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Swiss Chemical Society
Haus der Akademien
Postfach
3001 Bern
Switzerland
info@scg.ch
www.scg.ch

# Radicals in the Life of Industrial Polymer

P. Nesvabda[1]

[1]BASF Schweiz AG, Basel

Radicals play a fundamental role in the life cycle of synthetic polymers. Of the 300 million tons of industrial polymers produced worldwide every year about 50% are made by *radical polymerization* of monomers that are often stabilized against undesired premature polymerization by addition of *polymerization inhibitors*. Stabilizers are necessary to protect the majority of polymeric materials during their service life from *radical degradation processes* triggered by oxygen, heat or light. Modification of the polymeric architecture can be easily achieved via *radical polymer analogous reactions*. One of the most important developments in polymer science in the last 25 years is *controlled radical polymerization*. *Radical bearing redox-active polymers* are emerging as promising materials for example in energy storage application like organic radical batteries.

Our contributions to the above mentioned fields will be illustrated on the following examples:
a) Novel benzofuranone stabilizers[1-2] and related serendipity discovery of novel dyes[3-5]
b) Eco-friendly polymerization inhibitors[6-7]
c) First industrial realization of controlled radical polymerization[8-11]
d) Radicals bearing polymers for electrochemical applications[12-14]
e) Novel and safe radical initiators[15-17]

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# Selective attachment of Gold Nanoparticles on Asymmetrically Functionalized Janus Nanoparticles

F. Guignard[1], M. Lattuada[1]*

[1]Adolphe Merkle Institute - University of Fribourg

n recent years, the research in the field of nanoparticle has devoted much attention to the synthesis of anisotropic nanoparticles, also called Janus Nanoparticles. Their anisotropy may have different origins, such as having non-homogeneously functionalized surface or complex internal nanostructure. These special features render the nanoparticles much more interesting than their isotropic counterparts, especially regarding their self-assembling properties. Here, we describe the synthesis and the characterization of Janus Dumbbells asymmetrically coated with gold nanoparticles. This peculiar type of nanoparticles is prepared to be used as a template for catalytic Janus nanomotors, self-propelling in appropriate conditions.

We start by synthesizing polystyrene dumbbell-shaped nanoparticles in a three-step process, as has already been reported [1]. We then performed silane chemistry to selectively bring amino groups on the surface of one hemisphere of the dumbbells only. This is possible thanks to presence of silanol groups on the surface of the first hemisphere [2].

To selectively cover one hemisphere of the dumbbells with gold nanoparticles, two different approaches were tested. In the first case, we prepared negatively-charged gold nanoparticles (coated with citric acid) by a Turkevick-like method. In proper conditions, we then mixed the two types of nanoparticles. Due to electrostatic interactions between the amino groups on the polystyrene dumbbells and the citrate groups on the gold nanoparticles, the latter selectively attached on one hemisphere, while the other remains naked.

Another synthetic approach is to reduce the gold salt directly in the presence of the functionalized polystyrene dumbbells. In a similar way as in the first method, the asymmetric distribution of amino groups on the dumbbells will lead to the selective nucleation and growth of small gold nanoparticles only on one hemisphere.

On top of interesting plasmonic properties, gold nanoparticles are also known to act as “seeds” for the growth of platinum nanoparticles (or shells). An asymmetric distribution of such catalytic nanoparticles can lead to self-propulsion of the dumbbells in appropriate conditions (i.e. with $H_2O_2$ fuel). Evaluation of the drawback and advantages of the different method used for the synthesis of gold-coated dumbbells will be discussed.

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# Multi-stimuli responsive films designed through layer-by-layer assembly of PAA-b-PNIPAM block copolymers for biomedical applications

A. Osypova[1,4], C. Pradier[2,5], C. Jérôme [3], J. Landoulsi[2,5], S. Demoustier-Champagne [4]

[1]Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Protection and Physiology, St.Gallen, [2]Sorbonne Universités, Paris, France, [3]Center for Education and Research on Macromolecules (CERM), University of Liege, Liège, Belgium, [4]Institute of Condensed Matter and Nanosciences, Université catholique de Louvain, Louvain-la-Neuve, Belgium, [5]CNRS, Laboratoire de Réactivité de Surface, Paris, France

Smart or so-called stimuli-sensitive materials that reversibly respond to the environmental changes have opened numerous routes in biomedical fields, such as protein separation, surface properties control, medical diagnostic etc [1]. In regard to bioanalytical tools development, pH and temperature responsive macromolecules are the most profoundly studied systems [2,3]. Immobilization of this kind of smart macromolecules is the key step in the fabrication of biosensing elements.

In the present work, we report on the design and elaboration of multi stimuli-responsive thin films. For this goal, we employed the robust and versatile layer-by-layer (LbL) assembly approach to incorporate block copolymers made of poly(acrylic acid) PAA and poly(N-isopropylacrylamide) PNIPAM with tunable and well-defined block lengths. The combination of ellipsometry, quartz crystal microbalance (QCM-D) and infrared data revealed the possibility to build up $(PAH/PAA\text{-}PNIPAM)_n$ multilayers. The responsive properties towards application of different stimuli were evaluated by monitoring the adsorption of proteins (ovalbumin, bovine serum albumin) by means of QCM-D while varying (i) temperature, (ii) pH, (iii) ionic strength or a combination of all these stimuli. It emerges that temperature has a strong impact on the amount of adsorbed proteins, in accordance with the expected behavior of PNIPAM. In addition, the adsorbed amount of protein estimated by QCM-D measurements indicates that basic pH (~8) and/or low ionic strength ($10^{-5}$M) conditions are not favorable for protein adsorption while low pH (~4) and/or high ionic strength ($10^{-1}$M) changes the surface to protein attractive state.

In short, these new PNIPAM block copolymer-based LbL coatings are easy to build on substrates of various nature such as gold or silica and present highly tunable features [4]. This makes therefore them ideal candidates to be employed for applications requiring the control of protein adsorption, such as protein separation or cell culture.

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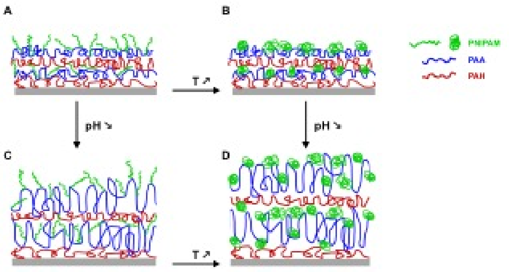

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# Developing New Strategies to study colloidal Nanocrystals using Dynamic Nuclear Polarization NMR Spectroscopy

L. Piveteau[1,3], T. Ong[1], B. J. Walder[2], A. Rossini[2], L. Emsley[2], C. Copéret[1]*, M. V. Kovalenko[1,3]*

[1]Department of Chemistry and Applied Biosciences, ETH Zürich, Vladimir Prelog Weg 1-5, Züirch CH-8093, Switzerland, [2]Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale de Lausanne (EPFL), Lausanne 1015, Switzerland, [3]Empa-Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, Dübendorf CH-8600, Switzerland

Nuclear magnetic resonance (NMR) is one of the most powerful analytical techniques to characterize molecules (solution NMR) and materials (solid-state NMR), including colloidal or powdered nanocrystals (NCs). However, NMR is suffering of inherently poor sensitivity, especially when it comes to isotopes other than $^{1}$H, $^{13}$C, $^{19}$F and $^{31}$P, which makes most of the NCs difficult to study or not accessible by NMR.

We showed in earlier work that dynamic nuclear polarization (DNP) NMR represented a practicable solution to the sensitivity problem described above.[1] However, few NC solutions yielded mentionable signal due to aggregation at the experimental conditions of 100 K required for DNP NMR. Insertion of the NCs into meso-silica hindered them from precipitating and maintained all the NCs within reach of the radicals for efficient polarization transfer leading to significant NMR signal enhancement. This novel, universally applicable, extremely simple and inexpensive methodology for sample formulation makes use of commercially available materials (meso-silica) and pristine colloidal NC solutions in their native environment avoiding the adverse effects of the isolation of NCs, such as powdering or re-dispersion.[2] Eventually, the combination of conventional and DNP NMR permits the selective study of the NC core, NC surface or capping ligands, should they be of organic or inorganic nature.

Nevertheless, new insights into chemical bonding (coordination, connectivity, interatomic distances, *etc.*) and composition (oxidation state, distribution in and on the NC, *etc.*) of NCs are restricted to systems with high symmetry and little site disorder. Else, the broad signals from different species overlap and make the spectrum interpretation superficial if not impossible. 2D-spectroscopy turned out to be an elegant tool to overcome this difficulty, by visualizing interactions or by increasing resolution through the isolation of line broadening effects. [2, 3]

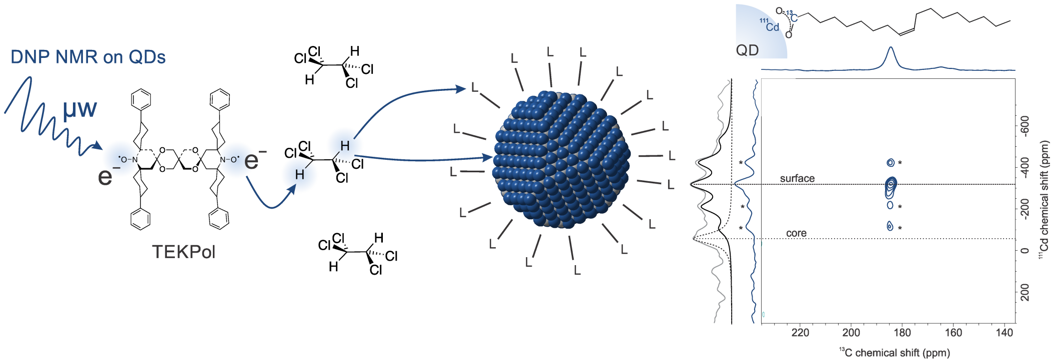

**Figure:** (left) Polarization transfer mechanism of DNP NMR leading to enhanced signal intensity of atoms of the ligand, at the surface or inside the NC. (right) D-HMQC-R$^{3}$ spectrum displaying connectivity of the oleate ligand to the surface cadmium species, which can easily be distinguished from the core (chemical shift, CSA).

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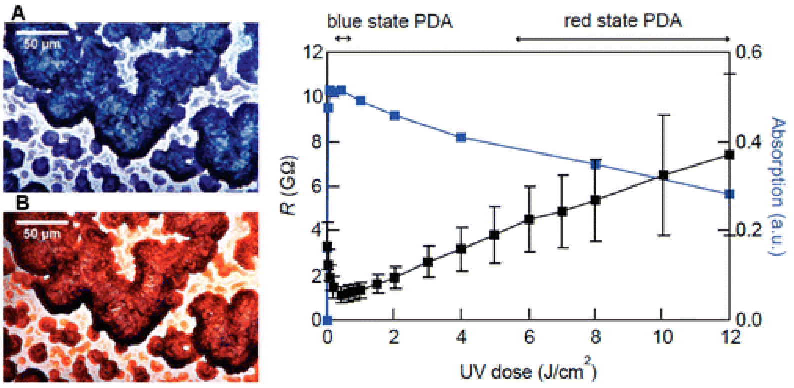
# Combined Electrical and Optical Characterization of Polydiacetylene

C. Girard-Reydet[1], R. D. Ortuso[1], M. Tsemperouli[1], K. Sugihara[1]*

[1]Department of Physical Chemistry, University of Geneva, Quai Ernest Ansermet 30, 1211 Geneva 4, Switzerland

Polydiacetylene (PDA) is a conductive polymer that has mechanochromism. When the polymer is exposed to mechanical stresses, change in temperature (thermochromism), pH (ionochromism), and so forth, the structural perturbation can be seen by the change in its color. Although it presents interesting electrical and optical properties, the relationship between these signals has rarely been investigated. We studied the correlation between the electrical conductivity and the absorption spectra of PDA. Upon UV irradiation, PDA absorption spectra presented a blue shift, which coincided with the decrease in the electrical conductivity.



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# Retort tie-layer: the development of a solution for barrier retort structures

E. Kupsch[1]

[1]Dow Europe GmbH, Bachtobelstrasse 3, 8810 Horgen, Switzerland

The presented work aims at the development of adhesive resins for steam sterilizable film applications in food and medical packaging that promote the adhesion between polypropylene and oxygen / carbon dioxide gas barrier polymers like polyethylene vinyl alcohol (EVOH) and polyamide (PA). Generally the adhesive resin design is based on maleic anhydride grafted polymers. The different challenges between polyethylene and polypropylene grafting are discussed. To overcome these deficiencies for the adhesive resin design, a Dow developed compatibiliser for polypropylene/polyethylene blends was used in the adhesive resin formulation. The concept of the compatibilising polymer is demonstrated with an electron microscopy analysis of blends containing different ratios of polypropylene, polyethylene and compatibiliser. Finally it could be demonstrated that in multi-layer extruded film the resulting adhesive resin formulation proves to be high in adhesion strength to polypropylene, polyethylene vinyl alcohol and polyamide without performance loss after the steam sterilization process.

# Phosphorescent oxygen sensors produced by spot-crazing of polyphenylenesulfide films

C. Toncelli[1,4], O. V. Arzhakova[2], A. Dolgova[2], A. L. Volynskii[2], J. P. Kerry[3], D. B. Papkovsky[4]

[1]Empa, Swiss Federal Laboratories for Materials Science and Technology. Laboratory for Protection and Physiology. Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland, [2]Department of Polymer Chemistry, Moscow State University, Leninskie Gory, Moscow, Russian Federation, [3] Department of Food Science and Nutrition, University College Cork, Cork, Ireland, [4]Biochemistry Department, University College Cork, Cavanagh Pharmacy Building, Cork, Ireland

Detection of molecular oxygen (O2) by a non-chemical, reversible, contactless optical method is of high utility for many areas including industrial process control, environmental monitoring, biological detection, medicine and food packaging [1]. Conventional O2 sensors are usually produced by making a polymeric cocktail in an organic solvent, applying it on a substrate and drying, polymerizing or curing liquid precursors. These processes usually involve toxic solvents or monomers (e.g. styrene), in significant amount and with considerable wastage [2]. Recently, solvent crazing of polymers in physically active liquid environments (PALEs) have shown an attractive alternative for the encapsulation of optical transducers in semi-crystallnie polymer matrix [3]. The creation of a nanoporous structure (5–15 nm pores with a narrow size distribution and volume porosity up to 55–60%) is achieved by tensile drawing in a suitable solvent which, in the presence of the additive, allows the encapsulation of the dye by diffusion forces in one-pot approach.

In the present work, phosphorescent oxygen sensors based on platinum benzoporphyrin and palladium benzoporhyrin dyes encapsulated in polyphenylenesulfide (PPS) films by the spot-crazing method are described. The new polymer matrix enables simple, one-step production of discrete, high-performance O2 sensors using a low toxicity solvent 2-butanone, low overall strain (8%), low amounts of solvent and precise spatial control. The resulting nano-structured sensor materials display markedly enhanced brightness, high photo-, mechanical and chemical stability.

Their structural and physico-chemical properties were characterized by differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), optical microscopy and phosphorescence lifetime imaging microscopy (PLIM). The PPS sensors show a high degree of lateral and in-depth homogeneity on the micro- and macro-scale, as revealed by confocal microscopy, linear Stern–Volmer plots and single exponential decays. Operating in phosphorescence lifetime mode, optimised sensors show stable O2 calibrations in the range of 0.1–100 kPa O2, low temperature dependence (linear in the range 10–50 °C), low cross-sensitivity to humidity and high reproducibility (RSD 1.5% at 21 kPa and 0.5% at zero O2). This technology facilitates the production of low-cost disposable O2 sensors and their integration in large scale industrial applications such as packaging.

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# 100% Renewables-Based Polyethylene Furanoate (PEF) for the "Green Bottle" Via Ring-Opening Polymerization

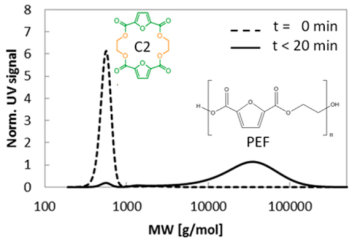
J. Rosenboom[1], G. Storti[1], M. Morbidelli[1]*

[1]ETH Zurich

Along the shift of our societies from fossil-fuel based economies towards more sustainable civilizations, polyethylene furanoate may replace one of the world's dominant fossil-based plastics, polyethylene terephthalate (PET). Recent efforts were invariably based on polycondensation followed by solid-state post-polymerization (PC-SSP), which is burdened with the necessary removal of condensation byproducts to reach high conversions and molecular weights, and thus typically requires reaction times in the order of days[1,2]. We present ring-opening polymerization (ROP) as a faster and living synthesis route to reach sufficiently high molecular weight PEF for commercial applications such as bottles, textiles, medical grafts, etc.[3].

Cyclic PEF monomers (cyOEF) can be derived from the 100% renewables-based building blocks 2,5-furandicarboxylic acid and ethylene glycol via depolymerization of short PEF oligomers in suitable solvents. Within 4 hours, cyOEF are formed with a selectivity of 80% towards cyOEF. The 20% unconverted linears and solvents can be recycled to maximize material use. Purification of cyOEF from residual linears via silica gel adsorption to yield ›99% cycles is essential for ROP to deliver 1) sufficiently high molecular weights, 2) reproducible reaction control and 3) colorless products. cyOEF were subjected to catalytic ROP at temperatures up to 280oC using tin catalysts such as FDA-approved tin octoate, the application of which could simplify the entry to regulated food packaging market, to form PEF chains in yields of ›95% and molecular weights equivalent to a PET bottle (~60'000 g/mol). Absolute molecular weight measurement is essential for process development, which we perform with laser scattering (MALS) and diffusion (DOSY) NMR [4]. Cyclic monomers do not have end-groups and thus render byproduct removal unnecessary, allowing for complete conversion to high molecular weight PEF within less than 20 min. Combined with cyOEF synthesis time, ROP outperforms commonly applied PC-SSP by about a factor of 10. Compared with PET, the higher glass transition temperature (85oC vs. 73oC) and lower melting point compared (215oC vs. 260oC) of PEF indicate higher thermal stability and easier processing of the final bottles. An at least 5x higher oxygen diffusion barrier complements the advantageous properties of PEF.

While the scale-up to larger (kilogram) volumes and processing towards actual bottles is ongoing, the advantageous synthesis of PEF via ROP opens a new and promising pathway not only towards the highly anticipated "green bottle", but also enables advanced molecular architecture control of furan based polyesters through a "living" polymerization, e.g. for branching and block copolymers, which is infeasible with the current process based on PC-SSP.



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# Force-Induced Cis-to-Trans Isomerization of Carbon-Carbon Double Bond Using Atomic Force Microscopy

M. Radiom[1], P. Kong[2], P. Maroni[1], A. Kilbinger[2], M. Borkovec[1]*

[1]Department of Inorganic and Analytic Chemistry, University of Geneva, Sciences II, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland, [2]Department of Chemistry, University of Fribourg, Chemin du Musée 9, 1700 Fribourg, Switzerland

Numerous examples of carbon-carbon double bond containing molecules exist in chemistry and biology. An attribute of these molecules is that their *cis* and *trans* isomers normally present different physical and chemical properties. Thus isomerization of double bond is a necessary process that naturally occurs or is artificially induced via irradiation, thermally or by catalysts to deliver specific function. So far the effect of mechanical force on isomerization of double bond has not been investigated. We present our results on force-induced *cis*-to-*trans* isomerization of double bond at the level of single polymer molecules containing *cis* double bond. Three double bond containing polymers, namely **P1**, ***cis*-PB** and **PB**, were used. The structures of these polymers are shown in figure 1(a).

Upon stretching *cis* double bond containing polymers to elevated forces using atomic force microscopy, a sudden relaxation in force and increase in elongation of polymer was observed in the force versus extension profile. The transition is attributed to isomerization. An example of force-induced isomerization in **P1** is shown in figure 1(b). Investigation of exclusively single bond containing polymers did not show any trace of isomerization. Our results reveal an isomerization force of 800±60 pN as shown in figure 1(c). This force is slightly lower that the force associated with breaking of covalent bonds and rings ~ 1-2 nN [1,2]. Our results show that the mechanical force can be used to trigger isomerization of double bond. Our results also open the possibility of a new class of force-responsive polymers based on mechano-isomerization of double bond.

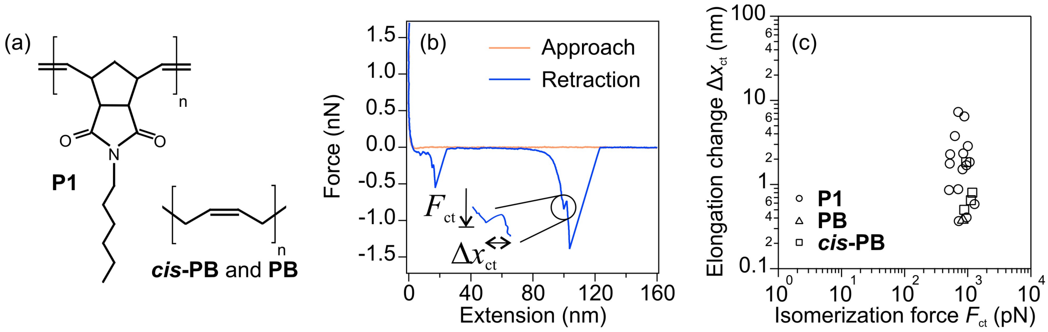

Figure 1: (a) Structural formulas of the *cis* double bond containing polymers used in this study: newly synthesized polymer **P1**, *cis*-1,4-polybutadiene (***cis*-PB**, 98% *cis* double bonds) and *cis*/*trans*-1,4-polybutadiene (**PB**, 36% *cis* double bonds). (b) Force versus extension of **P1** showing an isomerization event. The onset of *cis*-to-*trans* isomerization is denoted by force $F_{ct}$ that accompanies an elongation change $\Delta x_{ct}$. (c) The elongation change $\Delta x_{ct}$ of **P1**, **PB**, and ***cis*-PB** as a function of the *cis*-to-*trans* isomerization force $F_{ct}$.

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# Biomimetic Polymersomes through a Symbiosis of Organic and Polymer Chemistry

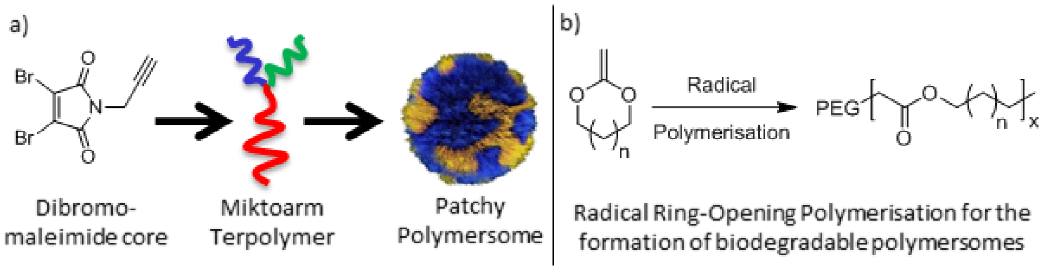
J. Gaitzsch[1], G. Battaglia[2], W. Meier[1]*

[1]University of Basel, [2]University College London

The chemical versatility polymers is one of the major benefits of polymersomes.[1] However, even more potential can be unlocked if polymer chemistry is combined with organic chemistry to obtain the polymer.

Polymersomes usually have a surface without any domains, which represents a major drawback with respect to natural vesicles. We accomplished stable domains by synthesising a miktoarm star terpolymer based on dibromomaleimide (see figure).[2] Translated from organic chemistry it proved to serve as a highly stable linker to form a miktoarm star terpolymer, which enabled the formation of polymersomes with stable domains (see figure). In order to make the patches visible, we translated the TAD chemistry, recently translated from organic chemistry, towards a method for polymer conjugation.[3]

One gap however, the development of smart and degradable polymersomes is only filling slowly. This is mainly due to the fact that ring-opening polymerisation does not tolerate the unprotected amines or alcohols necessary. By using controlled radical ring opening polymerisation (CoRROP) from cyclic ketene acetals (CKAs), this issue can be overcome. [4]The first key for this polymerisation is the monomer synthesis, hence the organic chemistry required. In very recent studies and ongoing research we aim at showing that CKAs are well accessible and how well CoRROP from cyclic ketene acetals can be used to create biodegradable polyesters unavailable from other polymerisation techniques.



Radical Ring-Opening Polymerisation for the formation of biodegradable polymersomes

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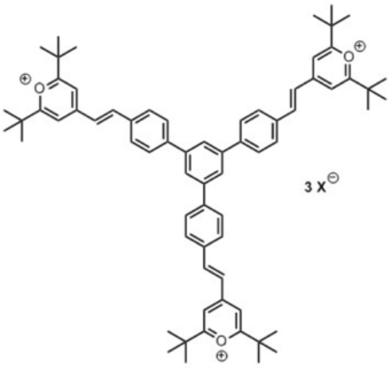
# A novel two-dimensional polymer synthesized by [2+2]-cycloaddition on the multigram scale

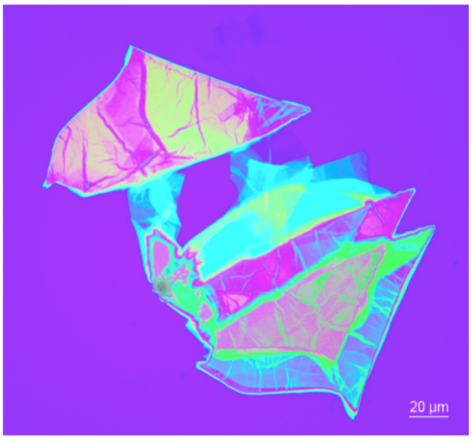
R. Z. Lange[1], G. Hofer[1,2], T. Weber[1,2], A. D. Schlüter[1]*

[1]ETH Zürich, [2]X-ray platform

Building on the results in topochemistry by Enkelmann, Novak, Wagener and Wegner[1-2] and inspired by the advances made by Hasegewa in the 1970s on linear polymers synthesized *via* [2+2]-cycloadditions in the single crystalline state[3], we introduce a new 2DP employing a styryl pyrylium dimerization reaction.[4]



**1a-d**



We here report the effortless, inexpensive and large scale (up to 28 g) synthesis of the pyrylium based triolefinic monomers 1a **–** d (a: X = ½ $SnCl_6^{2-}$ , b: X = $TfO^-$, c: X = $BF_4^-$, d: X = $ClO_4^-$), their crystallization into layered single crystals and their light induced polymerization into a novel 2D polymer. The process of polymerization leaves the single crystal largely intact and the molecular structure of the 2D polymer obtained can therefore be proven by X-ray diffraction.

Single layers of 2DPs can be isolated by immersing the crystals in a suitable solvent at 20 **–** 80 °C. The crystal elongates in an accordion-like manner so that sharp edges of thinner sheet-packages emerge. As the exfoliation proceeds, sheet-packages as thin as just a few layers or even monolayers of 2DP detach. Atomic force microscopy (AFM) of such a dispersion deposited on a $SiO_2$/Si-wafer reveals that the thinnest features have an overall approximate thickness of 1.5 – 2.5 nm, which likely corresponds to one monolayer.

Compared to existing anthracene-based 2DPs, the presented system has several advantages:
- Facile monomer synthesis from inexpensive starting materials
- Access to large crystals
- Rapid exfoliation into thin sheets

Because of the ionic nature of this polymer, intrinsic properties (electrical conductivity, porosity, non-linear optical behavior) are expected that differ from the known 2DPs. The evaluation and tuning of these properties (*e.g.* by altering the counter ion) is part of ongoing research.

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