

FIRST CONFERENCE OF PHD STUDENTS AT FACULTY OF CHEMICAL ENGINEERING

November 26, 2003

KINETICS OF DELAMINATION IN PP NANOCOMPOSITES

Ágnes ÁBRÁNYI, László SZÁZDI and Béla PUKÁNSZKY

Department of Plastics and Rubber Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary
and
Institute of Chemistry
Chemical Research Center
Hungarian Academy of Sciences
H-1525 Budapest, P.O. Box 17.

e-mail address: Lszazdi@mail.bme.hu

Supervisor: Béla Pukánszky

The development of nanocomposites induced much interest recently and it might evolve into one of the latest evolutionary steps of polymer technology. This new class of materials appears to offer attractive potentials for the diversification and new applications of conventional polymeric materials [1]–[3]. Nanocomposites can be prepared by various routes, the exfoliation of layered silicates during processing has become a quite efficient technology for the preparation of polyolefin-based nanocomposites [4]. The homogeneously dispersed thin clay layers are claimed to increase stiffness and strength considerably already at very low filler contents.

In this study, we prepared nanocomposites using several polypropylene matrix materials with various MFI values and an organophilized montmorillonite treated with stearyl-amine. The kinetics of exfoliation was followed by series of measurements. The time of homogenization and shear rate applied was varied in a wide range. The change in the gallery structure of the montmorillonite was followed by wide angle X-ray scattering and the mechanical properties of the composites were also measured. For some matrices the distance of the galleries depends on the time of homogenization, while it remains constant for others. We found that the degradation of the matrix polymer influenced the extent of the delamination. Contrary to expectations, the shear stress does not influence the extent of exfoliation, the intensity of the WAXS scattering peak characteristic for MMT is inversely proportional to torque (*Fig. 1*). The fact that larger shear stress is accompanied by less exfoliation needs further study and explanation.

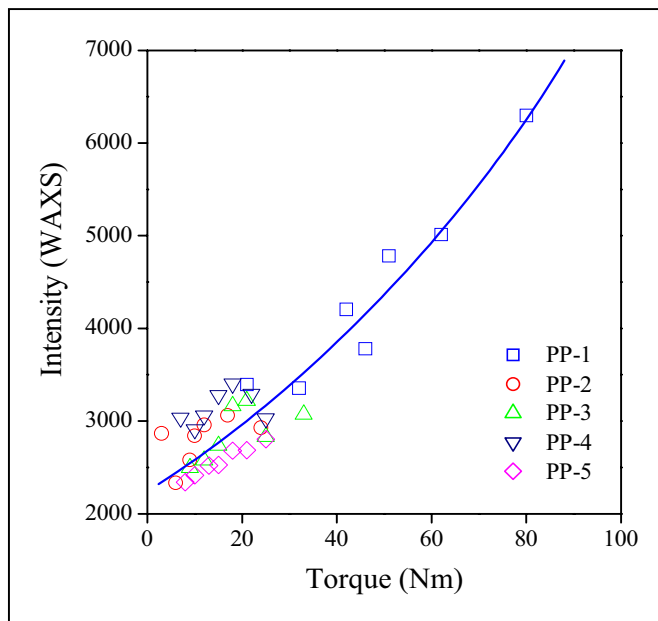


Fig. 1. Effect of shear stress on the extent of exfoliation for various PP polymers during mixing

References

- [1] ÁBRÁNYI, Á. – SZÁZDI, L. – PUKÁNSZKY, B., Delamináció kinetikája polipropilén nanokompozitokban, *Műanyag és Gumi*, (in press).
- [2] POZSGAY, A. – CSAPÓ, I. – SZÁZDI, L. – PUKÁNSZKY, B., Preparation, Structure, and Properties of PVC/Montmorillonite Nanocomposites, *Materials Research Innovations* (in press).
- [3] POZSGAY, A. – FRÁTER, T. – SZÁZDI, L. – MÜLLER, P. – SAJÓ, I. – PUKÁNSZKY, B., Gallery Structure and Exfoliation of Organophilized Montmorillonite; Effect on Composite Properties, *European Polymer Journal* (in press).

COMPUTER SIMULATION OF PREPARATION OF NANOSTRUCTURED THIN LAYERS BY WET COLLOID CHEMICAL METHOD

Attila AGOD

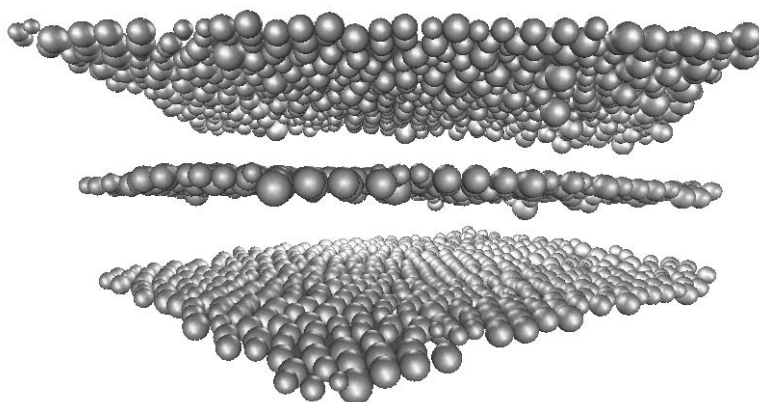
Department of Physical Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: aagod@mail.bme.hu

Supervisor: Zoltán Hórvölgyi

By forming the structure of a thin layer on the nanometer scale, we can manipulate its macroscopic properties to our advantage. The electrical, magnetic, optical or heat-insulating features of the layer are affected not only by the individual properties of the particles but also by their position within the layer.

The wet colloid chemical approaches to form nanostructured thin layers is highly favoured as it is cheaper than the rival technologies and enables the production of multilayers and sandwich structures. A molecular dynamics computer simulation of structure formation of nanoparticles at a liquid-fluid interface will be presented in the lecture. Existing and prospective applications will also be demonstrated.



Structure of Stöber silica system at water-air interface (simulation result)

The simulation is primarily used to interpret the results of film balance experiments [1]. However, it can also be applied to investigate the structure dependent optical properties of the thin layer. The compression of Stöber silica nanoparticles at water-air interface has been the subject of an intensive experimental study. The character of the interactions between particles and the effective refractive index of the layer can be determined from the measured surface pressure–area isotherms on

the basis of simplified model assumptions (e.g. monodisperse system, hexagonal ordering). The simulation can be used to assess the systematic errors associated with these assumptions and thus to introduce corrections [2]. A new method will be proposed to characterise the wettability of nanoparticles. Finally, a possible collapse mechanism of the layer will be discussed.

References

- [1] TOLNAI, GY. – AGOD, A. KABAI-FAIX, M. – KOVÁCS, A. L. – RAMSDEN, J. J. – HÓRVÖLGYI, Z., Evidence for Secondary Minimum Flocculation of Stöber Silica Nanoparticles at the Air-Water Interface: Film Balance Investigations and Computer Simulations, *J. Phys. Chem. B*, **107** (2003), pp. 11109–11116.
- [2] AGOD, A. – TOLNAI, GY. – ESMAIL, N. – HÓRVÖLGYI, Z., Compression of Nanoparticulate Arrays in a Film Balance: Computer Simulations, (Accepted, *Progress in Colloid & Polymer Sci.*).

AROMATIC COMPLEXES – COMPLEX AROMATICITY?

István Péter BAKK

Department of Inorganic Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisor: László Nyulászi

Aromaticity is still an important and widely used concept in chemistry. Originally, it has been used to describe the specific chemical behaviour of benzenelike compounds. Nowadays the presence or the lack of aromaticity is widely used to explain and predict the chemical behaviour of unsaturated rings. The concept is extendable to saturated rings, cage compounds and even transition structures. To quantify the classical qualitative concept of aromaticity, several methods have been and are being worked out. The investigated criteria are generally based on physically determinable properties like the geometric (i.e. bond equalisation), energetic (special stability relative to the nonaromatic reference), or magnetic measures (i.e. shielded $^1\text{H-NMR}$ signals). While the consequences of the aromaticity on certain physically measurable or computable properties were extensively discussed, the quantification of the ‘specific’ reactivity, however, has not been attempted.

Complexation with metals is a special reaction of aromatic compounds, which resulted in remarkable systems such as ferrocene or dibenzenechromium. These compounds are now textbook examples and other aromatic systems are known to bond metals and even non-metals in a similar way. This complexation mode is often attributed to the specific aromatic electronic structure.

In my work, investigating the complexation reaction of aromatic compounds, I was trying to answer to the following questions:

- Can the formation of metal complexes qualitatively be related to the extent of aromaticity?
- Does the complexation change the aromaticity of the parent molecule?

To answer these questions I have investigated a set of five and six membered heterocycles, that are known to represent a large variety in aromatic measures, and complex metals including Li^+ and d-elements η^5 - and η^6 -, respectively. The investigations were carried out by quantum-chemical methods.

In order to get a view of the extent of the aromaticity of the used compounds, I have determined and compared the values of the most commonly used and accepted measures trying to cover most criteria. In the case of five- membered heterocycles good correlations were found. Some of the measures were capable to measure, how much the complexation changes the aromaticity of the rings. These measures have shown both in the case of five- or six- membered heterocycles, that the complexation does not affect the aromaticity of the ligand. This result proposes a possibility to

experimentally determine the aromaticity of the ligands by using the data from Li-NMR.

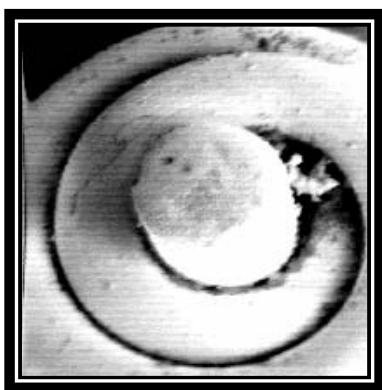
Comparing the complex formation energies with the values of aromatic measures shows that the formation of the complex is determined by multiple factors, and aromaticity has a small contribution only. Since Li^+ is a pure electron acceptor in the complex formation, the stability of the complex is determined by the electron donating ability of the heterocycles. The largest contribution comes from HOMO and HOMO-1, since these two π orbitals are at much higher energies than the rest of the MO-s. Thus, we have considered the sum of these orbital energies and found good correlation with the complexation energy for different heterocycles.

RESEARCH OF ELECTRON EMISSION PROPERTIES OF TUNGSTEN CATHODES

Ildikó BECK

Department of Atomic Physics
Surface Physics Laboratory
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisors: Katalin Josepovits Vargáné
János Sneider



For light fitting manufacturers the most important goals are to satisfy all consumer requirements and the increasing expectations of environmental protection. For this reason they develop energy-saving and environment-friendly light sources. My field of research is the investigation of the electron emission properties of high pressure sodium lamps that were manufactured by GE Hungary Inc. Tungfram Lighting. These lamps are used as outdoor lights.

Inside lamps arc discharge is initiated between two tungsten electrodes. For this discharge the atoms in the closed gas space must be ionized, which produces free charge carriers. In this process electrons emitted by the tungsten electrodes have leading role [1]. Electrons leave the tip of the electrodes at high temperature by thermic electron emission. The higher is the electron emission, the lower is the work function of the metal. The light flux of lamps can be increased by optimal planning of a low work function and maintaining its value during the entire operation time. This way longer life expectancy and high light flux can be ensured for a long period [2].

In order to achieve lower work function the surface of cathodes are covered with emission material. During the lamp operation Ba as a main component of emission material diffuses to the tip of cathode to lower the work function of electrons compared to the tungsten surface.

To have more knowledge about lamp operation it is necessary to determine the critical temperature of Ba diffusion and how it is able to lower the work function.

To achieve the above parameters we investigated model samples and the surface of the cathodes by surface analytical methods as X-ray Photoelectron Spectroscopy and Auger Electron Spectroscopy and Work Function Spectroscopy as well. During the investigation we obtained information about the lateral distribution of chemical elements and local work function.

Our measurements contribute to the discovery of all electron emission processes during operation of the lamps.

References

- [1] DEBRECZENI, G. – KARDOS, F. – SINKA, J., *Fényforrások*, Műszaki Könyvkiadó, Budapest 1985, pp. 10–30.
- [2] DE BOER, J. H., *Electron Emission and Adsorption Phenomena*, Cambridge University Press, London 1935, pp. 353–358.

INVESTIGATION OF BIOCATALYSTS AND BIOCATALYTIC PROCESSES AND THEIR SYNTHETIC APPLICATIONS

Viktória BÓDAI

Institute for Organic Chemistry
and
Department of Agricultural Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

The primary aim of my research was to investigate the enzyme production of thermophilic filamentous fungi strains and to study the lipase/carboxylesterase activities applied effectively as a general biocatalyst in organic synthesis practice. Investigation of these enzyme products in common and novel biocatalytic processes was also a part of my research work.

45 thermophilic filamentous fungi (18 are not identified yet) were cultivated in shaken flasks in two different media, and the supernatants were assayed for lipase/carboxylesterase activities using olive-oil, *p*-nitrophenyl palmitate and *p*-nitrophenyl butyrate as substrates. The 90 crude enzyme powders (acetone precipitated supernatants) were tested as biocatalysts in organic solvents.

Although hydrolases (lipases/esterases) were detected in numerous thermophilic fungi strains, only a few have been evaluated as synthetic biocatalyst yet. Therefore, we thought worthwhile to characterize the biocatalytic abilities of enzymes from thermophilic fungi by two typical enantioselective processes. Both enantiomers (2-acyloxy-1,3-propanediols) and enantiotopic selectivity (1-phenylethanol, glycerine-carbonate, *trans*-cycloalkane-1,2-diol monoacetates, 1-(benzofuran-2-yl) ethanols, 1-(benzotiazol-2-yl)-ethanol) were assayed by desymmetrization by enzymatic acetylation with vinyl acetate.

The tested biocatalysts proved to be comparable to the commercially available enzymes with respect to the degree of enantiomer selectivity, whereas they exhibited a wider range of enantiotopic selectivity than the most common commercial enzymes.

According to the initial goals several biocatalysts have been produced for general application. Among the enzyme preparations investigated in organic synthetic reactions a number of biocatalysts have been found, which catalyze processes at a rate and with a selectivity similar to that of commercially available enzymes. In a few cases, the other enantiomer product was successfully recovered by use of our enzyme preparations. The most significant of our results was the production of an enzyme preparation (BUTE-3b), which catalyzed the processes with even greater selectivity than the commercially available enzymes. The submission of the patent engaged in this enzyme preparation is being considered.

References

- [1] BÓDAI, V. – PEREDI, R. – BÁLINT, J. – EGRI, G. – NOVÁK, L. – SZAKÁCS, GY. – POPPE, L., *Adv. Synth. Catal.*, **345** No. 6–7 (2003), pp. 811–818.
- [2] BÓDAI, V. – NOVÁK, L. – POPPE, L., *SynLett*, (1999), pp. 759–761.
- [3] BÓDAI, V. – OROVECZ, O. – SZAKÁCS, GY. – NOVÁK, L. – POPPE, L., *Tetrahedron: Asymmetry*, **14** (2003), pp. 2605–2612.
- [4] PAIZS, CS. – TOŠA, M. – MAJDIK, C. – BÓDAI, V. – NOVÁK, L. – IRIMIE, F.-D. – POPPE, L., *J. Chem. Soc., Perkin 1*, **21** (2002), pp. 2400–2402.
- [5] PAIZS, CS. – TOŠA, M. – BÓDAI, V. – SZAKÁCS, GY. – KMECZ, I. – SIMÁNDI, B. – MAJDIK, C. – NOVÁK, L. – IRIMIE, F. D. – POPPE, L., *Tetrahedron: Asymmetry*, **14** (2003), pp. 1943–1949.

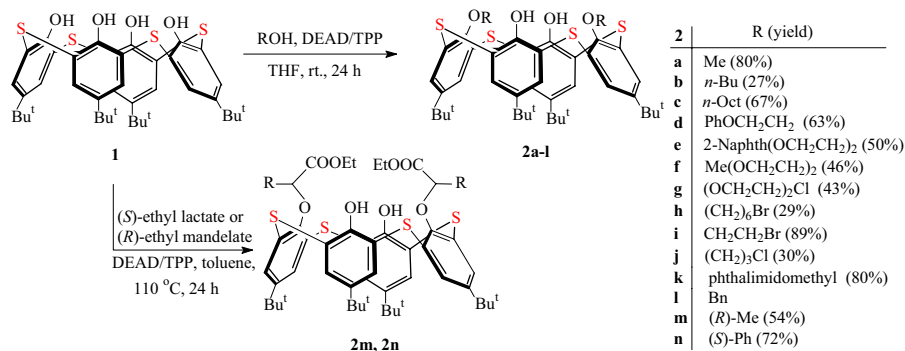
SELECTIVE REACTIONS OF THICALIX[4]ARENES

Viktor CSOKAI

Department of Organic Chemical Technology
 Budapest University of Technology and Economics
 H-1521 Budapest, Hungary

e-mail address: vcsokai@mail.bme.hu

Supervisor: István Bitter



The large number of calixarene derivatives is partly ascribed to the regio- and conformation selective reactions developed during the last decades. Similar regioselective reactions, at least with the same efficiency, have not been found in thiacalixarene chemistry. The lack of regio and stereoselectivity in the weak base mediated partial *O*-alkylation and acylation reactions of thiacalix[4]arenes can be attributed to the substantially reduced differences between the OH acidities and the 15 % larger cavity as compared with the calixarene counterpart. We have studied the cycloalkylations of thiacalixarenes in order to collect further data on the reaction and to obtain novel receptor molecules. As the cyclization of thiacalixarenes with tetra- and pentaethylene glycol derivatives could not be stopped at intermediate stage affording monocrowns in an efficient way, we have attempted to synthesize otherwise these new receptors. To overcome the problems arising in the base mediated alkylations, the Mitsunobu reaction appeared to be an attractive alternative to *O*-alkylation. This reaction has been unprecedented in thiacalixarene chemistry. The alkylation of phenols with alcohols effected by the triphenylphosphine/diethyl azodicarboxylate system is well-documented in the literature. The reaction was performed with a series of primary alcohols using TPP/DEAD in THF at room temperature and the clean formation of 1,3-dialkoxythiacalix[4]arenes was achieved. Under these conditions

the reaction generally stops at disubstitution and the tri- or tetraalkoxy products could not be isolated. These successes of the selective alkylations of thiacalixarene with Mitsunobu reaction prompted us to explore the possibility of intramolecular ring closure between thiacalix[4]arenes and oligoethylene glycols under these conditions. The reactions were performed in toluene with *p-tert*-butylthiacalix[4]arene using commercial di-, tri- and tetraethylene glycols, aza and benzo analogues. The short chained diethylene glycol under this condition gave an intermolecular coupling product of dimer structure. This compound is the first representative of a koiland-type multicavity receptor in the thiacalixarene series where two thiacalix units are connected by glycol chains. In conclusion, we have demonstrated for the first time the selective *O*-alkylation of *p-tert*-butylthiacalix[4]arene with a series of alcohols under the Mitsunobu protocol, thus opening a simple access to intermediates containing reactive functional groups which are not available by other methods.

LIQUID AMMONIA TREATMENT OF LINEN FABRICS

Barbara DORNYI and Emília CSISZÁR

Department of Plastics and Rubber Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary
e-mail:ecsiszar@mail.bme.hu

Liquid ammonia treatment induces intracrystalline swelling of cellulose and it is very effective in enhancing certain end-use properties, such as dimensional stability, tensile strength, resistance to abrasion, crease recovery, as well as handle and appearance. Liquid ammonia treatment has also considerable influence on the rate and degree of conversion of the subsequent heterogeneous cellulose reactions. Although a number of shorter studies and comprehensive reviews have been published regarding the swelling with liquid ammonia, most of them concentrated on cotton and only a very few publications focused on liquid ammonia treatment of linen and linen-containing fabrics. Our starting assumption is that liquid ammonia treatment could be an appropriate technology for manufacturing of linen and linen containing woven fabrics with excellent easy-care and wearing properties, as well as for producing of high quality and luxurious tablecloths and apparel textiles from linen.

The objective of this research work is to evaluate the influence of liquid ammonia treatment on the properties of linen and linen/cotton fabrics. The presentation concentrates on the mechanical properties of the fabrics, such as dimensional stability, appearance after washing, wrinkle recovery angle (WRA), breaking load and elongation, abrasion resistance, air permeability, drapeability and stiffness, resulting from swelling in liquid ammonia. Effects of liquid ammonia treatment on colour and fine structure of the substrates are also discussed.

References

- [1] CSISZÁR, E. – DORNYI, B. – SOMLAI, P. – BORS, A., Cellulóz alapú szálanyagok folyékony ammóniás kezelése. A folyékony ammóniás kezelés megvalósítása, *Magyar Textiltechnika*, **LV(3)** (2002), pp. 85–87.
- [2] CSISZÁR, E. – SOMLAI, P. – DORNYI, B., Lenszövetek folyékony ammóniás kezelése, IN-TECH-ED '02 Műszaki fejlesztés és oktatás a textil- és ruházati iparban, *TMTE 2002*, (2002), pp. 138–142.
- [3] CSISZÁR, E. – DORNYI, B. – SOMLAI, P. – BORS, A., Cellulóz alapú szálanyagok folyékony ammóniás kezelése. A folyékony ammóniás kezelés hatása a cellulóz szerkezetére, *Magyar Textiltechnika*, elfogadva.

PREPARATION OF NOVEL INDOLE DERIVATIVES BY SUZUKI-REACTION

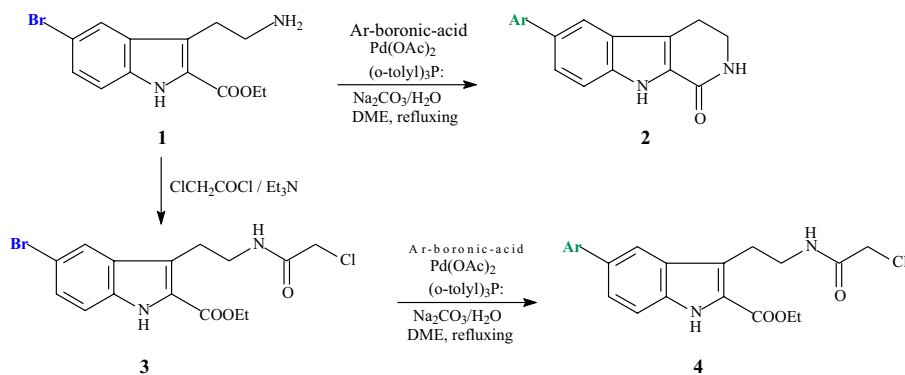
Melinda FEKETE and Lajos NOVÁK

Institute for Organic Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: kain@mail.bme.hu

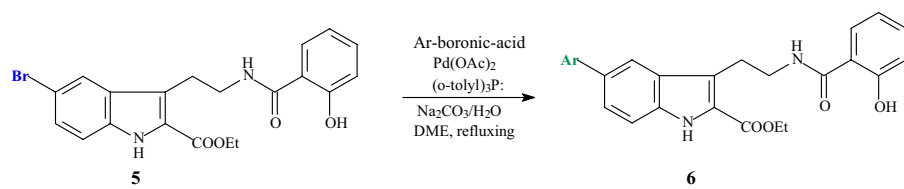
The indole skeleton is a common feature of many drugs. Some of them have effect on the serotonin receptors. Since the serotonin is the mediator of both periferial and central nervous systems, its receptors are new targets in the development of drug design against migrain, depression and schizophrenia.

The aim of our research is to elaborate novel indole derivatives affecting the serotonin nervous system. Namely, with the modification of position 5 in the compounds **1**, **4**, and **5**. We try to introduce new ring in positions 4 and/or 2 with the acylation of these compounds followed by ring closure.



Ar =

phenyl
4-methylphenyl
4-phenoxyphenyl
3,5-bis(trifluoromethyl)phenyl



Ar =

3,5-difluorophenyl
3,5-bis(trifluoromethyl)phenyl

References

- [1] FEKETE, P. – KOLONITS – NGO THI HIEN – NOVAK, L., Manuscript in preparation.

REACTION OF HETEROCYCLIC TRIALKYLPHENYLPHOSPHINE OXIDES AND DIMETHYL ACETYLENEDICARBOXYLATE

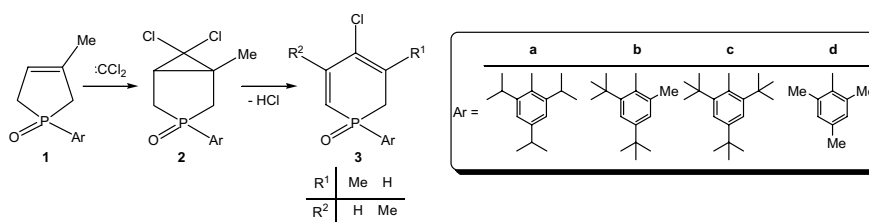
Henrietta FORINTOS

Research Group of the Hungarian Academy of Sciences at the Department of Organic Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

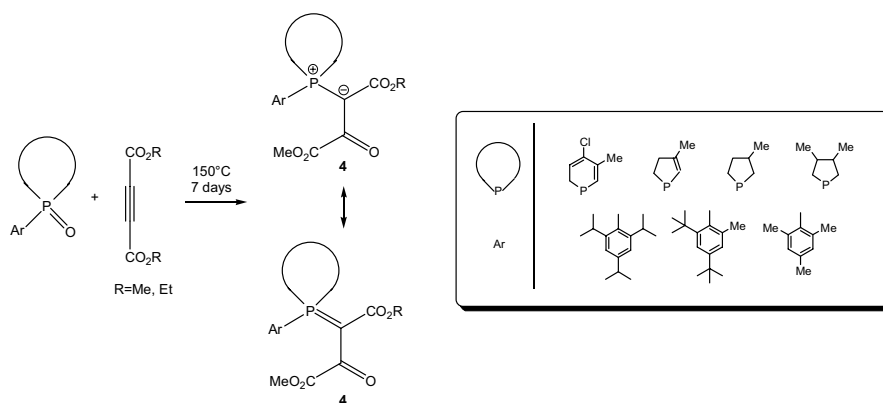
e-mail address: hforintos@mail.bme.hu

Supervisor: György Keglevich

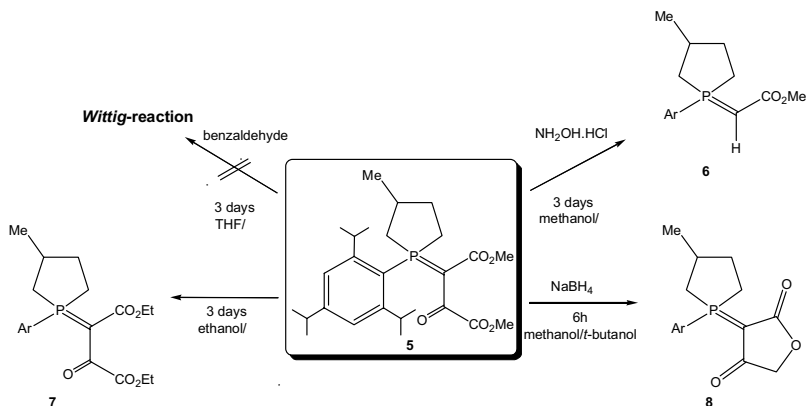
We synthesised 5- (**1–2**) and 6-membered (**3**) *P*-heterocycles with sterically demanding substituents as tri-*isopropylphenyl* (**a**), di-*tert*-butyl-methylphenyl (**b**), tri-*tert*-butylphenyl (**c**), and trimethylphenyl (**d**) on the phosphorus atom.



We found that the reaction of dihydrophosphinine oxides and DMAD at 150 °C (in a bomb) leads to phosphonium ylide **4**. The reaction is of general value and was extended to 5- and 6-membered cyclic phosphine oxides with different trialkylphenyl substituents on the phosphorus atom.



The strong delocalisation has an effect on the reactivity of the stabilised phosphonium ylide **5** in Wittig reaction, so **5** would not enter into reaction with benzaldehyde. Aiming at the synthesis of the corresponding oxime, **5** was reacted with hydroxylamine hydrochloride. The result of the reaction was, however, another phosphorane/ylide (**6**). This reaction may be the consequence of the attack of hydroxylamine on the β -keto group, or took place to the effect of hydrochloric acid. Phosphonium ylide **5** was subjected to reduction by an excess of sodium borohydride. To our surprise, a (phospholane-1-ylidene)-furan-2,4-dione (**8**) could be isolated from the reaction mixture.



**PREPARATION, VIBRATIONAL SPECTROSCOPY AND AB INITIO
STUDY OF THE UNSTABLE CF₃CNO MOLECULE AND ITS FUROXAN
RING DIMER**

Balázs HAVASI

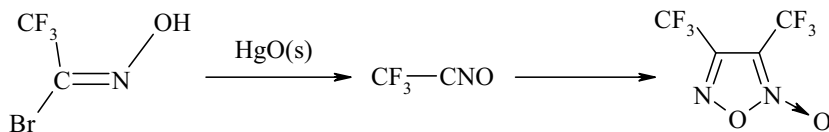
Department of Inorganic Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisors: Tibor Pasinszky
Nicholas P.C. Westwood

Small nitrile-oxides are short-lived, reactive intermediates and their isolation in the pure state is not possible. They are widely used in organic syntheses by *in situ* generation and subsequent 1,3-dipolar reaction with various substrates. In condensed phase they dimerize into the stable furoxan ring dimer.

Recent works have demonstrated a propensity for simple nitrile oxide molecules (XCNO, X = Br¹, NC², Cl³) to exhibit quasi-linear behaviour with the precise potential surface strongly dependent on the nature of the substituent X. The structural and spectroscopic properties of the unstable CF₃CNO molecule have, hitherto, not been investigated experimentally but, nevertheless, are of interest because of issues arising from the linearity or non-linearity of the CCNO frame.

In this work the unstable trifluoroacetonitrile *N*-oxide molecule, CF₃CNO has been generated in the gas phase with the solid-gas reaction of HgO(s) and CF₃BrC = N–OH in the highest yield and it was studied by gas-phase mid-infrared spectroscopy. Condensation of this molecule and subsequent revaporization leads to the formation of the stable ring dimer, bis(trifluoro)methylfuroxan also investigated by gas-phase FTIR.



Scheme: Preparation of CF₃CNO and its stable dimer

Thermolytic cleavage of aryl and alkyl furoxans were also successfully used for preparation and spectroscopic investigation of the unstable nitrile oxides. The reverse reaction suggests a similar opportunity to study the thermolysis of bis-(trifluoromethyl)furoxan.

The spectroscopy provides a detailed investigation into the vibrational character of the two molecules, and is supported by calculations of the harmonic vibrational frequencies; using density functional theory, B3LYP method with a 6–311+G(2d)

basis set and coupled-cluster calculations using CCSD(T) method with cc-pVDZ basis set. The ground state structures of both molecules were also investigated at the B3LYP level of theory, with the CF_3CNO species further investigated using coupled-cluster. The CCSD(T) method suggests a bent (C_s) structure for CF_3CNO with the B3LYP method suggesting a C_{3v} structure with a linear CCNO chain. The results suggest that CF_3CNO exhibits strong quasi-linear behaviour.

The monomolecular isomerization and dimerization are feasible loss processes for nitrile oxides, also for this unstable molecule, so the relative stability of CF_3CNO with respect to the known cyanate (CF_3OCN), isocyanate (CF_3NCO) and fulminate (CF_3ONC) isomers, and the mechanism of the dimerization process to the ring furoxan were studied with density functional theory.

References

- [1] PASINSZKI, T. – WESTWOOD, N. P. C., *J. Phys. Chem.*, **99** (1995), p. 6401.
- [2] PASINSZKI, T. – WESTWOOD, N. P. C., *J. Phys. Chem. A*, **100** (1996), p. 16856.
- [3] PASINSZKI, T. – WESTWOOD, N. P. C., *J. Phys. Chem. A*, **102** (1998), p. 4939.

ProfiSens – A PROFILE ANALYSIS SUPPORTING SOFTWARE IN FOOD SENSORY TESTING

János HESZBERGER

Department of Chemical Information Technology
Chemical Engineering Faculty
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisors: Klára Kollár–Hunek
Zoltán Kókai

Designing and implementing sensory tests can be effectively aided by the application of IT (Information Technology) tools as well as of Mathematical Statistics. Depending on the available resources different levels of computerization are possible:

- Computerization covers only the design of the experimental plan and the questionnaires
- Data input is computerized by OCR technology, too. (Optical Character Recognition) This level includes a computerized data analysis.
- The test is performed using the electronic copies of questionnaire files, data collection occurs by network.

The Sensory Laboratory of Faculty of Food Sciences (BUESPA) has a specially designed sensory booth system, which was established in accordance with the relevant ISO standards. The researchers of the Department of Chemical Information Technology (BUTE) and of the Sensory Laboratory (BUESPA) created a profile analysis supporting software, the ProfiSens. The language of the software is Visual Basic for Excel, it consists of several modules and UserForms. Its main functions are the following:

- Creates kitchen lists and score sheets for the assessors,
- Collects data from the completed score sheets,
- Performs statistical data evaluation, and diagrams of the results.

We have used the first version of the ProfiSens in the 2002/2003 academic year in research and in education as well. In this paper I discuss the results of both mentioned fields, and show the newly developed parts of the software.

I wish to express my gratitude to my PhD supervisor, Klára Kollár-Hunek, to the leader of the Sensory Laboratory, Zoltán Kókai, and to the head of Postharvest Department (BUESPA) Gábor Kollár for allowing me to take part in this research since 2001.

References

- [1] ISO 11035:1994 Sensory Analysis – Identification and Selection of Descriptors for Establishing a Sensory Profile by a Multidimensional Approach.
- [2] KÓKAI, Z. – HESZBERGER, J. – KOLLÁR-HUNEK, K. – KOLLÁR, G., A New Software as a Tool of Food Sensory Tests, *Hungarian Journal of Industrial Chemistry*, **30** (2002), p. 235.
- [3] KÓKAI, Z. – HENZE, E. – HESZBERGER, J. – KÁPOLNA, B. – SZABÓ, R., IT Support for Exploring Sensory Quality of Sustainable Grown Apple Varieties, *Proc. of EFITA'03*.
- [4] KÓKAI, Z. – HESZBERGER, J. – KOLLÁR-HUNEK, K. – SZABÓ, R. – KOLLÁR, G., Fogyasztói és szakértői érzékszervi vizsgálatok informatikai támogatása, *Proceedings of MKN'02*, Veszprém, Hungary, 2002, p. 177.
- [5] KOLLÁR, G. – VICZIÁN, ZS. – FÜSTÖS, ZS. – HUNEK, K., Problems and Results of Computer Aided QAS in Food Industry and Bioengineering, *Computers & Chem. Eng.*, **23** (1999), p. 687.
- [6] KOLLÁR, G. – KÓKAI, Z. – HENZE, E. – HESZBERGER, J. – KOLLÁR-HUNEK, K., Minőség és környezetkímélés – vizsgálat a rezisztens almafajták piaci versenyképességéről, *Proc. of VIII. Nemzetközi Vegyészkonferencia*, Kolozsvár, 2002, ISBN 973-85809-8-6, p. 176–180.

COMPUTED LONG-RANGE EFFECTS IN Gly_n (n = 2 – 8) OLIGOPEPTIDES

Viktória HORVÁTH, Zoltán VARGA, Attila KOVÁCS and István HARGITTAI

Department of General and Analytical Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Structure elucidation of biological compounds, the knowledge of their functions in organisms, and the understanding of the mechanisms of their reactions are of high priority in biomedical sciences. As relatively small amounts of energy – even a couple of kilojoules per mole – may play important roles, relatively high precision is required in their computational studies-, while cost considerations must also be kept in mind.

The purpose of our study was the mapping of variations in energy, geometry, and hyperconjugation in β -sheet oligoglycines at increasing chain length from the dipeptide to the octapeptide. The structures were optimized with a DFT method, [1]–[3] followed by perturbation energy analysis [4].

The stabilizing energy of the oligopeptide chain was calculated as the energy difference between two consecutive peptides relative to the energy difference between the dipeptide and the tripeptide. According to our computations, the stabilizing energy of the oligopeptide chain increases gradually with increasing chain length; for the octapeptide it is 2.3 kJ/mol more than for the tripeptide.

We have observed the most conspicuous change in the length of the hydrogen (H) bonds. With increasing chain length, the terminal H-bond shortens by 0.03 to 0.04 Å, whereas the in-chain H-bonds shorten by 0.02–0.03 Å. The strengthening of H-bonds is in accordance with increasing stability, which is a consequence of an in-chain cooperative effect. The propagation of such an effect may be facilitated by the delocalized N – C = O groups connecting 5-member H-bonded rings in the β -sheet structures.

Among the other bond lengths the change of the N-terminal C = O bonds (0.003 Å) and the lengthening of in-chain C = O bonds (0.02 Å) is significant; among the bond angles the terminal C_α – C = O and C – C_α – N are the most sensitive (change of 0.5°), while the in-chain angles altered only by 0.2–0.4°. The most significant change (4°) resulted in the N-terminal N – C_α – C = O torsion angle.

Our perturbation energy analysis suggested a correlation between the C = O bond lengths and hyperconjugation interactions at these bonds as well as between the two C_α – H bond lengths of the N-terminal amino acid and the energy contributions of hyperconjugation.

References

- [1] BECKE, A. D., *Phys. Rev. B*, **38** (1988), p. 3098.
- [2] LEE, C. – YANG, W. – PARR, R. G. , *Phys. Rev. B*, **37** (1988), p. 785.
- [3] VOSKO, S. H. – WILK, L. – NUSAIR, M., *Can. J. Phys.*, **58** (1980), p. 1200.
- [4] GLENDENING, E. D. – BADENHOOP, J. K. – REED, A. E. – CARPENTER, J. E. – BOHMANN, J. A. – MORALES, C. M. – WEINHOLD, F., *NBO 5.0*, Theoretical Chemistry Institute, University of Wisconsin; Madison 2001.

**INVESTIGATION OF AMINO-CLAISEN REARRANGEMENT IN THE
SYNTHESIS OF THE DERIVATIVES OF
*Phenserine***

Imre KIRÁLY, Gábor HORNYÁNSZKY, and Lajos NOVÁK

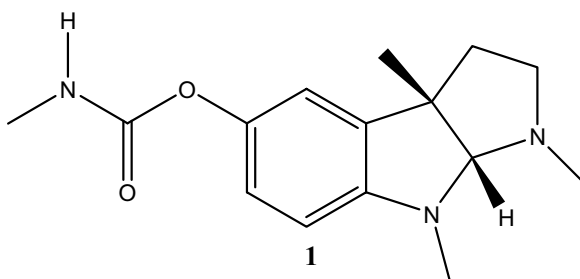
Institute for Organic Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: kiraly@mail.bme.hu

One of the most common dementia associated with aging is Alzheimer's disease, which can cause the loss of abilities like memory or learning and finally can destroy the personality itself. Although the disease cannot be cured, some acetylcholinesterase (AChE)-inhibitors can soften its progression.

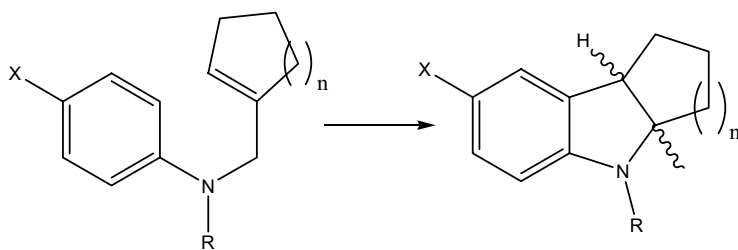
Phenserine (1) appears to be an excellent AChE-inhibitor in the treatment of Alzheimer's disease by its selectivity, low toxicity and high absorption in brain.

Its framework can be synthesized theoretically by using amino-Claisen rearrangement, which can provide a simple and relatively short method.



Amino-Claisen rearrangements are not frequently used in organic synthesis due to the high temperature required and the low yields, although Lewis-acids can moderate the reaction conditions.

We aimed to synthesize *Phenserine* (1) congeners and investigate the amino-Claisen rearrangement between different rings and examine the influence of different substituents attached to the ring system.



References

- [1] KIRÁLY, I. – HORNYÁNSZKY, G. – KOLONITS, P. – NOVÁK, L., Manuscript in Preparation.

INTERNAL PLASTIFICATION OF CELLULOSE ACETATE TO PRODUCE BIODEGRADABLE POLYMER

Szilvia KLÉBERT, Bianka VIDÉKI and Béla PUKÁNSZKY

Department of Plastics and Rubber Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary
and
Institute of Chemistry
Chemical Research Center
Hungarian Academy of Sciences

Supervisor: Béla Pukánszky

Nowadays considerable interest is being focused on biodegradable polymers. Cellulose derivatives could be appropriate materials for production of compostable and biocompatible polymers. Cellulose acetate has been widely used in the industry, and is also a potentially biodegradable plastic, although at higher degrees of substitution biodegradation proceeds rather slowly [1]. Unfortunately cellulose diacetate has limited processibility due to its relatively high glass transition temperature. Thus, plasticization of cellulose diacetate is necessary. The traditionally used external plasticization has often led to the bleeding of the plasticizer. Internal plasticization could be successful to avoid this problem [2]. The aim of our research activity is to find internal plasticizers which also improve the biodegradation of the cellulose acetate polymer besides plasticizing it. In the course of our research program we synthesised cellulose acetate-based polycaprolactones. Cellulose-acetates with different degrees of substitution were reacted with ϵ -caprolactone in melt, in an internal mixer. The ring opening polymerization of ϵ -caprolactone was initiated by the non-substituted OH groups in cellulose acetate [3, 4]. The polymerization reactions of ϵ -caprolactone were carried out for 30 min. at various temperatures in the presence of a small amount of stannous octoate as catalyst, as a function of the amount of catalyst, ϵ -caprolactone, the reaction temperature and other reaction conditions. Thermal and viscoelastic properties were studied by DSC (Differential Scanning Calorimetry), TG (Thermogravimetric Analyses) and DMTA (Dynamical Mechanical Thermoanalysis). The samples have also been tested by FTIR (Fourier-Transform Infrared Spectroscopy), X-ray diffraction analyses, GPC (Gel Permeation Chromatography) and MALDI-TOF (Matrix-Assisted Laser Desorption/Ionization Mass Spectrometry). The selective grafting of caprolactone oligomers onto CAs effectively increases the mobility of the cellulose backbone and – as PCL is known as a representative biodegradable and biocompatible polymer – expectedly accelerates the decomposition of the material. At present we are working on the replacement of ϵ -caprolactone in order to achieve more efficient plasticization.

References

- [1] BUCHANAN, C. M. – GARDNER, R. M. – KOMAREK, R. J., *J. Appl. Polym. Sci.*, **47** (1993), pp. 1709–1719.
- [2] LEE, S. – SHIRAISHI, N., *J. Appl. Polym. Sci.*, **81** (2001), pp. 243–250.
- [3] HATAKEYAMA, H. – YOSHIDA, T. – HATAKEYAMA, T., *J. Thermal Analysis and Calorimetry*, **59** (2000), pp. 157–168.
- [4] YOSHIOKA, M. – HAGIWARA, N. – SHIRAISHI, N., *Cellulose*, **6** (1999), pp. 193–212.

DEVELOPMENT OF FLAME RETARDED POLYMER SYSTEMS

Andrea MÁRTON, György MAROSI, Péter ANNA, György BERTALAN and Emese ZIMONYI

Department of Organic Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: gmarosi@mail.bme.hu

Supervisor: György Marosi

In recent years a great proportion of conventional structural materials are replaced by polymers in the fields of transportation, building and electronic industries. Increasing application of polyolefins (polypropylene, polyethylene) can be recognised due to their good recyclability and their favourable properties/price relation. The proportion of flame retarded types among commercial polymers is much lower than desirable. The more and more extensive use of polymers, underestimating the necessity of flame retardancy, led to dramatic events recently. Examples are the fires in the Mont Blanc tunnel (1999, 30 casualties), in an Austrian funicular tunnel (2001, 150 casualties), and in a serious bus accident in Spain in 1996 (47 casualties), where the passengers died either directly due to burning or due to evolved toxic gases.

The formation of protective surface layer (that limits the heat- and mass transfer through the surface) during burning is one of the fire retardancy mechanisms. One of the most effective ways for flame retarded formulation of polymers is the application of intumescent flame retardant additives consisting of ammonium polyphosphate and polyols as main components.

Application of this type of additives is limited due to their low water-stability and the low melt-viscosity of the polymer that leads to dripping and spreading of flame. (The flow of the molten polymer is of great importance in the case of fire. Always-changing surface of an easily flowing polymer does not allow a continuous barrier layer to develop on its surface.)

In this work polyboroxo siloxanes (BSil), synthesised from siloxane oligomers and boric acid were claimed to improve the performance and stability of ammonium polyphosphate-based intumescent systems [1, 2]. The ceramic-like barrier formed during combustion was investigated by X-ray photoelectron spectroscopy (XPS).

Further improvement on fire retardancy was achieved applying modified montmorillonite clay [2, 3]. The fire retardant mechanism of these nanocomposites corresponds to the mechanism of intumescent system, as we proved using surface analytical methods. Nanoparticles may accumulate on the surface of polymer during burning and form a protective barrier layer.

The fire retarded polymers developed within a EU5 Project in cooperation with many Hungarian companies (Pemü, Ikarusbus, Rati, Émi, Imag) were adapted

to functional applications in the fields of transportation, building and electronic industries.

References

- [1] MAROSI, GY. – MÁRTON, A. – ANNA, P. – BERTALAN, GY. – MAROSFŐI, B. – SZÉP, A., Ceramic Precursor in Flame Retardant Systems, *Polymer Degradation and Stability*, **77** (2002), pp. 259–265.
- [2] MAROSI, GY. – ANNA, P. – MÁRTON, A. – BERTALAN, GY. – BÓTA, A. – TÓTH, A. – MOHAI, M. – RÁCZ, I., Flame Retarded Polyolefin Systems of Controlled Interphase, *Polymers for Advanced Technologies*, **13** (2002), pp. 1–9.
- [3] MAROSI, GY. – MÁRTON, A. – SZÉP, A. – CSONTOS, I. – KESZEI, S. – ZIMONYI, E. – TÓTH, A. – ALMERAS, X. – LE BRAS, M., Fire Retardancy Effect of Migration in Polypropylene Nanocomposites Induced by Modified Interlayer, *Polymer Degradation and Stability*, **82** (2003), pp. 379–385.

THE INFLUENCE OF TRANSPARENCY BY DIFFERENT TYPES OF HIGHLY ACTIVE NUCLEATING AGENTS IN POLYPROPYLENE SYSTEMS

Alfréd MENYHÁRD*, Béla PUKÁNSZKY**, József VARGA*, Gábor NAGY***
and Ágnes MESTER***

*Department of Plastics and Rubber
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

**Chemical Research Center of Hungarian Academy of Sciences
Research Laboratory of Materials and Environmental Chemistry

***Tisza Chemical Works Ltd.

Introduction

Today the polypropylene is one of the most commonly used polymer. It has crystalline structure, and its morphological structure dramatically influences the properties of the polymer. The crystalline structure can be modified by adding nucleating agent to the polypropylene. With this technique the properties of the product can be changed in wide range. In the past few decades a continuous study was carried out on the department in this field. Those nucleating agents, which have advantageous effect on the transparency are called clarifiers. In the present study the effect of different nucleating agents were examined.

Results

Six different types of clarifiers were used during this study. Some of these types influence the transparency of the product dramatically. According to our study, the highly active nucleating agents enhance the transparency, when the size of the spherulites decreases radically, and they became as small as the wavelengths of the light. The most advantageous effect can be achieved by using the traditional sorbitol-based clarifiers, which are widely used in the industrial practice. On the other hand, numerous processing difficulties can happen by using these additives. For example, due to the poor homogeneity, the product will be hazy.

It can be established, that some of the highly active phosphor-based nucleating agents can be used as clarifiers. These two types of clarifiers have different modes of action. In *Fig. 1* these two different modes of action can be seen.

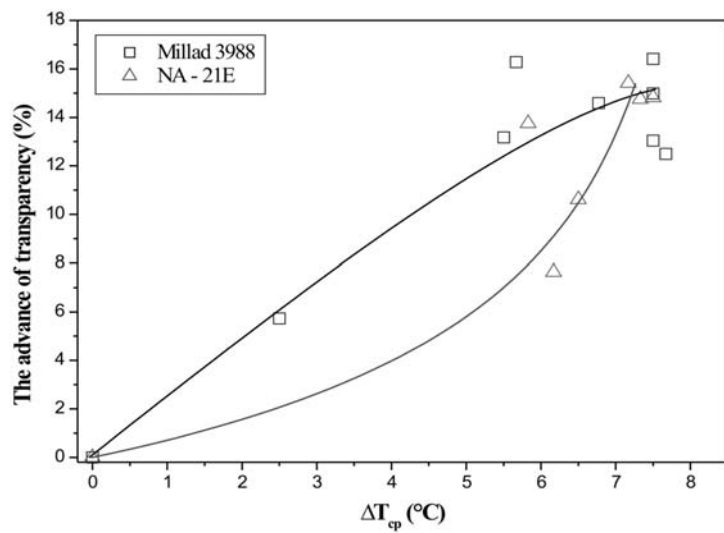


Fig. 1. The influence of transparency in the case of using the two most advantageous clarifiers

References

- [1] VARGA, J. – BELINA, K., *Műanyagok Fizikája*, 2003, Budapest manuscript.
- [2] WUNDERLICH, B., *Macromolecular Physics*, Academic Press, New York, London, Vol. 2. Crystal Nucleation, Growth, Annealing. 1976.

RESEARCH OF BIOTECHNOLOGICAL/BIOCONVERSIONAL METHODS FOR PRODUCTION OF GLYCEROL DERIVATIVES

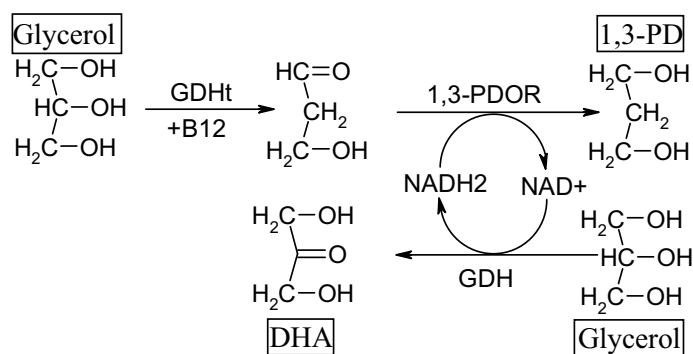
Áron NÉMETH

Department of Agricultural Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisor: B. Sevela

Glycerol, which is a byproduct of biodiesel formation, is a widely used, low cost raw material. The accessibility of glycerol supports its use in 1,3-propanediol (1,3-PD) and dihydroxyacetone (DHA) production. 1,3-PD is produced synthetically and biologically over 150.000 t/yr for polymer production purposes whereas DHA is used in the cosmetic industry.

The goal of my research work is to develop an enzyme catalized system, which can produce these two products from glycerol in a coenzyme-coupled reaction:



In order to realize our goal production of three key enzymes (glycerol-dehydratase (GDHt), 1,3-propanediol-oxydoreductase (1,3-PDOR) and glycerol-dehydrogenase (GDH)) must be performed by fermentation, analytical methods of these enzymes should be developed, the enzymes must be at least partially purified, and enzyme stability examinations must also be carried out. In the first part of my work I focused on the production of the enzymes and I developed a new effective cultivation process [1], [2], [3]. Furtheron I began the stability checks of partially purified 1,3-PDOR. The first enzyme reactions were carried out successfully in a model membrane reactor. Kinetic models were fitted to the measured fermentation as well as enzyme reactor performance data.

References

- [1] NÉMETH, Á. – KUPCSULIK, B. – SEVELLA, B., 1,3-Propándiol dehidrogenáz előállítás *Klebsiella pneumoniae*-val MTA Élelmiszertudományi Komplex Bizottsága, Magyar Élelmészeti Tudományos Egyesület és Központi Élelmiszer-tudományi Kutatóintézet 307. Tudományos Kollokviuma, Budapest, 2002 02. 22. presentation.
- [2] NÉMETH, Á. – KUPCSULIK, B. – SEVELLA, B., 1,3-Propanediol Dehydrogenase Production by *Klebsiella pneumoniae* DSM2026. 4th European Symposium on Biochemical Engineering Science, Delft, 2002 08. 28-31. poster presentation.
- [3] NÉMETH, Á. – KUPCSULIK, B. – SEVELLA, B., 1,3-Propanediol Oxidoreductase Production with *Klebsiella pneumoniae* DSM2026. *World Journal of Microbiology and Biotechnology*, **19** (2003), pp. 659–663.

SPIN-PHILICITY AND SPIN-DONICITY OF SUBSTITUTED CARBENES, SILYLENES, GERMYLENES AND STANNYLENES

Julianna OLÁH

Department of Inorganic Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

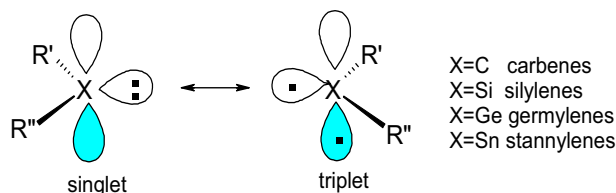
Supervisor: Tamás Veszprémi

One of the rapidly going fields of today's computational chemistry is the density functional theory (DFT). This field provides precise definitions of long known, but so far only vaguely defined chemical concepts such as the electronegativity, hardness, softness etc. All these indices may help any chemist to better understand the observed reactions, phenomena. Although newer and newer indices appear in the literature, it is always important to provide them with a clear interpretation and to examine them on a large set of molecules. Recently, two new indices have been introduced: the spin-philicity and spin-donicity indices [1]:

$$\text{Spin-philicity: } \omega_s^+ \equiv \frac{(\mu_s^+)^2}{2\eta_{ss}^0}, \quad \text{spin-donicity: } \omega_s^- \equiv \frac{(\mu_s^-)^2}{2\eta_{ss}^0},$$

where μ_s^\pm are the spin potentials and η_{ss}^0 is the spin hardness.

The divalent forms of the group 14 elements (carbenes, silylenes, germylenes and stannylenes) form a perfect set of molecules to investigate these indices. These compounds can have singlet or triplet ground state (*Scheme 1*) depending on the substituents and the atomic number of the central atom.



Scheme 1. Molecules with singlet and triplet ground states

In our work [2] we studied the spin-related DFT-based indices, such as the spin potentials, spin-hardness, spin-philicity and spin-donicity numbers. We performed quantum chemical calculations on a large set of carbenes, silylenes, germylenes and stannylenes using 25 different substituents. We discuss in detail the analogy between the electrophilicity and spin-philicity/spin-donicity indices. The same method was used to derive them, but serious differences arise from the fact that the

hardness of the molecule is positive, while the spin hardness is always negative. Our results demonstrate that the sum of the spin potentials calculated in the singlet and triplet states correlates excellently with the vertical singlet-triplet energy gap; this correlation is independent of the central atom. We have found a very good linear relationship between the spin-philicity and spin-donicity indices and the vertical singlet-triplet energy gaps. Although these indices may be used to describe both ground state and excited state properties, we only investigated ground state properties. We found that molecules with larger vertical energies possess larger spin-philicity and spin-donicity numbers, which is in accordance with the fact that molecules with larger vertical energies are better spin-catalysts. The derived maximal spin acceptance/spin release ($\Delta N_{s,\max}$) values are also in accordance with the observed spin catalytic power of several spin catalyst molecules.

References

- [1] PÉREZ, P. – ANDRÉS, J. – SAFONT, V. S. – TAPIA, O. – CONTRERAS, R., *J. Phys. Chem. A*, **106** (2002), p. 5353.
- [2] OLÁH, J. – DE PROFT, F. – VESZPRÉMI, T. – GEERLINGS, P., *J. Phys. Chem. A* **108** (2004), p. 490.

ACTIVITY CHANGE IN SOFTENING ENZYMES DURING SOUR CHERRY MATURATION AND STORAGE

Rita PERLAKI

Biochemistry and Food Technology Department
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: rperlaki@mail.bme.hu

Supervisors: Etelka Kovács

e-mail: kovacs@cfri.hu

Microbiology Department, Central Food Research Institute

Ferenc Örsi

Biochemistry and Food Technology Department

Sour cherry is an important human diet in consequence of its high antioxidant capacity and mineral content. The sour cherry fruit cannot be stored a long time. During storage firmness decreases very fast due to sensitivity to microbiological damages.

The aim of our research was to investigate the sour cherry cell wall break-down (pectin decomposition). The activity of β -galactosidase and polygalacturonase enzymes were determined as a function of fruit ripeness and storage time. The morphological parameters and the colours of the samples were also measured as a function of ripeness.

Rhamnogalacturonan (RG) is a branched heteropolymer in which D-galacturonic acid residues alternate with L-rhamnose residues. All RGs have side chains attached to the O4 of the rhamnosyl residues. Many of them are rich in arabinose and galactose.

Polygalacturonase (PG) hydrolyses the α -1,4 linkage between two adjacent galacturonic acid residues within the pectin backbone. β -galactosidase (β -gal) hydrolyses galactose molecules [1].

Enzymes were analysed in 2002 and in 2003 [2]. In 2002 two different sour cherry cultivars KÁNTORJÁNOSI and PÁNDY 279 were harvested at various times, and stored for 40 days at 4 °C, 90% RH. Sour cherries cv. KÁNTORJÁNOSI were harvested as a function of ripeness stages (green, breaker/pit hardening, pink, light red, red and dark red). These fruits were not stored. In 2003 KÁNTORJÁNOSI and PÁNDY 279 cultivars were examined as a function of ripeness stages.

It was established that the activity of β -galactosidase enzyme of sour cherry (cv. KÁNTORJÁNOSI) decreased between green and breaker stages, then continuously increased up to red stage, then slowly decreased (2002). In the next year the results were similar but the absolute values were higher in 2002.

The activity of β -galactosidase enzyme in stored sour cherries (cv. KÁNTORJÁNOSI) decreased in the first part of the storage (12–16 days) then increased

till the end of the storage (2002). In 2003 the activity of β -galactosidase increased from harvest day till the end of the storage in both cultivars.

The activity of polygalacturonase enzyme decreased during ripening and increased as a function of storage time in all cultivars (2002). Similar results were found in 2003.

These researches are coordinated by the Research Institute for Fruitgrowing and Ornamentals Budapest (expert: Dr. T. Kállay) and Central Food Research Institute (supervisor: Dr. E. Kovács).

Research also was supported by the National Scientific Research Foundation, Hungary (T 034401).

References

- [1] SEYMOUR, G. B. – KNOX, P. J., *Pectins and their Manipulation*, USA/Canada: CRC Press, 2002, pp. 157–159.
- [2] KOVÁCS, E. – VAN BUREN, J. P. – PITIFER, L. A. – HOCH, H. C. – TERHUNE, B. T., Effects of Irradiation and Storage on Cell Wall Structure of Golden Delicious and Empire Apples, *Acta Alimentaria*, **26** (1997), pp. 171–190.

A PILOT STEAM CRACKING PLANT TO QUALIFY RAW MATERIALS

Attila PINTÉR

Department of Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisor: Antal Tungler

Pyrolysis (high temperature steam cracking) of hydrocarbons to olefins is the largest petrochemical process. Feedstock selection is almost the most important aspect in product yields. There are some models which predict the olefin yield under altering working conditions and using different feedstocks. The availability of the most reliable and accurate model is restricted so we tried to build a laboratory pyrolysis reactor to qualify feedstocks.

The device has to operate under industrial conditions (temperature and residence time), but in laboratory scale and after some hours run enough product has to be produced to make material-balance. We tried to assert these aspects by the reactor design.

The flow profile in commercial reactors is very turbulent ($Re \sim 90000$). Calculations were carried out whether similar flow can be generated in pilot plant or not. Our reactor is working in laminar flow range ($Re \sim 700$). This fact is the most important running condition difference between a commercial and our pilot plant reactor.

The gases arisen in the process of pyrolysis experiment are analyzed by gas-chromatography.

The behaviour of the pilot plant shows much similarity to the commercial reactor but there are some differences that generate the deviation of the yield structure measured at commercial and pilot plants. The change of ethylene and propylene yields follows the trends found in the literature and are in good accordance with industrial results. The apparatus is appropriate to steam-crack complex mixtures and to make comparative measurements.

FIRST ENANTIOSELECTIVE SYNTHESIS OF α -AMINOPHOSPHINATES

Andrea SZABÓ*, Imre PETNEHÁZY*, Zsuzsa M. JÁSZAY** and László TÓKE**

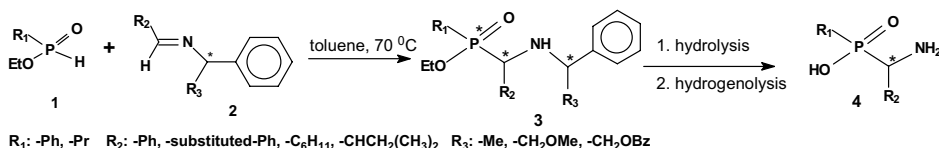
*Department of Organic Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

**Organic Chemical Technology Research Group of the Hungarian Academy of
Sciences
H-1521 Budapest, Hungary

In the past twenty years, considerable attention has been paid to the synthesis of α -aminophosphonic and α -aminophosphinic acids, because the phosphinic acids are the phosphorous analogues of α -aminocarboxylic acids, and therefore have biological importance both in itself and as building blocks for peptides. Despite of their importance, there is no enantioselective synthesis for α -aminophosphinic acids.

The most obvious route for the synthesis of α -aminophosphinates is the Kabachnik-Field reaction involving the addition of H-phosphinates to a C = N double bond. Using imines prepared from optically active amines and aldehydes, the addition results in a mixture of four diastereomeric pairs due to the attack of the prochiral phosphinate to the prochiral C-centre of the C = N bond.

Here, we disclose the first simple enantioselective synthesis of α -aminophosphinates by the addition of H-phosphinate to chiral imines, in the absence of catalyst [1].



As model compounds we have chosen chiral imines prepared from aliphatic and aromatic aldehyde and chiral amines, such as (S)- α -methylbenzylamine, (S)- α -methoxymethylenebenzylamine and (S)- α -benzyloxymethylenebenzylamine.

After the hydrolysis and hydrogenolysis we observed an enantiomeric ratio of α -aminophosphinic acids modest to excellent. The very simple chiral auxiliary α -methylbenzylamine and its methoxy and benzyloxy derivatives exert good/excellent chiral induction in the case of the addition of ethyl phenylphosphinate to imines and modest to good in the case of addition of ethyl propylphosphinate to imines. Since the absolute configuration of one member of α -aminophosphinic acids (R_1 , $\text{R}_2 = \text{Ph}$ **4a**) is known [2], namely (R), one might assume the same configuration

for **4** (*R*) as all these compounds have negative sign of optical rotation as that of **4a**. The *S* configuration in both type of chiral auxiliary induces *R* configuration on the α -carbon atom.

Calculations on the minimum energy of the stable conformation for the four diastereomeric pairs of **3** were performed. According to these, two major diastereomers were found to be more stable, therefore dominating among the four. These two diastereomers (which contain (*R*) chirality on the α -carbon atom) were identical with the major isomers in our experiments.

References

- [1] SZABÓ, A. – JÁSZAY, ZS. – TÓKE, L. – HEGEDŰS, L. – PETNEHÁZY, I., *Tetrahedron Lett.*, **44** (2003).
- [2] BELOV, YU. P. – RAKHNOVICH, G. B. – DAVANKOV, V. A. – GODOVIKOV, N. N. – ALEKSANDROV, G. G. – STRUCHKOV, YU. T., *Izv. Akad. Nauk. SSSR*, **5** (1980), p. 1125.

EFFECT OF CHOLESTEROL ON THE STRUCTURE OF THE FULLY HYDRATED DIPALMITOYL-LECITIN/WATER LIPOSOMES IN THE PRETRANSITION RANGE

Krisztián SZEGEDI

Department of Physical Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: szegedi@math.bme.hu

Supervisor: Attila Bóta

The studies on model membranes are fundamental for studying and understanding the changes of the physico-chemical properties of biological membranes. The model membranes are made of the major lipid components of the biomembranes (phospholipids, such as dipalmitoyl-phosphatidylcholine /DPPC/) and water. Any additional third molecule can drastically affect the structural characteristics and the thermotropic behaviour of the lipid/water system. The cholesterol plays an important role in the complex membrane mechanisms of the living cell, so the studies of the interactions between cholesterol and the lipid bilayer have an elementary role in understanding the function of the membrane cholesterol.

The DPPC/water system was studied in the temperature domain of the pre-transition in the biologically relevant range of cholesterol concentration by using small and wide angle X-ray scattering, differential calorimetry and freeze-fracture electron microscopy. Depending on the cholesterol/DPPC ratio, drastic changes were observed in the layer arrangements, the surface morphology and in the phase transition behaviour, too. The pretransition vanishes in the studied concentration range and it gets a weak first order character in the same time. A significant phase coexistence can be observed at cholesterol concentration of 5%. According to the electron density profiles of the layers deduced from the SAXS pattern, it was revealed that the parent phases are perturbed in the transitional states and the changes related to the corresponding (gel and rippled gel) states of the pure system are different.

These structures exhibit an importance, and should be taken into account because the coexistence of the different gel phases means that opposite effects can take place in the same time in laterally separated regions, leading to complex membrane processes as well as new effects are present at the formed domain walls.

References

- [1] FINEAN, *Chem Phys of Lipids*, **54** (1990), pp. 147–156.
- [2] PABST et al., *Phys Rev E*, **65** (2000), pp. 4000–4009.
- [3] SZEGEDI et al., *HASYLAB Ann Rep.*, (2002), pp. 793–794.

UTILISATION OF BRIDGED P-HETEROCYCLES IN PHOSPHORYLATION REACTIONS

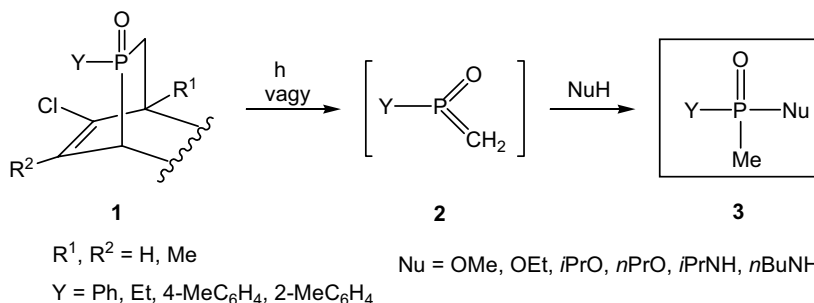
Helga SZELKE

Department of Organic Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: hszelke@mail.bme.hu

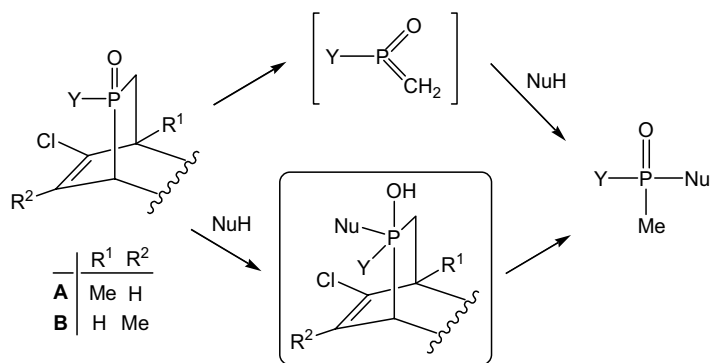
Supervisor: György Keglevich

Our aim was to prepare bridged P-heterocycles (**1**) that are useful in the generation of methylenephosphine oxides (**2**). These reactive intermediates – generated by UV light and thermo induced fragmentations – can be utilized in phosphonylations and phosphinylations.



One of the advantages of the mild UV-light mediated fragmentation-related phosphinylations/phosphonylations is the easy synthesis of P-derivatives with four different substituents (**3**). The efficiency of the phosphorylations through the thermally induced generation of methylenephosphine oxides (**2**) were somewhat decreased by the inevitable polymerisation of the reactive intermediate.

While the thermoinduced phosphinylations obviously take place through an elimination–addition (EA) mechanism involving methylenephosphine oxide (**2**) as the intermediate, the photochemically initiated phosphinylations may also involve a novel addition–elimination (AE) route by an intermediate with a pentavalent pentacoordinated phosphorus atom (**4**). We wished to utilise the newly synthesized aryl-precursors (**1**) to obtain new data on the mechanism of the photoinduced phosphinylations.



TIME RESOLVED GAMMA-SPECTROMETRY IN THE ACTIVATION ANALYSIS

László SZENTMIKLÓSI, Zsolt RÉVAY, Tamás BELGYA and Gábor L. MOLNÁR

Department of Nuclear Research
Institute of Isotopes and Surface Chemistry
Chemical Research Center
Hungarian Academy of Sciences

e-mail address: szentm@alpha0.iki.kfki.hu

Supervisors: Zsolt Révai
Department of Nuclear Research
Nagyné László Krisztina
Department of Physical Chemistry

The prompt-gamma activation analysis is a powerful, nondestructive analytical method for determination of the elemental composition in the samples.

Spectral interferences may frequently occur in gamma-ray spectra of activation analysis samples. A straightforward way is suggested to overcome these difficulties, where not just the conventional energy spectrum is utilized, but also the time-dynamic is recorded. This feature makes the identification of the radionuclides more reliable.

This method provides a solution based on the so-called *list-mode* feature of XIA's digital gamma-spectrometers. In this mode we can record the accurate time and energy information for each individual event, and convert them to useful analytical parameters (e. g. energy, amplitude, half-life) using a detailed off-line evaluation procedure.

During the evaluation we can reconstruct the usual energy spectrum in maximum 64k channels, or generate the decay curves of all occurring isotopes (this required several separate measurements in the conventional case). The evaluation of complete 3D region plots (counts versus energy and time) provides the more accurate information, but it needs a new approach of the evaluation procedure. In this talk the progress of the ongoing development will also be presented.

Since the count rate may vary an order of magnitude while the nuclides decay, the shape and the amplitude of the decay curves would be distorted without using an accurate dead-time correction. Whereas the spectrometer does not provide dead time correction in the list mode, the measured data should be corrected manually. Several independent methods for the correction of the dead time have been investigated.

Demonstration measurements have been carried out with samples containing nuclides of half-lives from minutes to hours (^{28}Al , ^{52}V , ^{20}F , ^{116m}In , ^{56}Mn , ^{64}Cu , ^{24}Na), to check the feasibility of the method. From the numerical fit of the decay curves we were able to determine the half-lives, with a good agreement with the

literature data (in most cases within $\pm 1\sigma$ uncertainty range), and we succeeded in decomposing overlapping peaks on the basis of their half-lives, although they were inseparable in the energy spectrum.

ANALYSIS OF MULTICOMPONENT SYSTEMS BY RAMAN MICROSCOPY

Andrea SZÉP, György MAROSI, Péter ANNA and Judit PÓTI

Department of Organic Chemical Technology
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

e-mail address: gmarosi@mail.bme.hu

Supervisor: György Marosi

The scope of an analytical process applicable for characterizing multicomponent systems is basically determined by the sensitivity of the method to the physical and chemical differences between the components and by the modifying and destructive effects caused during sample preparation and analysis. In order to answer the current questions emerging in material science, especially in the area of multicomponent polymer systems, high lateral and depth resolution with sensitivity for chemical characterization, good localizability and possibility for depth profiling are essential.

The development of multicomponent polymer systems requires for example a comprehensive knowledge about the interfaces. The Raman microscope is one of the most convenient instruments for analyzing the structural characteristics and changes in the interfacial region of multicomponent systems. This is confirmed by the results obtained in the field of packaging materials, nanocomposites, surface treated additives and basalt fibre reinforced composites. A Raman microprobe enables one to make local measurements at microscale as well, providing information on the vibrational and vibrational-rotational states of the molecules without any sample damaging.

Most samples analyzed by the Jobin Yvon LabRam Raman microscope located in the Department could not be at all or could hardly be investigated by any other analytical method. In multicomponent polymer systems, the method may give valuable information about the individual layers, their surfaces, interfaces and interdiffusion effects [1]. In case of surface modified polymers or polymer additives we have found that not only the identification of coatings but also their chemical reactions can be followed by Raman microscopy [1, 2]. We have also investigated, whether the Raman microscope is suitable to follow the migration processes of nanofillers towards the surface induced by heat treatment. We could show that the method is able to detect the slight changes on the surface [1]. A great benefit of Raman microscopy is that, in principle, it requires no sample preparation. It makes possible for example the exact spectroscopic monitoring of the thermoanalytical process, such as crystallization [1]. Not only solid materials but also solutions could be measured using Raman scattering. Raman microscopic monitoring of

the synthesis of reactive surfactants was supported by the fibre optic device of the instrument [3].

References

- [1] SZÉP, A. – MAROSFŐI, B. – BERTALAN, GY. – ANNA, P. – MAROSI, GY., Analysis of Multicomponent Polymer Systems by Raman Microscopy, *Macromolecular Symposia*, **202** (2003), pp. 269–280.
- [2] ANNA, P. – ZIMONYI, E. – MÁRTON, A. – SZÉP, A. – MATKÓ, SZ., – KESZEI, S. – BERTALAN, GY. – MAROSI, GY., Surface Treated Cellulose Fibres in Flame Retarded PP Composites, *Macromolecular Symposia*, **202** (2003), pp. 245–254.
- [3] MATKÓ, SZ. – ANNA, P. – MAROSI, GY. – SZÉP, A. – KESZEI, S. – CZIGÁNY, T. – PÖLÖSKEI, K., Use of Reactive Surfactants in Basalt Fiber Reinforced Polypropylene Composites *Macromolecular Symposia*, **202** (2003), pp. 255–268.

ELECTRICALLY ADJUSTABLE THERMOTROPIC WINDOWS

András SZILÁGYI

Department of Physical Chemistry
Budapest University of Technology and Economics
H-1521 Budapest, Hungary

Supervisor: Miklós Zrínyi

Several attempts have been made recently to develop smart windows, which can moderate light and heat intensities. These materials can be used to substantially reduce glare and so to increase the thermal and visual comfort. Another promising area of their application is in greenhouses and water-boiling systems for optical and thermal control. These materials are also good candidates for large displays.

Recently, the development of thermotropic hydrogels, which may be used for constructing intelligent windows, has met growing interest. In order to construct an adaptive gel-glass, I have placed a thin intelligent polymer gel layer between two glasses or transparent plastic sheets. These windows are completely transparent and very similar to commercial windows in their external features. Their optical properties are not disturbed by the gel. Adaptability of gel-glass is provided by the intelligent polymer layer.

Optical properties (e.g.: its transparency) of the gel are significantly influenced by environmental stimuli, like temperature changing or presence of electric field. This environmental sensitive glass becomes cloudy when the stimulus exceeds a critical value. It becomes transparent again if it is reduced under this value.

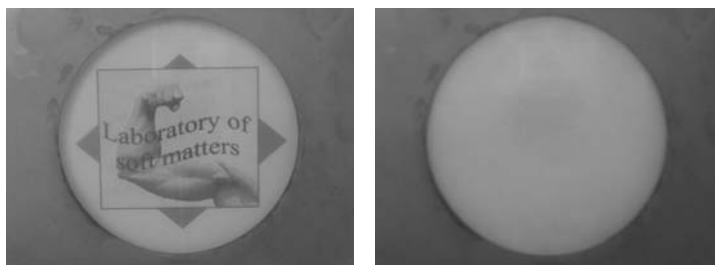


Fig. 1. The transparent – opaque transition of gel-glass as a result of audio frequency AC current

Based on the phase transition of polymer gels, a novel electrically adjustable window, which includes a gel layer, has been developed in our laboratory. Unlike other electrically controlled structures, the optical properties of the gel layer are

abruptly modified by the Joule heat of audio frequency AC current. The so-called gel-glass becomes opaque when the temperature exceeds a critical value and changes back to its original transparent state when it is cooled down again. This method results in fast control and relatively low operational cost. Two types of gel-glasses – active and passive structures – have been developed and investigated. In the lecture I will demonstrate the structural build-up and working of these novel electrically adjustable thermotropic windows. Experimental studies have been made at different frequencies and voltages. Influences of two types of audio frequency AC current signal – sine and square – have been investigated. The optical properties, as well as the energy balance of the systems, have been reported [1].

References

- [1] GYENES, T. – SZILÁGYI, A. – LOHONYAI, T. – ZRÍNYI, M., *Polym. Adv. Technol.*, **14** (11–12) (2003), pp. 757–762.