International Polymer Physics Meeting To Honour Prof. F. J. Baltá Calleja on his 70th Birthday



"Advances in Nanostructure and Physical Properties of Polymer Materials

and Nanocomposites"

Madrid, 23rd-24th October 2006



Instituto de Estructura de la Materia

Serrano 113, 119, 121, 123

http://www.iem.cfmac.csic.es/fmacro/

October 23rd

- 9:00 Welcome, *Prof. José V. García Ramos*, Director of the *Instituto de Estructura de la Materia, CSIC*.
- 9.10 Opening Remarks, Prof. Francisco J. Baltá Calleja.

Nanostructures and Crystallization Processes

Chairman: Prof. Eric Baer

9:30 The Essential Novelty brought to Crystallization by Linear Molecules

Prof. David C. Bassett, Univ. Reading

10:00 The Origin of Flow-Induced Crystallization in Entangled Polymer Melts

Prof. Benjamin S. Hsiao, Stony Brook Univ. NY

10:30 Crystallization-Induced Confinement in PET and its Connection with Mechanical, Dielectric and Calorimetric responses

Dr. Marco Pieruccini, CNR Messina

Coffee Break

11:00 – 11.30

Chairman: Prof. David C. Bassett

11:30 Nanostructures in Block Copolymers with Liquid-Crystalline Amphiphilic Molecules

> Prof. Wim H. de Jeu, FOM Inst. Atomic Mol. Phys., Amsterdam

12.00 Benefits and Potentials of High Performance DSC (HPer DSC) for the Study of Crystallization and Melting of Polymers

Prof. Vincent B. F. Mathot, SciTe The Netherlands Katholieke Universiteit Leuven Belgium

Academic Session

(in Spanish language)

12:30 Prof. José V. García Ramos, Director of IEM.

Lunch 13:30 – 15:30

Multicomponent Systems, Nanocomposites and New Polymer Materials

Chairman: Prof. Ben Hsiao

15:30 Multicyclic Polymers – A New Architecture

Prof. Hans R. Kricheldorf, Univ. Hamburg

16:00 Forced Assembly into Polymer Nanolayers: Creating Polymers Plus

Prof. Eric Baer, Case Western Reserve Univ.

16:30 Incorporation of Carbon Nanofibres into Single Polymer Polypropylene Composites

Prof. Ian M. Ward, Univ. Leeds

Break 17:00 – 17:30

Chairman: Prof. Wim H. de Jeu

17:30 Understanding the Polymer Interphase

Prof. Anne Hiltner, Case Western Reserve Univ.

18:00 Processing and Characterization of a Multi-Walled Carbon Nanotube/Polyetherester (PBT/PTMO) Masterbatch and its Blends

Dr. Georg Broza, Technic. Univ. Hamburg-Harburg

18:30 In-situ Polycondensation Method of Polymer/CNT Nanocomposites Preparation

Prof. Zbigniew Roslaniec, Technic. Univ. Szczecin

October 24th

Properties and Deformation Processes

Chairman: Prof. Georg H. Michler

10:00 Relating Texture and Local Mechanical Properties of some Semicrystalline Polymers by AFM Nanoindentation

Prof. Stefano Piccarolo, Univ. Palermo

10:30 Filler Size Effects on Deformation Mechanisms in Amorphous Nano-Composites

Prof. Hans H. Kausch, École Polytechnique Fédérale Lausanne

Coffee Break	11:00 – 11:30
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Chairman: Prof. Stefano Piccarolo

11:30 Nanomechanical Effects in Layered Polymer Systems

Prof. Georg H. Michler, Martin Luther Univ. Halle-Wittenberg

12.00 Application of Polymer Membranes in Waste Water Treatment

Dr. Axel Schönfeld, Federal Institute for Environmental Science Berlin

12.30 TEM Dark Field Investigation of the Buildup and Transformations of Polymer Single Crystals

Prof. Bernard Lotz, Institute Charles Sadron Strasbourg

13.00 Closing Session

Dr. Tiberio A. Ezquerra Head of the Department of Macromolecular Physics, Instituto de Estructura de la Materia, CSIC.

The Essential Novelty brought to Crystallization by Linear Molecules

David C. Bassett J. J. Thomson Physical Laboratory University of Reading, UK

In addition to chainfolding *per se* there are two associated factors fundamental to the inherent differences between the crystallization of short and linear molecules. Lamellar fold surfaces of monodisperse n-alkanes and polyethylene - the archetypal linear molecules - are planar with low crystallographic indices corresponding to $\sim 35^{\circ}$ tilt between the chain axis, **c**, and lamellar normals when grown slowly (Régime I). This indicates both a degree of ordering and the strong preference for more basal surface area than zero tilt provides. Moreover, unlike short molecules or extended-chain lamellae of the monodisperse n-alkanes, adjacent lamellae do not lie parallel but diverge linearly from branch points, generally giant screw dislocations (which is the basis of spherulitic growth). This is because, for long molecules, permanently or temporarily uncrystallized molecular segments, i.e. cilia, will occupy space adjacent to the fold surface, denying it to other crystallizing molecules and creating a short-range repulsive force as the morphology requires.

Greater divergence, accompanied for once-folded monodisperse n-alkanes and polyethylene by coherent twisting or banded growth, results for fast growth (Régime II). Then surfaces are not initially ordered but rough having insufficient time to organize before the growth surface advances. Additional divergence results and, with zero overall chain tilt, surfaces are highly stressed. Partial alleviation, with reduced free energy, is achieved by twisting, accompanying isothermal lamellar thickening employing the inherent strong longitudinal molecular motions, and the exploration of alternative fold conformations.

Accordingly, the two additional factors key to the characteristic novel behaviour of linear molecules are 1) that partly-attached molecules get in the way and impede crystallization causing the lamellar divergence underlying spherulitic growth and 2) that under typical fast growth rates, fold surfaces form disordered, giving additional divergence, and prone to reorganization. The associated surface stress will be particularly high in systems such as polyethylene whose preference is for chains to be tilted within lamellae; its partial alleviation by twisting is the origin of banded growth. The underlying distinction between fast and slow growth with their distinctive crystallization behaviours is whether or not fold surfaces have time to organize their packing before the next layer adds to the growth surface.

The Origin of Flow-Induced Crystallization in Entangled Polymer Melts

Benjamin S. Hsiao Department of Chemistry Stony Brook University, USA

A combined synchrotron small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) study of model polyethylene blends was carried out to investigate the origin of flow-induced crystallization in entangled polymer melts [1-9]. Results indicate that the formation of the shish-kebab structure in high molecular weight species can be attributed to the abrupt coil-stretch transition that occurs only in sections of the chain, rather than its entire contour length. Unexpected shish-kebab structure with multiple shish in a sheared polymer blend, containing 2 wt% of crystallizing ultra-high molecular weight polyethylene (UHMWPE) and 98 wt% of non-crystallizing polyethylene copolymer matrix, was observed by field-emission scanning electron microscopy (FE-SEM) examinations of the solvent-extracted UHMWPE component [10]. SEM results indicated that the shish-kebab entity contained several independent shish, instead of a single shish as conventionally observed in dilute polymer solutions or thin films. Both scattering and microscopy data confirmed the hypothesis that two populations of chain segments (stretched and coiled) in UHMWPE are induced by shear, where the stretched segments form the basis of the multiple shish and the coiled segments crystallize into the kebabs following a diffusion-controlled process.

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Crystallization-Induced Confinement in PET and its Connection with Mechanical, Dielectric and Calorimetric responses

Marco Pieruccini Istituto per i Processi Chimico-Fisici CNR, Messina, Italy

The interplay between structure formation and relaxation dynamics, as a manifestation of nano-confinement, is analyzed in the case of semi-crystalline PET. Dynamic mechanical thermal analysis and calorimetry on cold-crystallized PET reveal the occurrence of a rubber-to-glass transition during the annealing of colddrawn PET at low temperatures (100 °C $\leq T \leq$ 140 °C). This process is viewed as an effect of confinement caused by the tendency of the crystalline domains to grow. The free energy associated to the density fluctuations is the key quantity in terms of which this effect can be discussed, in a framework resembling the Adam-Gibbs approach to the description of the glass transition. A re-analysis of the (approximate) PET structural data by means of this model reveals that confinement-induced vitrification takes place when the linear dimensions of the constrained regions are close to the density autocorrelation length. Cold-drawing causes the latter to increase by a factor of ~ 2 along the orientation direction, with respect to the isotropic case. The asymptotic decay of the α -relaxation worked out from the dielectric response, is put in relation with the lacking amount of free energy associated to those density modes which are quenched by confinement. The model is found to describe these observations consistently.

Nanostructures in Block Copolymers with Liquid-Crystalline Amphiphilic Molecules

Wim H. de Jeu FOM Institute for Atomic and Molecular Physics Amsterdam, The Netherlands

We present a surface X-ray study of the morphologies of thin films of P2VP*b*-PEO diblock block copolymers complexed with amphiphilic molecules. The latter consisted of wedge-shaped molecules having a sulfonic group at the tip and were incorporated via protonation of P2VP. The degree of neutralization was varied from 25% via 50% till 100% [1]. X-ray reflectivity of thin films exhibit in all cases microphase-segregated patterns comprising smectic layers of the complexed P2VP blocks oriented parallel to the substrate throughout the whole film. In addition a specific substrate layer is observed that is different for each of the degrees of complexation. For the 50% complex AFM and GISAXS indicate embedded amorphous cylindrical PEO domains stabilized perpendicular to the substrate by the smectic layering of the ligands. The results can be understood using the ABC triblock model for smectic liquid crystalline/amorphous block copolymers [2].

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Benefits and Potentials of High Performance DSC (HPer DSC) for the Study of Crystallization and Melting of Polymers

<u>Vincent B.F. Mathot</u>^{1,2}, Thijs Pijpers^{1,2}, Geert Vanden Poel³ ¹ SciTe*, The Netherlands ² Katholieke Universiteit Leuven, Belgium ³ DSM Resolve, The Netherlands

Recently, HPer DSC has been introduced [1] as a tool for measuring at high scan rates with commercial available instrumentation. Constant rates up to maximal 300 °C/min in cooling and 500 °C/min in heating are feasible. Such rates are much faster than achievable by 'standard' DSC, which operates typically at rates around 10 °C/min. Being able to choose optimum scanning rates (from low to high ones, using one device) for tackling a problem under study is one of the great benefits of HPer DSC [2, 3].

Advantages found hitherto are:

- Increased sensitivity;
- Access to quantitative measurements, including heat capacity measurements and determination of crystallinity as function of temperature;
- Increasing production;
- Improved way of study of kinetics;
- Study of reorganization phenomena; hindering of undesired phenomena like cold- and recrystallization; solid-solid transformations etc.;
- Matching rates occurring in daily practice;
- Mimicking of rates during processing, like extrusion and injection molding;
- Measuring on minute amounts from milligram down to the microgram level

 of materials, such as impurities, coatings, yields of fractionations (like HPer DSC on SEC fractions!) and combinatorial chemistry experiments;
- Possibility to run at low to high scan rates using the same device.

The presentation will provide examples of the benefits which come into reach. Though the examples will be given for polymers, the findings are of use for pharmaceutical raw materials and products too.

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Multicyclic Polymers – a New Architecture

Hans R. Kricheldorf, Lali Vakhtangishvili, Nino Lomadze, Gert Schwarz Institut für Technische und Makromolekulare Chemie University of Hamburg, Germany

Various activated difluoroaromatics were polycondensed with triphenols with optimization of the reaction conditions, so that gelation was avoided. Analogous polycondensations were performed with various diphenols and aromatic trifluoroketones. Soluble multicyclic polyethers, or in other words, soluble nanogels having molar masses up to 10^8 Da were obtained by these " $a_2 + b_3$ " polycondensations. Multicyclic poly(ether ester)s were prepared from trimesoyl chloride and monodisperse oligo(ethylene glycol)s. These poly(ether ester)s were found to dissolve all alkalimetal benzoates in contrast to the highly selective crown ethers. The multicyclic polymers possess a compact three-dimensional structure and are not capable of undergoing entanglements.

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Forced Assembly into Polymer Nanolayers: Creating Polymers Plus

Eric Baer Department of Macromolecular Science and Engineering Case Western Reserve University, Cleveland, USA

Lessons from biology have revealed that natural materials systems have architectures that are specifically designed to accommodate a unique spectrum of required properties. These architectures always have many scale levels that are bound together by interfacial coupling or adhesion. In recent years, new synthetic approaches have been used to develop macromolecular architectures that "self-assemble" into nano-scale morphologies. This lecture addresses another approach – the "forced-assembly" of synthetic polymers by continuous nanolayer coextrusion. Films can readily be created with thousands of layers containing two or more alternating polymers. Layer thicknesses have been made in the range of several microns down to less than ten nanometers by varying the number of layers and the layer composition.

Nanolayered films are of interest because of a potential for developing materials systems with novel mechanical, transport, electrical and optical properties. Since the radius of gyration of macromolecules can readily exceed the nanolayer thickness, the surrounding layers can be used to impart dimensional constraint at the molecular level. Perhaps the most spectacular application of polymer nanolayers is our development of bio-inspired axial, cylindrical and spherical gradient refractive index (GRIN) lenses. These are made by layering nanolayered polymer films into hierarchical structures with controlled refractive index gradients. The spherical lenses biomimic the octopus lens. They contain more than 5x105 nanolayers. Lenses of this type exhibit a wider field of view with less aberration than conventional lenses having no index gradients.

Incorporation of Carbon Nanofibres into Single Polymer Polypropylene Composites.

Ian Ward, Peter Hine, Richard Foster and Vivien Broome IRC in Polymer Science and Technology University of Leeds, UK

The incorporation of carbon nanofibres (CNF) into single polymer polypropylene (PP) composites has been explored in terms of optimisation of the production of the composites and preliminary studies of the structure and properties of the self reinforced composites. The production requires optimisation of three stages: incorporation of the CNF into the PP, orientation of extruded PP tapes by tensile drawing and hot compaction of the tapes.

The most significant improvement in properties (increased stiffness and reduced thermal expansion) was found for the incorporation of CNF into unoriented PP, which is the material that comprises the matrix phase of a single polymer composite. It was shown that although the incorporation of CNF into PP causes voiding at the tensile drawing stage these voids are closed and sealed by the hot compaction process so that completely consolidated composites can be produced.

Attempts have been made to apply composite modelling to these results, using dynamic light scattering and electron microscopy to obtain estimates of the fibre aspect ratios in the hot compacted composites.

The improvement in the mechanical properties of the oriented hot compacted composites is more valuable at high temperatures where the PP matrix shows a major reduction in stiffness. A result which could be of some importance is that the peel strengths of the woven CNF/PP composites show a four-fold increase over the unfilled woven PP composites, and this is increased two-fold again by the addition of a maleic anhydride compatibiliser.

Understanding the Polymer Interphase

Anne Hiltner Department of Macromolecular Science and Engineering Case Western Reserve University, Cleveland, USA

When two immiscible polymers are brought into intimate contact, highly localized mixing of polymer chains creates an "interphase" region. We have fabricated materials that are entirely interphase by forced assembly of two immiscible polymers. Assemblies of thousands of alternating layers of two glassy polymers, with individual layer thickness on the nanometer size scale of the interphase, were created by layer multiplying coextrusion. Various combinations of poly(methyl methacrylate), polycarbonate, and a series of styrene-acrylonitrile copolymers were studied. The properties of the interphase materials were probed with conventional tools of polymer analysis. Continuous nanolayers were observed directly using atomic force microscopy. Interphase thickness, extracted from the layer thickness dependence of oxygen permeability, showed the predicted dependence on the interaction parameter and correlated with interphase strength as measured with the Tpeel test. Interphase specific volume, as determined by density, exhibited both positive and negative deviations from constituent additivity. The deviations correlated with the change in free volume hole size from positron annihilation lifetime spectroscopy, but did not correlate directly with the χ parameter. The origin of the deviations was found in the nature of chain packing in the interphase, as evidenced by non-additivity in entanglement molecular weight. The volumetric effects accounted for the glass transition behavior of the interphase material.

Processing and Characterization of a Multi-Walled Carbon Nanotube/Polyetherester (PBT/PTMO) Masterbatch and its Blends

<u>G. Broza</u>, K. Schulte Polymer Composites Section Technical University Hamburg-Harburg, Germany

Thermoplastic elastomers (TPEs) with carbon nanotubes (CNT) have the potential to be structured materials. This is mainly due to their superior mechanical properties and the possibility of conventional processing. In this contribution we will report on the evaluation of the effect of multi walled carbon nanotubes (MWCNT) on the properties of poly(etherester)(PBT/PTMO) blockcopolymers, as a function of the volume content of MWCNT.

The aim of the work is to achieve a preferably high dispersion of multi walled carbon nanotubes (MWCNT) in a PBT/PTMO matrix. The PBT/PTMO were milled, mixed, extruded and granulated to obtain a masterbatch with 10.00 wt. % MWCNT. In addition, five samples with different weight percentages of MWCNT were produced by repeated milling, mixing and, extruding, followed by injection moulding the masterbatch and the PBT/PTMO.

The samples were characterised by electron microscopy, dynamic-mechanical analysis, and tensile testing. SEM image shows uniform nanotubes distribution in the matrix. Significant tubes pullout can be observed in the photograph and agglomerates in the matrix have not been identified yet.

Adding a small amount of CNT was enough to improve the thermomechanical properties of the nanocomposites. The Young's modulus, and tensile strength, monotonically increased with added amount of MWCNT in the PBT/PTMO matrix. However, when the content of MWCNT increased from 0.5 wt.% to 2.0 wt.%, the strength and the strain of the nanocomposites decreased.

In all nanocomposite materials, the incorporation of MWCNT causes an increase in the stiffness. The storage modulus is increased by the stiffening effect of the nanotubes, which is particularly significant at temperatures between T = -80 °C and + 175 °C. Tan δ shows the same glass transition for all samples.

In-situ Polycondensation Method of Polymer/CNT Nanocomposites Preparation

Zbigniew Roslaniec Institute of Materials Science and Engineering Szczecin University of Technology, Poland

Polymer nanocomposites including those containing carbon nanotubes appear to be of particular significance. Polymer nanocomposites based on thermoplastic polyesters (PET, PBT), polyamide 12, poly(ether-ester) elastomer and carbon nanotubes have been prepared and investigated. The nanocomposites were obtained (in situ) by introducing the fillers into the reaction mixture and the synthesis of polymer by polycondensation in the molten state. The nanotubes were dispersed in laurolactam, ethylene glycol, 1,4-butanediol or polytetramethylene glycol (depending on the polymer matrix) using ultrasonicator and ultra-high speed stirrer. Structure of mixture and polymer nanocomposites have been investigated by TEM, SEM and AFM. Some physical properties of the resulting nanocomposites have been also studied.

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Relating Texture and Local Mechanical Properties of Semicrystalline Polymers by AFM Nanoindentation

Stefano Piccarolo Dip Ingegneria Chimica dei Processi e dei Materiali Università di Palermo, Italy

AFM not only shows outstanding resolution for describing material texture, it is also ideally suited to determine its mechanical properties. Nanoindentations performed by AFM force curves on several polymers show that the contact between the tip and the sample is dominated by elastic behavior with negligible plastic deformation once suitable experimental conditions are identified. The local modulus so determined is representative of the continuum material behaviour and, if samples are homogeneous, i.e. if the homogeneity extends up to the macroscopic scale, the elastic modulus determined by nanoindentation is very close to the macroscopic one. However upon decreasing the load, penetration decreases and indentation size becomes comparable with the underlying texture thus giving the possibility to identify individual components mechanical properties rather than the bulk properties.

Nanometer scale morphological order of macroscopically amorphous polyesters, obtained from the melt at moderate cooling rates, was shown in the past. The influence of such order on mechanical properties, evaluated through AFM nanoindentations, is reported in this study on a PET/PEN blend. Results show that nanoindentations conducted at relatively high load, with penetration depths of the order of 100nm, confirm the information obtained from mechanical tests at micrometer scale, i.e., microhardness. On the other hand, true nanometer scale indentations (<40nm) are seen to discriminate between the mechanical properties of the nanophases formed during solidification.

Filler Size Effects on Deformation Mechanisms in Amorphous Nano-Composites

Hans-Henning Kausch¹, Georg H. Michler² ¹Institute of Materials, Federal Institute of Technology Lausanne (EPFL), Switzerland ²Institute of Physics, Martin Luther University Halle-Wittenberg, Germany

Fillers and modifiers have been employed from the very beginning of the industrial use of polymer materials - and about 75 years before the notion of macromolecule was born. Fillers are generally used to reduce cost as well as the thermal sensitivity of mechanical properties of the matrix material and to improve - if possible - strength and toughness. In this respect nano-scale reinforcement has attracted particular attention in recent years. In view of their small size nano-particles can often be incorporated into the crystalline morphology and /or the network of entangled chains. As a further consequence the average distances ID between nanoparticles are also drastically reduced even at relatively low filler concentrations. Secondly, the nano-particles provide ultra-high specific surfaces with (strong) interaction to the polymer matrix. Both characteristics influence the structure and the micro-mechanics of deformation, which were studied using three different nanocomposites: PS/alumina, PMMA/SiO2, and PC/carbon nano-tubes. It could be shown that good dispersion of (surface treated) nano-particles is achieved when using solution blending or electrospinning techniques. Limited interfacial strength essential for debonding and nano-void formation - favours plastic yielding of polymer matrix ligaments through local stress concentration at nano-voids thus resulting in energy dispersion and material toughening.

At small interparticle distances (of a few 10 nm) nano-particle modulated crazing was observed in PS, PMMA and PC. Interparticle distances in nano-particle filled PMMA nano-fibres amounted to around 32 nm, sufficient to reduce lateral constraints and enable thin-layer yielding, i.e. the homogeneous (plastic) deformation of the ligament of matrix material. Both effects increase toughness of the material without significant reduction of stiffness and strength.

Nanomechanical Effects in Layered Polymer Systems

Goerg H. Michler Institute of Physics Martin Luther University Halle-Wittenberg, Germany

The common feature of the group of amorphous, macroscopically brittle polymers, including polystyrene (PS), polymethylmethacrylate (PMMA), poly(styrene-acrylonitrile) copolymers (SAN), cyclic olefine copolymers (COC), and others is a brittle fracture at room temperature with elongations of break of about 5%. However, on the microscopic level these polymers show highly localized deformation zones. These zones are usually some µm thick and some 100 µm long and are composed inside of nanovoids and highly stretched fibrils. These crazes or craze-like deformation zones are precursors of cracks and initiate crack propagation and the brittle fracture [1, 2]. The degree of stretching of the polymeric material inside the deformation bands reaches some 100% and is limited by the total stretching of the entanglement network [1]. It shows that the macromolecules in principle are able to large deformations, if some morphological conditions are fulfilled [3].

Following this idea, there are some structurally modified polymers where the usually brittle polymer can be deformed to a high degree, yielding an enhanced toughness [4]. Some examples will be discussed in the lecture:

- Linear and star block copolymers of PB and PS can be prepared with a lamellar morphology also if the PS content is up to about 80%. If the PS lamellae are thinner than 30 nm, they can be deformed at room temperature till to 250-300% (i.e. till to the limit of deformability of the entanglement network, this effect was called "thin layer yielding").
- Nano- and microlayered structures of blends of PS/PB blockcopolymers and homo-PS as well as from coextrusion technology reveal changes in toughness by reducing the layer thickness from some µm down to a few tens of nm.

These micro- and nanomechanical processes have been investigated using all microscopic methods, including scanning electron, transmission electron and atomic force microscopy using special micro-tensile devices enabling deformation tests of the materials at different temperatures, including in situ tests [2, 4]. Additional valuable information arises from micro-indentation studies of these polymers [4].

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Application of Polymer Membranes in Waste Water Treatment

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Membranes are used for treatment and purification of industrial wastewater especially for the goal to reuse these waters for certain purposes. Besides metallic and ceramic perforated membranes mainly polymer membranes are widely used. The most common polymers used for membrane bioreactors are made of Polysulfone, Polyacrylnitrile, Polyethersulfone, Polypropylene, Polyvinylidenfluoride, Cellulose acetate and Polyamide. In recent years polymer membranes have found their way into the treatment of municipal wastewater. This paper is concentrated on this application. A typical process for purification of municipal wastewater consists of primary, secondary and tertiary treatments. Primary treatment separates solid particles by using screens and grit separators. Secondary treatment consists of aerobic biological oxidation of liquid and fine particle organic pollution in the wastewater by activated sludge and a following clarification by sedimentation and gravel bed filtration to eliminate the surplus activated sludge. The tertiary treatment may consist of the removal of nitrogen compounds and phosphorus (the components That eutrophicate the receiving water bodies), procedures to reduce the infection potential a.s.o. Nevertheless the resulting effluent is not without turbidity and, what is more important, not hygienically safe. It can be disinfected chemically for discharge. However the effluent contains solved organic compounds that are poorly biodegradable or even persistent, between them are toxic, cancerogenic, mutagene and endocrine acting compounds. To solve the hygienic problems with respect to discharging treated municipal wastewater into water bodies like rivers, lakes and coastal waters and to improve the biological quality of these discharges, in recent years micro-,ultra-and even nanofiltration techniques using polymer membranes have entered into municipal wastewater technology. When the discharged water enters directly to bathing waters the application of biomembran reactors containing polymer membranes is the best choice to eliminate affection of swimming peoples by bacteria and viruses. The size und number of such treatment plants is increasing year by year. By 2006, around 100 municipal full-scale plants with a capacity >500 p.e.(population equivalent) are in operation in Europe. The largest membrane bioreactor plant worldwide was commissioned in 2004 to serve a population of 80,000 p.e. (Kaarst, Germany).

It is now considered that for a green field and for a given treatment quality the capital cost of membrane bioreactor plants is comparable to a conventional scheme. However, the energy costs remain 30 to 50% higher. Should this discrepancy be reduced in the coming years, the membrane bioreactor technology would become a state-of-the-art process for the municipal sector. Further optimisation of the polymer membranes and of the whole technology will make it to a common and competitive treatment alternative for purification of municipal wastewaters.

TEM Dark Field Investigation of the Buildup and Transformations of Polymer Single Crystals

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Dark field imaging is a most remarkable technical capability of electron microscopy, as it combines the diffraction and imaging modes. Using the electrons scattered by the material to form the image enables a detailed mapping of its internal structure, and gives access to various defects and/or growth processes. The presentation deals with insights gained on polymer single crystal growth and structural changes as illustrated by old and (very) recent work from this laboratory: (i) preservation of helical hands in a crystal-crystal transformation (isotactic Poly(1-butene Form II to Form I) (ii) progress of a crystal-crystal transformation along invariant strain planes (poly(ethylene-carbon monoxide), β - α phase transformation) (iii) in polymer single crystal growth, determination of the extent of lateral spread (both average and distribution) and density of secondary nucleation, two fundamental parameters of polymer growth theories for which only estimates were available (isotactic polyvinylcyclohexane).

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