PERIODICA POLYTECHNICA SER. CHEM. ENG. VOL. 48, NO. 2, PP. 117–154 (2004)

CONFERENCE OF MSC STUDENTS

Faculty of Chemical Enginering
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

November 9, 2004

ABSTRACTS

PREPARATION OF THERMOPLASTIC STARCH (TPS) AND ITS COMPOSITES: A STUDY ON THE RELATIONSHIP BETWEEN STRUCTURE AND PROPERTY

Kristóf BAGDI

Supervisor: Béla Pukánszky
Deparment of Plastics and Rubber Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

Consultant: Péter Müller
Department of Plastics and Rubber Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

In these days, the increasing amount of polymer waste is one of the most challenging problems the world faces, due to the large volume and the slow degradation of the polymeric products. The application of biodegradable polymers, which are primarily natural polymers such as starch and cellulose, can be an alternative solution, since these materials are easily available at low cost, they are renewable, and fully degradable. Widespread usage of biodegradable materials is limited by their processability, e.g. the melting point of starch ($T_m = 257$ °C) is higher than its degradation temperature ($T_d = 230 - 250$ °C). However, by the application of plasticizers the starch can be transformed into a thermoplastic material.

In the experiments, using two different mixing procedures, we succeeded to produce composite materials with various mechanical properties and with different plasticizer contents. The samples were prepared with 30 and 60 wt% glycerol content, followed by structure and mechanical tests on them. Dried starch and dried glycerol plasticizer were used in the experiments since the presence of absorbed water hinders the polymer processing procedure. The products obtained exhibited good mechanical properties, but have failed with longer storage time due to the high water uptake as a consequence of the strong hydrophilicity of the starch. In

order to improve further the mechanical properties and the life time of the products, different composites were prepared and processed. First, thermoplastic starch nanocomposites were prepared by using differently surface treated layered silicates, then structure-property studies were performed on these samples.

The solution is expected to improve the processability of TPS composites as well as to decrease the shrinkage of injection molded products. It is planned to develop fiber reinforced thermoplastic starch systems, which are anticipated to have improved mechanical properties and lower shrinkage.

ON COMPUTING THE NONCENTRALITY PARAMETER OF THE NONCENTRAL F-DISTRIBUTION

Ali BAHAREV

Supervisor: Sándor Kemény
Department of Chemical Engineering
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: kemeny@mail.bme.hu

Power, size of detectable effects and sample size calculations for ANOVA tables are based on noncentral F-distribution and these calculations can be performed with the aid of sparse tables. When checking the table of Lorenzen and Anderson (1993), great differences between the values of this table and the values obtained by Patnaik's (1949) 2-moment central-F approximation were observed. This made it necessary to study the algorithms for computing the noncentrality parameter of the noncentral F-distribution and the accuracy of the approximations.

The most effective recursive algorithms use the noncentral beta function ratio

$$I_x(a, b; \lambda) = \sum_{j=0}^{\infty} \left(\frac{e^{-\lambda} \lambda^j}{j!} \right) I_x(a + j, b), \tag{1}$$

where $I_x(a, b)$ is the usual incomplete beta function ratio; a and b denote the half of the corresponding degrees of freedom and λ denotes the half of the noncentrality parameter. Thorough examination of the literature and exhaustive computations gave the following results. (i) For large values of the noncentrality parameter summation (1) should be started at a higher index to avoid under/overflow problems in recursive computations. The incorrect values of the table of Lorenzen and Anderson (1993) were caused by overflow problems. (ii) We can start the above summation from the lowest j and proceed toward higher indexes, the reverse way is to start at the highest j and proceed backward. Knüsel and Bablok (1996) stated that the forward way is instable due to numerical cancellation. Attempts were made but we failed to prove this statement. Several authors suggest starting from a value approximately equal to λ and then work 'outward' (increasing and decreasing j). More accurate results can be achieved by the opposite 'inward' technique, however there is no such published algorithm. (iii) Newton's iterative computation of the noncentrality parameter can be greatly speeded up by eliminating redundant steps (Ding, 1997). Taking all these guidelines into consideration a new algorithm was coded in Statistica Visual Basic and the table of Lorenzen and Anderson was corrected. The Statistica's built-in algorithm for power analyses was found to give correct values. A new and finite formula was derived for calculating noncentral F probabilities when b is integer by combining Sibuya's (1967) as well as Singh and Relyea's (1992) formulae.

Patnaik's (1949) 2-moment central-F approximation, Tiku's (1965) 3-moment central-F approximation and Severo and Zelen's (1960) normal approximation were

compared. The results are the same as Tiku's ones (1966). We computed the above-mentioned table by using these approximations and compared the theoretical value (0.10) and the real value of the type II errors. The most accurate is Tiku's 3-moment central-F approximation. Severo and Zelen's approximation is slightly less accurate than Patnaik's approximation but the easiest to compute. The accuracy of these approximations is satisfactory for practical purposes.

QUANTUM CHEMICAL INVESTIGATIONS ON DIMERISATION OF FLUORINATED PHOSPHORUS YLIDES

Zoltán BENKŐ

Supervisor: László Nyulászi
Department of Inorgarnic Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: nyulaszi@mail.bme.hu

The synthesis of stable phosphorus ylides often fails because of the dimerisation of the nascent molecules. Previous works have shown that the fluorine substitution at the phosphorus stabilizes the phosphorus ylides. The aim of my studies was to investigate if this stabilization would be strong enough to inhibit the dimerisation of these fluorinated molecules.

The dimerisation of F_3P=N-X and F_3P=CX_2 molecules (X=H, CN, COOH) were investigated by density functional calculations carried out at the B3LYP/3-21G(*), B3LYP/6-311+G** and B3LYP/aug-cc-pVTZ levels of theory. The geometries of the ylides F_3P=NH, F_3P=N–CN, F_3P=N–COOH, F_3P=CH_2, F_3P=$C(CN)_2$, F_3P=$C(COOH)_2$ and their dimers were optimized. The analysis of the molecular orbitals has shown the effect of back donation into the σ^* anti-bonding orbitals of PF_3 groups.

The dimerisation Gibbs free energy of F_3P=NH and F_3P=CH_2 molecules at 298K is negative at all investigated levels of the theory. It means that these two ylides would not be stable at room temperature. The transition states of the reactions were optimized, too. According to the calculations the Gibbs free energy barriers of the dimerisation is not high enough to inhibit the dimerisations of the nascent molecules. Because the enthalpies and entropies of these reactions are negative, a dissociation temperature of about 500 K could be estimated. Thus, the structure of these hitherto unknown ylides could be investigated by the pyrolysis of the respective dimers.

Further calculations were carried out on fluorinated phosphorus ylides with electron withdrawing groups at the C/N atoms, since earlier studies have shown that these groups stabilize the ylides in other reactions. The ylides with nitrile or carboxil groups are more stable then their dimers, thus these compounds are potentially synthesizable.

INVESTIGATION OF WETTABILITY OF MICROSPHERES AT FLUID-LIQUID INTERFACES IN FILM BALANCE

Sándor BORDÁCS

Supervisor: Zoltán Hórvölgyi
Deparment of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: horvolgyi@mail.bme.hu

Co-supervisor: Attila Agod
Deparment of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

The investigation of monoparticulate layers composed of microspheres in film balances can serve as a model for the fabrication of nanostructural layers by Langmuir-Blodgett technique.

In this model system the particles are observable by traditional optical microscopy, allowing us to explore the mechanisms of structure formation in the interfacial layer and also the wettability of particles.

Monolayers of 75 μm diameter glass beads with chemically modified surface were studied in Wilhelmy film balance. The wettability of surface modified particles at water-air and water-octane interfaces was assessed by optical microscopy. The film balance experiments focused on the collapse mechanism of the layer as a function of particle contact angles and the quality of the subphase. For the investigations a two-liquid film balance was built and a measurement controlling software was developed.

The experiments revealed that the collapse mechanism is determined by two factors: the adhesion work of a particle and the fluid-liquid interfacial tension. Microspheres dropped out from the interface if small adhesion work was coupled with high interfacial tension. In other cases particle monolayers got creased without particle removal. The investigations showed that the pre-wetting of the particle surface has an effect on the behaviour of the interfacial layer.

According to the literature the contact angle can be calculated if particles fall out during the collapse [1]. The results suggest that the calculated contact angles were significantly higher than the directly measured values. In case of drop-out collapse, the work to force the particles into the subphase was found to be much higher, than the total adhesion work of the particles. The discrepancies were interpreted in terms of the contact angle hysteresis, dynamic contact angles and other dissipative processes. As a result of the measurements the compression efficiency could be approximated, which will have a key role in nanoparticulate layer investigations.

Finally, the source of errors of film balance experiments were taken into consideration and corrections were recommended to eliminate the systematic errors.

References

[1] CLINT, J. H. – QUIRKE, N. J., Colloids and Surfaces A: Physicochem. Eng. Asp. 1993, 78, 277.

This work was supported by the Hungarian National Scientific Foundation for Research (OTKA T037643).

DEVELOPING A MATHEMATICAL MODEL OF THE FISSION YEAST CELL CYCLE: $cdc25^{op}$ AND $wee1^{op}$ MUTANTS DESCRIBED

Quynh CHI LE THI

Supervisor: Ákos Sveiczer
e-mail: quynhchi79@yahoo.com

The most fundamental requirement for life is cell reproduction. Cell cycle is the sequence of events by which a growing cell duplicates all its components and partitions them more-or-less evenly between two daughter cells. The events of the cell cycle of most organisms are ordered into dependent pathways in which the initiation of late events is dependent on the completion of early events. For example, chromosome segregation in eukaryotes is dependent on the completion of DNA synthesis. These processes are controlled by a considerably complicated regulatory molecular network called the cell cycle machinery. In the first half of the 20th century yeasts have become model organisms in different fields of cell biology. Since the late '50s *Schizosaccharomyces pombe* (also known as fission yeast) has been spotlighted through its favourable physiological features for example, its symmetrical division enables good synchronization techniques, which are necessary for cell cycle studies. During the last 40 years, *S. pombe* has become an attractive model organism in all chapters of cell cycle research, as well as in other physiological, genetic and biochemical studies. The full genome of *Schizosaccharomyces pombe* has been recently sequenced, indicating the importance of this species.

The aim of the present study was to test a recently published mathematical model of the fission yeast cell cycle by simulating some mutants which were not involved in former research. The first task was to adapt the original model from the DOS-based Time-Zero software to the Windows-based WinPP software. The adaptation was tested by simulating the cell cycle of wild-type cells and those 18 cell cycle mutants, which had been used to construct the original model. In all cases, simulations by both softwares gave results with high similarity. Afterwards, the model was developed in order to describe some further mutants. It has been long known how the behaviour of fission yeast changes if it over-produces either the *cdc25* or the *wee1* gene. These over-producing mutants either have multiple integrated copies of the corresponding gene, or gene transcription is controlled by a very strong constitutive promoter. Because the reversible phosphorylation and dephosphorylation of the Cdc2 subunit in MPF (promoted by the Cdc25 and the Wee1 proteins, respectively) are a crucial point in the regulation of the fission yeast cell cycle, our mathematical model should properly describe the phenotypes of these over-producing mutants. The main goal of my work was testing the model in this respect, and to examine if there were any discrepancies between the experiments and the simulations or not. In the former case, some parameters of the model should have been changed in order to decrease these discrepancies below the level of acceptance.

PREPARATION AND CHARACTERIZATION OF CARBON GELS

Orsolya CZAKKEL

Supervisor: Krisztina László-Nagy
Department of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: klaszlo@mail.bme.hu

Resorcinol – formaldehyde (RF) hydrogels were prepared from resorcinol (R) and formaldehyde (F) under controlled conditions. After solvent exchange three kinds of drying methods are available to get solid polymer gel: (1) heat treatment under inert atmosphere (resulting RF xerogel), (2) freeze drying (resulting RF cryogel) and (3) extraction with supercritical CO_2 (resulting RF aerogel). The dried gels can be converted to solid porous carbon xero-, cryo- or aerogels when pyrolysed in inert atmosphere.

The usage of this kind of carbons at the storage and conversion of electrical energy is promising. In some new kinds of capacitors the base of energy storage is the charge separation which appears at the electric double layer, on the electrode/electrolite interface. These systems are called electric double-layer capacitors (EDLC). The higher is the surface area of the electrode (carbon), the higher amount of energy can be stored. The molecules of the electrolite cannot enter the micropores, that is why it is important to have mesoporous electrode.

My aim was to optimize the synthesis conditions. I examined the effect of the reaction circumstances. The parameter I studied was the initial pH value of the resorcinol-formaldehyde solution, which was modified with diluted HNO_3. I compared the influence of the different drying methods on the pore structure of the gel. The effect of the carbonization parameters was also investigated as well as the stability of both the RF and the carbon gels.

Scanning electron microscopy was applied to visualize the carbon gels. The pore structure and the surface area of solid RF gels and carbon gels were determined with low temperature nitrogen adsorption measurements.

After drying all previously soft RF hydrogels became hard and brittle. SEM images showed that carbon cryogel has the finest structure: uniform microspheres with a diameter of about 30 nm form a chain-like structure, and these chains build a three dimensional matrix. The RF xero- and aerogel exhibit a compact structure, the diameter of the building spheres is about 100 nm. The xero- and aerogel shrink during the drying process, while RF cryogel dries practically without shrinkage. All the RF gels are stable, the specific surface area ranges from 111 to 572 m^2/g. The freeze-dried RF gel has the highest specific surface area, total pore volume, and mean pore diameter. All these polymer gels are mesoporous.

The structures of the carbon gels are strongly determined by the structures of the precursor RF gels. After the pyrolysis the compact structure of xero- and aerogel is maintained, while the loose structure of the cryogel is changed, the chains

form two-dimensional ribbons. In all the three cases, during carbonization, the specific surface area increased drastically (730–2240 m^2/g). The main reason of this phenomenon is the formation of micropores, which is caused by self-activation and chemical vapor deposition (CVD). These micropores give the 22–61% of the total porosity. Examining the effect of the time and the temperature of the carbonization, it can be stated that changes in any of them modify the structure of the carbon gels, and affect basically the micropore region. The carbon xero- and aerogel are found to be stable in time. In contrast carbon cryogel is ageing, the specific surface area decreases with time.

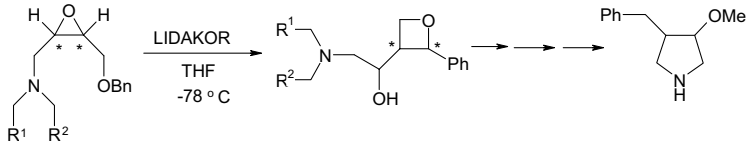
As the pore sructure and the BET surface area of the carbon gel were found to depend on the initial conditions of the synthesis and the drying and carbonizing method, carbons with high surface area and controlled pore structure can be prepared.

SYNTHESIS OF NEW OPTICALLY ACTIVE OXIRANCE, OXETANE AND PYRROLIDINE DERIVATIVES

Ferenc FARKAS

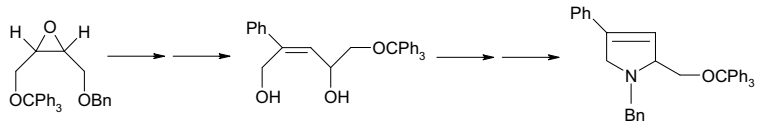
Supervisor: Angelika Thurner
Ferenc Faigl
Research Group and Department of Organic Chemical Technology
Hungarian Academy of Sciences
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: ffaigl@mail.bme.hu

Chiral oxiranes and oxetanes as well as 3,4- or 2,4-disubstituted pyrrolidine derivatives can serve as valuable intermediates of optically active drugs in pharmaceutical research. In order to get such compounds, a new enzyme-catalysed kinetic resolution of (*Z*)-2-benzyloxymethyl-3-hydroxymethyloxirane (**1**) was developed. The optically pure enantiomers (**1**) were transformed into new aminomethyl derivatives (**2**, **3**), then superbase induced stereoselective rearrangement process provided the corresponding new chiral oxetane derivatives (**4**, **5**). New, 3,4-disubstituted pyrrolidines (e.g. **6**) were prepared from oxetanes **4** and **5** in three steps.



2 R^1 = Me, R^2 = Ph **4** **6**
3 $R^1 = R^2$ = Ph **5**

Enzyme catalysed kinetic resolution of another (*Z*)-oxirane derivative **7**, followed by a two-step, superbase induced rearrangement process served the corresponding optically active *cis*-but-2-ene-1,4-diol **8**. This compound yielded the new 2,4-disubstituted dihydropyrrole derivative **9** via mesylation and consecutive reaction with benzylamine.



7 **8** **9**

STUDY OF THE BIOSYNTHESIS OF GLUTEN-FORMING POLYPEPTIDES OF WHEAT USING HPLC

Adrienn GUÓTH

Supervisor: Radomir Lásztity
Department of Biochemistry and Food Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: lasztity@mail.bme.hu

Wheat is the most highly cultivated grain crop in the world due to its unique technological properties connected with gluten. Since early research work in the 18th and 19th centuries it became clear that gluten, formed from storage proteins (monomeric gliadin and polymeric glutenin) of wheat endosperm, plays the main role in determining bread-making quality of wheat. Based on studies of correlations between gluten composition and technological quality of wheat it has been suggested that the spectrum of gluten forming polipeptides, coded on chromosomes of wheat, fully determines the quality. However, recent studies showed that in addition to polypeptide composition the interactions of polypeptides and the mechanism of polymerisation play also an important role.

The research work and its results to be presented in this paper are a part of the complex research programme connected with the aim to give deeper insight in processes mentioned above. The aims of research work were the followings: (1) adaptation and development of RP-HPLC methods suitable for separation of gliadin subunits, (2) study of the in vivo biosynthesis of gluten polypeptides during kernel development.

A wheat cultivar with known HMW-GS composition, grown on experimental field of Agricultural Research Institute of Hungarian Academy of Sciences in Martonvásár has been used. Samples were taken from 12th to 53th days after anthesis and after determination of nitrogen and moisture content lyophilized and stored at -18 °C.

A RP-HPLC method was used for separation of gliadin and glutenin polypeptides. A Perkin-Elmer LC 200 DAD HPLC chromatographic system (USA) was applied with Vydac C18 (USA) column. The results may be summarized as follows:

1. The experiments confirmed that the optimized RP-HPLC method may be successfully used for separation of polypeptides and may be also useful for variety identification.
2. The rates of biosynthesis both of total gliadin and total glutenin subunits are changing during kernel development and it seems, it may be characterized by two maxima.

Differences were observed also in the rate of synthesis and accumulation of individual gliadin components and glutenin subunits. E.g. the accumulation rate

of omega gliadin with low hydrophobicity, although it starts first after anthesis, is in later stage of kernel development much lower than that of other (alpha+beta) gliadins.

Among glutenin subunits the accumulation of LMW-subunits starts earlier and its rate is higher than that of HMW-subunits.

Concerning the sequence of start of translation it was obsereved, in accordance with some findings published by other researchers, that the synthesis of gliadin components and HMW-subunits starts earlier after anthesis than that of LMW-subunits. Among HMW subunits first the Dx-type subunit may be detected in the kernel. Later all HMW-subunits are synchronously synthetized.

Whether the LMW-subunits remain in monomeric form until HMW-subunits will be synthetized or their polymerization starts earlier, this should be clarified by further investigations.

STUDY ON THE SWELLING AND SWELLING KINETICS OF COMPOSITE POLY(DIMTEHYL-SILOXANE) NETWORKS

Tibor HAJSZ

Supervisor: Miklós Zrínyi
HAS-BUTE Laboratory of Soft Matters
e-mail: zrinyi@mail.bme.hu

Consultant: Genovéva Filipcsei
Department of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

Many useful engineering materials, as well as living organisms have a heterogeneous composition. The components of composite materials often have contradictory, but complementary properties. Fillers are usually solid additives that are incorporated into the polymer to modify the physical properties. Fillers can be divided into three categories: those that reinforce the polymer and improve its mechanical performance, those that are used to take-up space, and thus reduce material cost. The third, less common category is when filler particles are incorporated into the material to improve its responsive properties. Smart soft composites are valuable materials for several technological applications e.g. vibration control.

Composite materials consisting of rather rigid polymeric matrices filled with magnetic particles are long known and called magnetic elastomers. These materials are successfully used as permanent magnets, magnetic cores, connecting and fixing elements in many areas. These traditional magnetic elastomers have low flexibility and practically do not change their sizes, shapes and elastic properties in the presence of external magnetic field.

The new generation of magnetic elastomers represents a new type of composites, consisting of small (mainly nano and micron-sized) magnetic particles dispersed in a highly elastic polymeric matrix. The combination of polymers with magnetic materials displays novel and often enhanced properties. The magnetic particles couple the shape of the elastomer to the external magnetic fields. All of the forces acting on the particles are transmitted directly to the polymer chains resulting in either locomotion or deformation. Shape distortion occurs instantaneously and disappears abruptly when external fields are applied or removed, respectively. Combination of magnetic and elastic properties leads to a number of striking phenomena that are exhibited in response to impressed magnetic fields. Giant deformational effect, tuneable elastic modulus, non-homogeneous deformation and quick response to magnetic field open new opportunities for using such materials for various applications.

Elastic materials with tailor-made anisotropy can also be prepared under external field. The anisotropy manifests itself in both direction dependent elastic modulus and direction dependent swelling.

BIORECOGNITION WITH CHEMICALLY MODIFIED GOLD NANOTUBULES

Lajos HÖFLER

Supervisor: Róbert E. Gyurcsányi
Institute for General and Analytical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: robertgy@mail.bme.hu

The application of nanotubules for the development of chemical sensors is a new but extremely promising research area. Since the diameter of the nanotubules is comparable with the dimensions of the biological macromolecules, the selective binding of macromolecules inside of a nanotubule should result in significant changes of the ion transport through the nanotubule. Therefore, our long term goal is the development of label-free ion-channel mimetic biosensors based on nanotubules for the detection of macromolecules of biological origin, such as DNA and proteins. A selective biorecognition requires the chemical modification of the nanotubules with suitable bioprobes that will bind the analyte. The probe-analyte complex formed will change the cross section of the nanotubule and/or the electrical charge of the internal wall resulting in changes in the flux of different marker ions through the nanotubule. The proof of principle of the novel biosensing technique has been previously demonstrated by our group by using the biotin-avidin model system resulting in a detection limit of 10^{-8} M for avidin. The nanotubules were formed by template synthesis in the nanopores of track etch polycarbonate membranes. The present research work developed further the methodology by the optimization of the experimental parameters and implementing novel detection techniques. By using microcontact printing the external surface of the gold nanoporous membrane was blocked with a biocompatible thiol resulting in a very significant, four orders of magnitude improvement of the detection limit (10^{-12} M). The selectivity of the method was investigated with bovine serum albumin (BSA, 66 kDA) a protein similar in size with the avidin (68 kDa). While the specific binding of the avidin to the biotin monolayer confined to the internal surface of the nanotubules resulted in the decrease of the ion flux, the non-specifically bound BSA has been removed by the washing step implemented between incubation and detection and had no effect on the flux of the marker ions.

For maximal efficiency, in the future, the complete miniaturization of the measuring setup and its integration in a microfluidic system will be necessary. Preliminary experiments performed by using a miniaturized flow-through transport cell have already resulted in a 100 fold sensitivity increase of the ion flux determinations.

MECHANISTIC STUDY OF 1–2 HYDORGEN SHIFTS

Oldamur HOLLÓCZKI

Supervisor: László Nyulászi
Department of Inorganic Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: nyulaszi@mail.bme.hu

The 1–2 hydrogen shift from the singlet carbenes leading to the more stable double bonded isomers is a well known reaction. In the present work a computational study has been carried out to compare the reaction barriers of the monomolecular and the bimolecular processes. Despite the importance of this reaction in the previous mechanistic studies the monomolecular pathway has been explored almost exclusively. With the exception of the methyl, and silylcarbene (where the $-CH_2^-$, or $-SiH_2^-$ groups formed by the movement of the proton act stabilizing on the carbene) the monomolecular proton transfer is prohibited by a high barrier.

The bimolecular process has a low activation energy, in many cases it proceeds even without an energy gap. The reason of the stability of this transition structure is twofold, as has been shown by a Bader analysis of the electron density. When two (singlet) carbenes approach each other a hydrogen bond forms, stabilizing the dimeric structure. In the course of the reaction the proton moves off from the carbene toward the other reacting molecule. During this motion the bridging hydrogen forms a real bond with the second molecule, while the original chemical bond becomes a weak hydrogen bond. The breaking and the formation of the two bonds are a simultaneous processes, thus the energy investment needed to break one bond is compensated by the formation of the other bond. In case of the monomolecular process, however, the formation of the new bond commences only after the breaking of the first one. Although the activation entropy has a significant effect on the barriers of the bimolecular reactions (ca. 40 KJ/mol at room temperature), the activation Gibbs-free energies are low in the bimolecular process, being smaller in every case than 30 KJ/mol).

Assuming the bimolecular mechanism, previous experimental results in literature could be explained.

A MATHEMATICAL MODEL FOR THE REGULATION OF CELL DIVISION

Orsolya KAPUY

Supervisors: Béla Novák, Béla Győrffy
Molecular Network Dynamics Research Group
Budapest University of Technology and Economics and
Hungarian Academy of Sciences
H–1521 Budapest, Hungary
e-mail: kapor20@freemail.hu

Cellular behaviour is controlled by complicated molecular networks and the dynamic properties of these networks determine the physiology of cells. Self-reproduction is a fundamental characteristic of cells, and a very similar network coordinates the multiplication of simple eukaryotic cells as well as cells in multicellular organisms. Due to this similarity of controls, cell reproduction can be studied on simple eukaryotes (like yeasts) instead of complicated human cells. The regulation of cell division is best characterized in fission yeast, a rod-shaped organism which divides by synthesizing a septum in the middle of the cell. The regulatory network that is responsible for the control of cell division in fission yeast is called the septation initiation network (SIN for short).

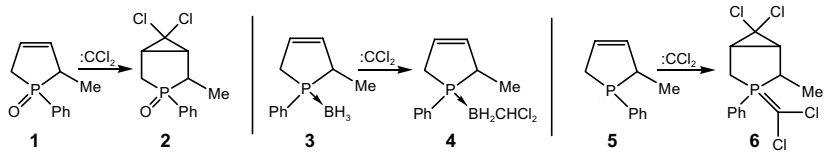
We have developed a simple mathematical model of the SIN and we have analysed this model with computer simulations. We show that the SIN behaves like an adaptive system in its response to the mitosis inducing Cdc2/Cdc13 kinase activity. The SIN is inactive both at low and at high kinase activity; it gets transiently activated only when Cdc2/Cdc13 kinase activity drops from high (mitotic) to low (G1) value. We show that this behaviour is a consequence of the dual action of Cdc2/Cdc13 kinase on the SIN pathway: it activates the upstream segment and inhibits the downstream segment of the pathway. This dual control provides a robust adaptive behaviour if the two segments of the SIN operate on a slightly different time scale. Uncontrolled septation in sin^- mutants is due to malfunction of this regulatory network.

SYNTHESIS OF P-LIGANDS UTILIZED IN VARIOUS COMPLEXES

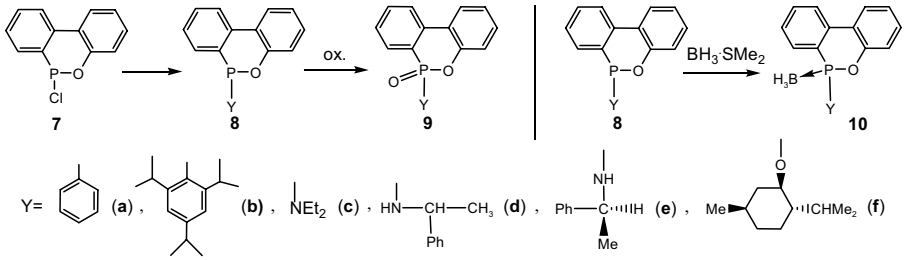
Andrea KERÉNYI

Supervisors: György Keglevich, Helga Szelke
Department of Organic Chemical Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
zsonoand@freemail.hu

The easily available 3-methyl-2,5-dihydro-1*H*-phosphole 1-oxides may serve as starting materials for 6- and 7-membered P-heterocycles. Therefore, we whished to explore how the 2-methyl-derivative (**1**) can be utilized in ring expansion and in functionalizations.



In the second part of our work we examined the substitution reactions of the chloro-dibenzooxaphosphorine (**7**). First, aryl-, diethylamino- and methylbenzylamino oxaphosphorine derivatives (**8**) were synthesized. In order to prepare optically active compounds, the chloro-oxaphosphorine was reacted with (*S*)-(-)-α-methylbenzylamine and (1*R*,2*S*,5*R*)-(-)-menthol. To get more stable derivatives, the phosphinites, phosphonamides and phosphonite (**8**) were converted to the oxides (**9**). The phosphines were also stabilized as borane complexes (**10**).



Finally, arylphosphinites (**8**) were reacted with dichlorodibenzonitrile platinum to afford two different stereoisomers (**11** and **12**). The *cis* and *trans* orientation of the ligands in the complexes is in accord with the stereospecific $J_{\mathrm{Pt-P}}$ couplings detected.

COMPARATIVE STUDY OF PARMESAN CHEESES BASED ON THEIR D- AND L-AMINO ACID CONTENTS

Katalin KISS

Supervisor: Dr. habil Livia Simon Sarkadi
Department of Biochemistry and Food Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: katalin_kiss@hotmail.com

The Parmesan cheese (Parmigiano-Reggiano) is one of the world's most popular and widely enjoyed cheeses. Parmigiano-Reggiano is intimately connected with the lands where it is produced. This brand, synonym of quality, is acknowledged only at the production that takes place in a precise geographical area, in Northern Italy.

The precise knowledge of its chemical composition has a great importance besides its role of nutritional-physiology and in addition the quality assurance aspects (the authenticity of origin).

The aim of my work was to study Parmesan cheeses originated from 3 different factories and manufactured by different technologies (traditional and ecological) based on their L-amino acid composition and their free D-glutamic acid and D-aspartic acid content. Since Parmesan cheese has a large size (width 46 cm and height 23 cm), one of its slices was divided into four parts in order to study the distribution of amino acid content in the cheeses.

Total L-amino acid content was determined after hydrolysis by 3 mol/dm^3 p-toluene sulphonic acid (containing 0.2% triptamine) using automatic amino acid analyser (Biotronik LC 3000). For determination of free L-amino acid content, cheese samples were extracted with 6% perchloric acid and analysed by amino acid analyser. The free D-amino acid content was determined by reversed phase high performance liquid chromatography (RP-HPLC) after perchloric acid extraction followed by forming diastereomeric derivatives with o-phthaldialdehyde (OPA) and 1-thio-β-D-glucose.

Concentration of total L-amino acids ranged from 221.98 mg/g to 446.25 mg/g in the cheeses. The essential amino acid content accounted for approximately 50% of the total amino acid content.

The Parmesan cheeses had a typical free amino acid profile, and the content of the free amino acids changed between 36.28 mg/g and 82.07 mg/g cheese. The most abundant free amino acids were glutamic acid, proline and lysine. Good correlation was observed between the main free amino acid concentrations and the ripening times of cheese. Among the other amino acids, the changes of arginine and ornithine were appropriate to distinguish traditional and ecological cheese-making technologies.

The amount of the free D-aspartic acid and D-glutamic acid increased during the ripening time. The D/L aspartic acid ratio seems to be a good marker in making

clear difference among the types of the Parmesan cheeses. The D/L glutamic acid ratio showed good correlation with the ripening time of Parmesan cheeses.

The results showed, that the free amino acid profile, D/L glutamic acid ratio and D/L aspartic acid ratio seem to be good parameters for the qualification of Parmesan cheeses.

COMPARATIVE STUDY OF THE ANTIOXIDATIVE EFFECT OF GLYCOSAMINOGLYCANES

Árpád KÖNCZÖL

Supervisor: György Tibor Balogh, PhD
Gedeon Richter Ltd., Technological Development Laboratory II.

Glucosaminoglycanes (GAG) (Hyaluronan; Chondroitin sulphate A, C; Heparin, etc.) are mucopolysaccharides built up of *N*-acetyl-D-glucosamine or *N*-acetyl-D-galactosamine disaccharides, characteristically. Except for hyaluronan, the saccharide chains of the other three GAGs are sulphated to various extent. GAGs are mainly present in the connective tissue of mammals (elements of the extracellular matrix) thereby taking part in an enormous number of physiological processes.

Significant portion of recent biochemical research is focused on the exploration and the potential of controlling methods (antioxidants) of processes with radical mechanism (development of immune response, inflammatory processes, lipide peroxidation, deactivation of enzymes, DNA impairments, functioning of electron transport systems) that play an extremely important role in the metabolism and the maintenance of homeostasis of biological systems. Recently, studies targeted to the role of GAGs in free radical processes, are mainly concentrated on hyaluronan, although, information on the antioxidant effect of chondroitin sulphate and heparin is also available. Despite this fact, comparative studies and studies examining the antioxidant profile of GAGs simultaneously, have not been published yet. Taking into consideration the physiological significance and the increased therapeutic application of GAGs, we found to be important to execute comparative studies.

In our experiments we tested the antioxidative effect of the four most important GAGs (Hyaluronan; Chondroitin sulphate A, C; Heparin) from physiological point of view and that of the fragments of hyaluronan with different molecular sizes against various reactive agents (hydroxyl radical, peroxynitrite radical anion and peroxyl radical) in *in vitro* modelling systems. Furthermore, we also studied the mechanism of the antioxidative effect of GAGs by following the change in the sulphate quantity liberating from radical attack in the interaction of GAGs against free radicals.

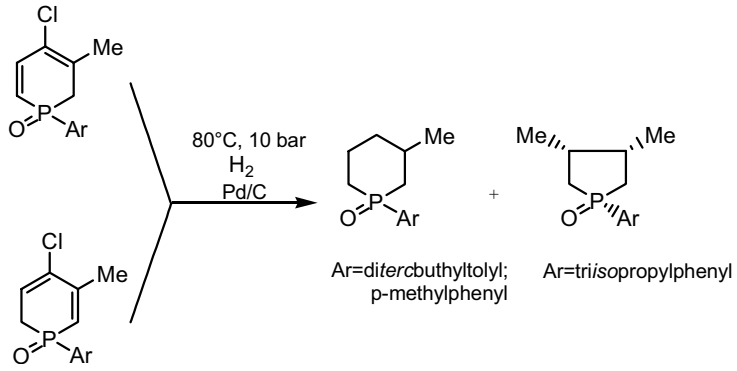
Based on our results we verified and compared the antioxidative effect of GAGs and moreover, we tried to specify the potential role of the mentioned GAGs in diseases accompanied by free radical release.

SYNTHESIS OF 1-ARYL-1,2,3,4,5,6-HEXAHYDROPHOSPHININE 1-OXIDES

Dóra Lengyel

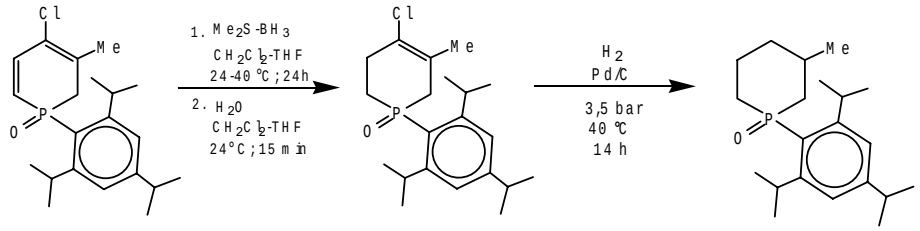
Supervisors: György Keglevich, Melinda Sipos
Department of Organic Chemical Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: lengyeldora@yahoo.co.uk

In the course of my work, new 1-aryl-1,2,3,4,5,6-hexahydrophosphinine oxides were prepared. These compounds can be used in syntheses and are of potential biological activity. The basic procedure involves catalytic hydrogenation of the corresponding 1,2-dihydrophosphinine oxides.

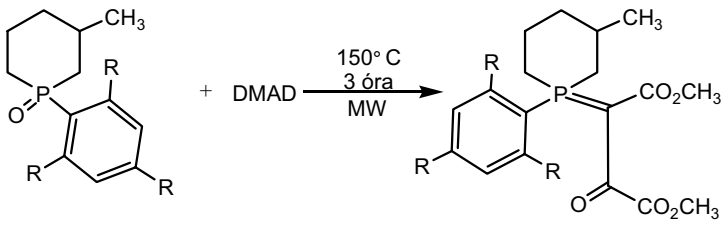


Due to a ring contraction side reaction, another route, the stepwise saturation of the double bonds of the starting dihydrophosphinine oxide was necessary for the synthesis of the 2,4,6-triisopropylphenyl derivative.

At first, the electron-poor double bond was saturated via hydroboration by dimethylsulfide-borane, then catalytic hydrogenation of tri*iso*propylphenyl-tetrahydrophosphinine oxide provided diastereomeric mixture of hexahydrophosphinine oxide.



Preexperiments of the reaction tri*iso*propylphenyl- and trimethylphenyl-hexahydrophosphinine oxides with dimethyl acethylenedicarboxilate provided the corresponding β-oxophosphoranes in an interesting and novel reaction.



R= i-Pr (**n**), Me (**o**)

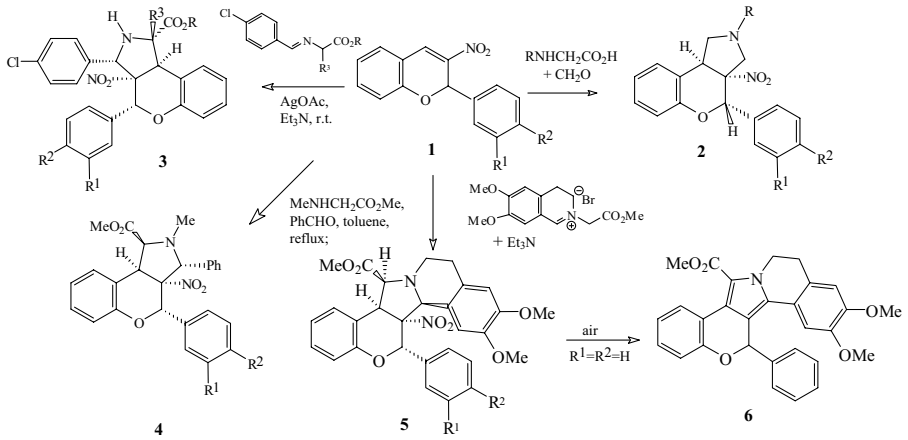
3-NITROCHROMENE DERIVATIVES AS 2π COMPONENTS IN 1,3-DIPOLAR CYCLOADDITIONS OF AZOMETHINE YLIDES

Gabriella MARTH

Supervisor: Miklós Nyerges
Department of Organic Chemical Technology
Research Group of the Hungarian Academy of Sciences
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: mnyerges@mail.bme.hu

The abundance of naturally occuring chromene and chromene derivatives and their interesting physiological properties along with the known selective dopamine D_3 receptor antagonist action of some benzopirano[3,4-*c*]-pyrrolidine derivatives suggested to study the easily available 2-aryl-3-nitrochromene derivatives (**3**) as 2π components in 1,3-dipolar cycloadditions of azomethine ylides.

The 3-nitrochromene derivatives (**1**) were prepared from the corresponding 2-aryl-nitroethylenes by the treatment with salicylaldehyde, in the presence of DABCO, without any solvent, in a single step. The 1,3-dipolar cycloaddition of these chromenes with various azomethine ylides has been investigated.



In the first set of experiments we used the most simple non-stabilized azomethine ylides which were generated from paraformaldehyde and sarcosine or *N*-benzyl-glycine using the decarboxylation method. These reactions proceed smoothly, to give the expected 3*a*-nitro-4-aryl-benzopirano[3,4-*c*]-pyrrolidines (2). The cycloaddition of **1** with the azomethine ylides derived from the imines of ethyl glycinate or phenylalanine ethylester in the presence of AgOAc and Et_3N occurred at room temperature giving cycloadducts (**3**) in 60–77% yield. The nitro-chromenes (**1**) reacted also easily with the dipole originated from methyl sarcosinate and benzaldehyde to yield the corresponding heterocycles (**4**). The cycloaddition of **1** with

the azomethine ylide derived from an isoquinolinium salt at ambient temperature with the exclusion of air gave rise to the formation of cycloadducts **5** in virtually quantitative yield as a single diastereoisomer. However, the solution of **5**, in the presence of air rapidly transformed into the pyrrole derivative **9**. The structures of all new compounds were elucidated by NMR spectroscopy using ^{1}H, ^{13}C, ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, ^{1}H-^{13}C HMQC and ^{1}H-^{1}H n.O.e. techniques.

THE POSSIBILITIES OF USING ETHANOL AS AN ALTERNATIVE FUEL IN DIFFERENT PARTS OF THE WORLD

Anna MELEG

Supervisor: Kati Réczey
Department of Agricultural Chemical Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: kati_reczey@mkt.bme.hu

Ethanol is an attractive alternative fuel which is already in use in different countries. Ethanol production for fuel purposes started due to the oil crisis in the 1970s. To reduce oil dependency is an important driving force to introduce ethanol as a fuel, but it is not the only one. To vote for use of ethanol as fuel in a given country different interests have to meet such as the interest of the agricultural sector and/or environmental considerations.

In Brazil, the country which is the greatest producer of ethanol, apart from the problems caused by the high oil prices, ethanol production also provided an outlet for sugar-cane sugar, reducing the problem caused by agricultural crisis. Due to the success of the Brazilian alcohol program (Proalkohol) the share of ethanol in the fuel market accounted for 50% in the 1980s. Although this number decreased to 30% in the last years it seems to be stabilized at this value what is far more than the average of the EU countries or the USA.

In the USA ethanol production is the interest dominantly of the corn producing farmers in the Mid-West region of the country, but it is also supported by continuously growing interests in the quality of the environment.

In the EU agricultural overproduction, set-aside fields and the EU Directive (2003/30/EC) are the main reasons motivating the introduction of fuel ethanol. In Spain and France the oil companies as stakeholders of distilleries have direct interest and also have control over ethanol production but in both countries the agricultural sector provides the main driving force for fuel ethanol production. Sweden is the only country where the use of fuel ethanol is driven mainly by environmental concerns and the future possibility of the increased use of ethanol depends on the development of the technology using lignocellulosic raw material.

Ethanol production is taking on in more and more countries (Peru, Thailand, China…) but their output is still far below that of the leading producers.

Ethanol is used in different ways such as in different blends in flexi fuel cars, as pure fuel, or as ETBE as derivative of ethanol with isobutene. Brazil is the only country where ethanol can be produced for lower price than gasoline. As the economic competitiveness with gasoline still remains an issue in most countries the use of ethanol seems to remain dependent on subsidies, tax exemption or other forms of support.

Although Hungary has unexplored capacities both for raw material cultivation and ethanol production, ethanol is not used in the transport sector at the present

conditions. In order to meet the requirements of the EU 2003/30/EC Directive the Hungarian Government set the national indicative targets to ensure the minimum proportion of biofuels in the fossil fuels. These indicative targets are far below the reference value for these targets given by the EU. A minimum use of bioethanol and biodiesel was proposed to complete these national indicative targets. It is also determined that ethanol can be used and promoted only in the form of ETBE, which decision is driven by financial interests. In order to achieve a more significant proportion of ethanol in the fuel market, collaboration of different members of the ethanol production and utilization is mandatory.

COMPLEX ANALYTICAL INVESTIGATION OF THE POLYMORPHISM OF FAMOTIDINE

Zoltán NÉMET

Supervisor: György Pokol
Department of General and Analytical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
Csaba Szántay, Jr.
Gedeon Richter Ltd

Tutors: Janisz Sztatisz
Department of General and Analytical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
Béla Hegedűs
Gedeon Richter Ltd

In the last few years the polymorphism of drug substances has become one of the focal issues of pharmaceutical research, development and quality control. This stems from various reasons. First, there is an increasing demand for the validated documentation of any polymorphic impurity in a drug substance. Secondly, polymorphism may have patenting implications involving fundamental market interests. Thirdly, the morphological composition of a substance may change during its shelf life, as well as because of the impact of the various technological processes related to production. For all these reasons it is essential to ensure an adequate analytical control of the polymorphs. This problem is rather challenging since the reliability of the various analytical tools is not *a priori* known for a given polymorphic system and the polymorph composition may be affected by sample preparation and/or the analytical measurement itself.

The target of our investigation was famotidine, a histamine H_2-receptor inhibitor produced by Gedeon Richter Ltd. which also holds a patent on the two, reproducibly preparable polymorph modifications of famotidine. The two forms exhibit a monotropic system: **A** is the thermodynamically stable form at all temperatures, while **B** is the kinetically favoured form.

Detailed characterization of the two forms is available in the literature, however, no data have been given as to the quantitative determination of mixtures of modifications. The aim of our study was therefore twofold: On the one hand we aimed at exploring the applicability (reproducibility, limit of detection, variance, potential polymorphic transition during the measurement) of the pertinent analytical methods (IR, Raman, XRPD, DSC, ssNMR) for the morphological characterization of famotidine. On the other hand we wanted to investigate whether the various effects associated with the technological procedure of production incur any change in the morphological composition. The problem became particularly interesting on

account of the fact that recently a Spanish group reported, based on DSC measurements, famotidine being vulnerable to polymorphic change under high pressure and grinding.

According to our results, grinding, pressurization and micronization does indeed appear to promote a marked **B** $\rightarrow$ **A** conversion as indicated by DSC. In contrast, however, the IR, Raman and XRPD results showed no such a transition.

We concluded that the polymorphic transformation is driven by heat in the mechanochemically activated sample during the DSC measurement. We assume that the **B** $\rightarrow$ **A** conversion proceeds via recrystallization from melt as well as solid-solid transition near the melting point.

Our results showed unambiguously that in the case of the polymorphism of famotidine the DSC method must be used only with utmost care. Statements regarding the polymorphic composition must be substantiated by the complex use of the pertinent analytical methods. These results are of substantial significance regarding the patent issues surrounding famotidine.

FEASIBILITY OF SEPARATING AZEOTROPIC MIXTURES BY CONTINUOUS HETEROGENEOUS EXTRACTIVE DISTILLATION

Katalin PAPP

Supervisors: Zoltán Lelkes, Endre Rév
Department of Chemical Engineering
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: lelkes@mail.bme.hu, ufo@sunny.vemt.bme.hu

Azeotropic distillation can be applied even if the newly formed heterogeneous azeotrope is not the lightest point of the system. Heterogeneous extractive distillation, as a novel separation process (see *Fig. 1*), is studied.

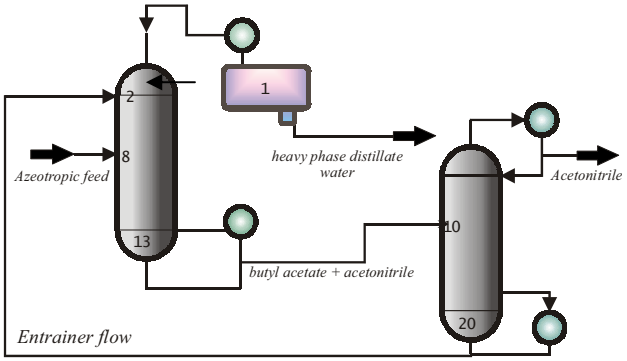


Fig. 1. The scheme of the Heterogeneous Extractive Distillation

These opportunities are demonstrated on the atmospheric system of acetonitril, water, and butyl acetate, the latter being the entrainer. Systematic methodology and criteria are developed for deciding on the feasibility of applying one, two, or three different (stripping, extractive, and rectifying) column sections in the new type of process. The process is feasible if one of the following criteria is satisfied:

Criterion 1: The stripping profile intersects the tie line of x_D.
Criterion 2: The rectifying and stripping profiles intersect.
Criterion 3: The extractive profile, started from a point of the stripping profile, intersects the tie line of x_D.
Criterion 4: The extractive profile connects the rectifying and the stripping profiles.

The process is attributed with both minimum and maximum reflux ratios. There is a critical reflux ratio below which the two-section variant is infeasible. Feeding the entrainer to the top, and thus applying an extractive and a stripping

section only, is feasible above this critical reflux ratio. Feeding the entrainer of the heterogeneous azeotropic process to a lower point of the main column, i.e. applying heterogeneous extractive distillation with three different column sections, is feasible both below and above this critical value.

The V/L, L/L, and V/L/L equilibria were described with the NRTL model, and were calculated using the BibPhyAddIn thermodynamic property server available as a Microsoft Excel macro. The feasibility method applies the usual simplifications, whereas the designed processes are rigorously computed with the commercially available steady state simulator Prosim Plus.

EXAMINATION OF THE GENETIC BACKGROUND OF EPIDERMOLYSIS BULLOSA SIMPLEX

Ráchel SAJÓ

Supervisors: Sarolta Kárpáti, Márta Csikós, Annamária Bóna
Department of Dermatology
Semmelweis University of Budapest

Ákos Sveiczer
Department of Agricultural Chemistry Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: rachelsajo@hotmail.com

BACKGROUND: Epidermolysis bullosa simplex (EBS) is an inherited skin disease characterized by skin and mucous membrane blistering upon mild mechanical trauma. The mutations of the keratin 5 (*KRT5*) and keratin 14 (*KRT14*) genes, responsible for the disease, were examined. The aim of the study was to identify the mutations in order to explore the genotype-phenotype correlation in detail, and to add new data to the mutation database.

METHODS: At first, DNA was isolated from the peripheral blood of the patients and their relatives. Then all the exons of the *KRT5* gene were amplified with polymerase chain reaction (PCR), and the products were examined with heteroduplex analysis in conformation sensitive gel (CSGE-HD). After purification, the sequences of the shift positive exons were determined by automatic sequencing. Mutations were verified with restriction endonucleases. Detecting mutations in *KRT14* was hampered by the presence of a highly homologous pseudogene. Because of their similarities, the pseudogene would also be amplified by PCR. After cleaving the *KRT14* pseudogene with restriction enzymes, while leaving the functional gene intact, only exons of the functional *KRT14* gene were amplified. After digesting its pseudogene, *KRT14* was treated in the same way as *KRT5*.

RESULTS: From the 11 examined patients with EBS symptoms, in three cases we identified the mutations, which were responsible for the disease. Two of them were novel, unpublished mutations (L136Q in *KRT14*, and R331G in *KRT5*), while the third change was shown in the case of a Japanese family (E170K in *KRT5*). Examination of other patients are under way.

SPECTROSCOPIC STUDY OF POTENTIAL PHOTOSENSITIZERS FOR PHOTODYNAMIC THERAPY

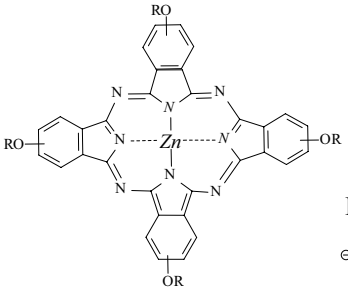
Klára SZEGLETES

Supervisors: András Grofcsik, Péter Baranyai, Tamás Vidóczy
Department of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: agrofcsik@mail.bme.hu, pbaranyai@mail.bme.hu,
tvid@chemres.hu

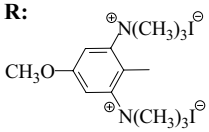
Photodynamic therapy (PDT) is a cancer treatment involving systemic administration of a tumour-localizing photosensitizer. This, when activated by the appropriate wavelength of light, interacts with molecular oxygen to form a toxic, short-lived species known as singlet oxygen, which is thought to mediate cellular death resulting in tumour eradication.

The first and still frequently used photosensitizer is a hematoporphyrin derivative (HpD), which has, however, several drawbacks. The most frequently studied classes of compounds are porphyrins, chlorins, bacteriochlorins, phthalocyanines (Pcs) and porphycenes.

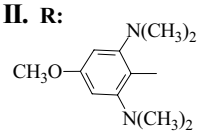
The aim of the present work was to study the photophysical parameters of some Pc derivatives (I–IV).



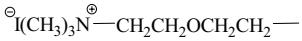
I. **R:**



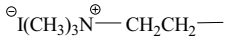
II. **R:**



III. **R:**



IV. **R:**



All of them are Zn-complexes and three are water-soluble cationic Pcs, which are expected to exhibit decreased aggregation in solution, and the possibility of photodynamic inactivation of certain cells.

For comparison the unsubstituted Zn(II)Pc was used.

The result of the measurements shows that the photophysical properties of compounds **I–II** fulfil the photophysical requirements for a photosensitizer in PDT. They have strong absorption around 680 nm, triplet lifetimes are around 300 μs in the absence of air and well below 1 μs in air saturated solutions, the quantum yields of singlet oxygen formation are higher than 0.5. On the other hand we were unable to prove triplet formation upon exciting **III** and **IV**. This is probably due to significant aggregation.

SYNTHESIS OF NEW, REACTIVE FLAME RETARDANT EPOXY RESIN

Nikoletta TÓTH

Supervisors: Andrea Toldy, György Marosi
Department of Organic Chemical Technology
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

The increased attention to safety requirements has accelerated the investigation of flame retardant plastics. In our days the use of halogenated flame retardants is still widespread but the halogen-free flame retardants (e.g. phosphorus-containing ones) are likely to take the lead as according to the latest legislation of the European Union the bromine-containing flame retardant additives are going to be banned from July 2006.

Epoxy resins are widely used (e.g. electronic and electrotechnical applications) due to their excellent properties, but the flammability of the organic matrix is a major limitation in areas requiring high flame resistance; hence their flame retardance is very important.

Our aim was to develop a simple and cost-effective preparation method for synthesizing phosphorus-containing amines which can be used both as crosslinking agent in epoxy resins and as flame retardant.

According to the thermal behaviour of the synthesized phosphorus-containing amines, it can be concluded, that their decomposition is endothermic, what is advantageous in the aspect of flame retardancy, just as the significant charring. Their further advantage is that they do not increase the viscosity of the epoxy resin.

The synthesized compounds were incorporated into epoxy resins. The enthalpy of the curing followed by DCS confirmed that they can replace the traditional curing agents. Furthermore, they perform an excellent flame retardant effect evaluated by LOI, UL-94 and Cone Calorimeter measurements.

The use of the synthesized new, reactive flame resistant epoxy resins in the electronic industry will contribute to the development of safer computers and other electronic equipment.

HYBRID PROCESSES BASED ON PERVAPORATION

Edit VALENTINYI

Supervisors: Péter Mizsey, Katalin Koczka
Department of Chemical Engineering
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

Hybrid separation systems based on pervaporation (PV) separating ethanol – water mixture are studied and compared. The following structures are studied:

1. Pervaporation with a subsequent distillation of the permeate and the distillate containing ethanol is fed back in to the feed stream of the PV. The retentate has the prescribed ethanol concentration (PV + D structure).
2. The feed is concentrated with distillation close to the azeotropic point. The distillate is processed in pervaporation unit until the prescribed purity is arrived (D + PV structure).
3. The feed is concentrated with distillation close to the azeotropic point. The distillate is processed in pervaporation over the azeotropic composition. The retentate of the pervaporation unit is distilled in an ordinary distillation column until the prescribed purity is achieved in the bottom (D + PV + D structure).

The aim is to determine the most economical hybrid separation structure on the total annual cost basis (TAC). The simulations are carried out with ChemCad flowsheeting software. According to the results the most favourable hybrid method is the D + PV structure but only if the pervaporation modules are in series. The same efficiency is achieved if the membranes are in parallel (same total surface) but the capital cost of the parallel membrane case is higher than that of the series membrane case because of the smaller membrane modules. In each case the capital cost of the membrane units is the main part of the total cost.

To process the feed first in pervaporation did not prove to be the best solution (PV + D) because the distillation as first separation method guaranteed a more economic solution.

The TAC of the D + PV + D structure is not too high compared to the others (PV + D and D + PV). This construction could be more effective in the case if pure ethanol is to be produced since the selectivity of the membrane is getting worth at too high alcohol concentration (higher than 99.5–99.8).

EFFECT OF COPPER IONS ON STRUCTURE OF LIPOSOMES

Zoltán VARGA

Supervisor: Attila Bóta
Department of Physical Chemistry
Budapest University of Technology and Economics
H–1521 Budapest, Hungary

In investigations of the effect of different chemical substances on biological membranes, the real systems are very complex, therefore liposomes (with other word: vesicles) are used as model systems. The liposomes can mimic the main features of the biological membranes because the characteristic double lipid layer is the same in both real and model systems. Phospholipids are the most frequent lipid components of the biological membranes, therefore these molecules are generally used to prepare liposomes. By dispersing phospholipids in water, multilamellar liposomes are formed with a concentric arrangement of alternating water and double-layered lipid shells. If a third, foreign molecule is added to the liposomes, their characteristic structure can be perturbed slightly or drastically depending on the concentration of the guest molecules.

In my work the features of the location of copper(II) ions dispersed in the dipalmitoylphosphatidylcholine (DPPC)-water liposomes were studied. The copper ions were added to the system in the form of $Cu(CH_3COO)_2$ in the small molar ratio regime (DPPC : Cu = 100 : 1). The copper(II)-acetate is a representative of the salts of toxic metal ions present in the environment and also in organisms. Generally, the salts of divalent metal ions cause drastic destruction in the regular layer arrangements of the liposomes, as is concluded from the small-angle X-ray and neutron scattering of these systems [1].

Small-angle and anomalous small-angle X-ray scattering (SAXS, ASAXS) measurements were carried out at the JUSIFA (B1) beamline at HASYLAB (DESY, Hamburg) in the regime of the scattering variable ($h = (4\pi/\lambda)\sin\Theta$) from 0.006 up to 0.5 1/Å) [2]. The selected energies were 8496 and 8975 eV, i.e. close to the K edge of the copper (8979 eV, measured by the absorption of both copper and copper-acetate). The measured scattering curves were also calculated by computer simulations involving Monte-Carlo method. During the calculations the main structural features of the layer structure and the subcell of the chain packing were varied to obtain the values of the characteristic parameters of the features considered.

Detecting the scattering curves at two energies of the X-ray, two anomalous scattering curves (ASAXS) can be obtained which exhibit great similarity, but the closer inspection shows that their shapes depend on the energy. Exactly, this difference provides information about the displacement of the copper ions. The copper ions are mainly located in large domains between the lamellae and only partly in the characteristic periodic water shells of the liposomes. The effects of the copper ions on the subcells were also investigated and the change of the WAXS profiles of the doped system was reconstructed by using model calculation. A correlation was

revealed between the size of the lateral domains in the lipid layer and the FWHM of the wide angle scattering peaks.

Consequently, the knowledge of the location of guest molecules in liposomes is of great importance in investigating their effect on biological membranes.

References

[1] HERBETTE, L. – NAPOLITANO, C. A. – MCDANIEL, R. V., *Biophys. J.*, **46** (1984), pp. 677–685.

[2] GOERIGK, G. – SCHWEINS, R. – HUBER, K. – BALLAUFF, M., *Europhys. Lett.*, **66** (2004), pp. 331–337.

SELECTIVE EXTRACTION OF St. JOHN'S WORT (HYPERICUM PERFORATUM L.)

Tünde VATAI

Supervisors: Béla Simándi, Erika Vági
Department of Chemical Engineering
Budapest University of Technology and Economics
H–1521 Budapest, Hungary
e-mail: tvatai@freestart.hu

St. John's Wort (SJW) has been used for various ailments since the Greeks (ca.400B.C.E). Paracelsus (ca.1540 C.E.) used it to treat mental disorders. The latter decade renewed the interest for St. John's Wort. Clinical researches documented its safety and efficacy for treating mild to moderate depression. The SJW medications are standardized to hypericin, hyperforin or both. Hyperforin cannot be extracted by conventional extraction. The two main components can be found in the same parts of the plant, but their accumulation is different. The hypericin level is the highest in the early bloom, the hyperforin accumulates in the later bloom. During my work 3 different plant samples were examined. Samle **1** was collected in the early bloom, sample **3** later. The sample **2** contained pithy parts , where less hypericin and hyperforin can be found. Soxhlet-extraction with four different polarity solvents (ethanol 96%, isopropanol, ethyl-acetate, *n*-hexane) was carried out. Pilot scale Soxhlet-extraction was done with ethanol (96%) solvent. Supercritical extraction was studied using carbon dioxide. Supercritical fluid extraction was demonstrated on a simple mathematical modell. The hyperforin and hypericin contents of the extracts were detected by thin layer chromatography. The quantity analysis was done at the Szeged University of Science. One of the main active agents, hypericin, was found to concentrate in polar solvents. The most effective extraction of hyperforin was achieved by using supercritical carbon dioxide. The selective extraction of the two main agents can be achieved. The hypericin concentration is the highest in extracts made by ethanol from a drug collected in the early bloom. The hyperforin most effective extraction can be achieved by using supercritical carbon dioxide, from a drug which is collected in later bloom. The extracts are stable on prolonged storage.

My further goal is preparing standardized preparations of St. John's Wort for both active components. According to the latest researches the flavonoid content of SJW is also important. I find it interesting to work out an extraction method for flavonoids.