Danish Polymer Centre is currently involved in three so-called *Centre Contracts*. The term covers a juridical collaboration between companies, research institutions and technological service institutes like the Danish Technological Institute. The aim of the Centre Contracts is to create a common effort in strategic research and development projects with a commercial appeal. They make it possible for companies to get access to the newest results in the fields of research and technological development. The Centre Contracts are also intended to support tangible renewals within Danish companies by uniting the best qualities and abilities of the industry, research institutions and technological service institutes.

At the present time the Danish Polymer Centre is involved in three different Centre Contracts:

MONEPOL: A project concerned with understanding the processes, which chemically and environmentally degrade polymers, in order to exploit this in future applications.

HYDECO: A project that deals with hygienic design and cleaning of process equipment in the comestible industry.

COMF: A project concerned with surface metrology and functionality.

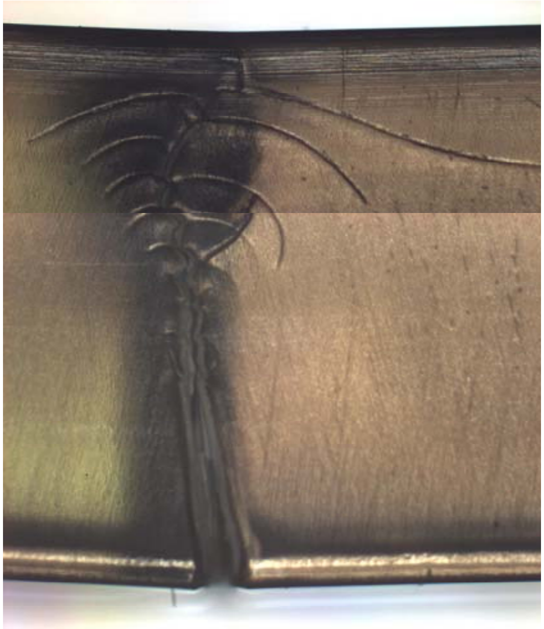

Fig. 1 Studies of environmental stress cracking of plastics, with the aim to make better performance materials. The figure shows optical microscopy photos of cracks in polycarbonate exposed to ethylene glycol monomethyl ether.

Patents and spin-off

Staff members of the Polymer Centre reported 5 disclosures in 2001 to managements at DTU and Risø. So far 3 of these have been filed as Patent applications. In 2001-02, three earlier patents licensed to Optilink A/B are under commercialisation with participation from the Polymer Centre. Additionally, in return for patent rights transferred to Cartificial A/S, the Polymer Centre (at Risø) has received stocks in accordance with new governmental regulations. At the same time the Polymer Centre works under contract with Cartificial A/S to develop the patented materials into registered devices.

Other Types of Cooperation

Apart from Centre Contracts, the Danish Polymer Centre has good experience with other kinds of industrial cooperation like Master projects, Ph.D. projects and specific investigations.

Fig. 2 Experimental set-up for simulating materials wear due to continued exposure to friction, pressure etc.

The procedure of contacting the Danish Polymer Centre, with respect to a specific assignment, has been facilitated by the decision to employ two *Project Pilots*; i.e. commercially minded personnel with scientific backgrounds within research, development and processing, who are experienced in project management. Their jobs are either to help directly, if the task lies within their personal field of expertise, or to direct the company to the right persons within the Polymer Centre. The normal contact procedure for a company is to make an enquiry by phone or mail. The Project Pilot then sets up a meeting with the relevant persons, in which the needs, aims and economy are defined. After this the project or task is started.

Often it is an advantage for the company to have only one contact person from the Polymer Centre, and the Project Pilots act as task or project managers at the Polymer Centre on behalf of the company. This initiative constitutes a new way, in which small companies can easily make inquiries about actual problems or research projects.

Apart from Centre Contracts and specific assignments, the Polymer Centre is also cooperating with the industry in a number of EU-projects as well as in a few large research and development projects.

Industrial collaborators:

- Borealis A/S
- Coloplast A/S
- Danfoss A/S
- Gram Technology ApS
- Grundfos A/S
- Lego A/S
- Løgstør Rør A/S
- Maersk Medical A/S
- Mallinckrodt A/S
- Medicotest A/S
- Novo Nordisk A/S
- Novozymes A/S
- NKT Research A/S
- Optilink A/S
- Radiometer A/S
- Roblon A/S

For further information please contact:
Sune Lund Jensen, Hasse Buus, Kristoffer Almdal, and Kell Mortensen

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