

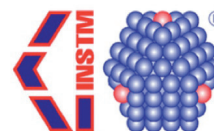
Proceedings of the Milan Polymer Days conference - MIPOL2017

What's going on in polymer science

Milan, Italy, 15-16 February 2017



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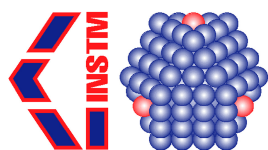


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SCIENTIFIC PROGRAMME

The conference presentations will consist of plenary lectures (PL), invited lectures (IL), oral presentations (OP) and posters (P)

Wednesday, February 15th, 2017

08:30 Registration

09:20 Opening ceremony

Francesco Demartin, University of Milan, Head of Chemistry Department

Elisabetta Ranucci, University of Milan, Conference Chair

Chairperson: Paolo Ferruti, University of Milan, Italy

09:40 PL **Julio San Roman**, CSIC, Madrid, Spain

Playing with the composition of synthetic polymeric systems for the preparation of self-assembling systems and their application in drug delivery

10:20 IL **Mario Malinconico**, IPCB-CNR, Pozzuoli, Italy

Synthesis of functionalized amphiphilic copolymers for the realization of multi-targeted nanoparticles

10:40 OP **Daniela Maggioni**, University of Milan, Italy

Transition-metal complexes of purpose tailored biocompatible and biodegradable polymers for imaging and therapy

10:55 Coffee break

Chairperson: Julio San Román, CSIC, Madrid, Spain

11:10 IL **Roberta Cavalli**, University of Turin, Italy

Polymer-based core-shell nanoparticles

11:30 IL **Minna Hakkarainen**, Royal Institute of Technology (KTH), Stockholm, Sweden

Strategies for utilizing biobased and recycled resources for tailor-making polylactide properties

11:50 IL **Francesco Cellesi**, Politecnico di Milano, Italy

Design and synthesis of complex macromolecular architectures for applications in nanomedicine

12:10 IL **Francesco Trotta**, University of Turin, Italy

Cyclodextrin-based nanosponges: a versatile class of cross-linked polymers

- 12:30 OP **Dario Puppi**, University of Pisa, Italy
Additive manufacturing of biomedical polymeric scaffolds with dual-scale porosity
- 12:45 OP **Yves M Galante**, ICRM-CNR, Milano, Italy
Aerogels of enzymatically oxidized galactomannans from leguminous plants: versatile delivery systems of antimicrobial compounds and enzymes

13:00 Lunch

Chairperson: Jaime Grunlan, TEXAS A&M University College Station, USA

- 14:00 PL **Brigitte Voit**, Leibniz Institute for Polymer Research, Dresden, Germany
Hyperbranched polymers in coating and blends
- 14:40 IL **Apostolos Avgeropolous**, University of Ioánnina, Greece
Complex architecture copolymers and terpolymers: synthesis, characterization and self-assembly
- 15:00 IL **Enrico Dalcanale**, University of Parma, Italy
Stimuli responsive polymers via molecular recognition
- 15:20 IL **Chiara Gualandi**, University of Bologna, Italy
Electrofluidodynamic techniques to design functional polymeric materials for biomedical application
- 15:40 OP **Nicolò Mauro**, University of Palermo, Italy
Graphene oxide surface functionalization of polymeric scaffolds for the recruitment and thermal ablation of tumor cells

15:55 Coffee break

Chairperson: Minna Hakkarainen, Royal Institute of Technology (KTH), Stockholm, Sweden

- 16:10 IL **Serge Bourbigot**, University of Lille, France
Flame retarded polymers: how to fight against fire?
- 16:30 IL **Jaime Grunlan**, Texas A&M University, USA
Super gas barrier nanocoatings for packaging film from water-based polyelectrolyte solutions
- 16:50 IL **Federico Carosio**, Politecnico di Torino, Italy
Flame protection of polymers through green step-by-step surface modifications
- 17:10 OP **Anna Rita De Corso**, University of Applied Science and Arts of Southern Switzerland, Switzerland

A layer by layer assembled barrier to impart flame retardancy to polypropylene substrate

- 17:25 OP **Lilian Medina**, Royal Institute of Technology (KTH), Stockholm, Sweden
Biobased nanocomposites combining strength, stiffness and fire-retardant properties

19:30 Social Dinner

Thursday, February 16th, 2017

Chairperson: Apostolos Avgeropoulos, University of Ioánnina, Greece

- 09:00 PL **Peter Dubruel**, Ghent University, Belgium
3D printing of hydrogel building blocks: going biopolymers or synthetic?
- 09:40 IL **Elisa Passaglia**, ICCOM-CNR, Pisa, Italy
Functional polymers through post-reactor modification reactions
- 10:00 IL **Alessandro Pegoretti**, University of Trento, Italy
Fiber/matrix interphase engineering in polymer composites with graphene and graphene oxide
- 10:20 OP **Andrea Dorigato**, University of Trento, Italy
Novel electrically conductive polymer nanocomposites for industrial applications
- 10:35 OP **Daniele Rigotti**, University of Trento, Italy
Polyvinyl alcohol reinforced crystalline nanocellulose in 3D printing application

10:50 Coffee break

Chairperson: Vincenzo Busico, University of Naples, Italy

- 11:05 IL **Oscar Chiantore**, University of Turin, Italy
Polymers for art conservation
- 11:25 IL **Concetto Puglisi**, IPCB-CNR, Catania, Italy
Characterization of complex polymer systems by MALDI mass spectrometry
- 11:45 OP **Massimo Mella**, University of Insubria, Italy
Killing bacteria via ion-complexing insoluble polymers
- 12:00 OP **Lorella Izzo**, University of Salerno, Italy
pH-Sensitive nanoaggregates: controlling swelling via copolymer structure and chemical composition

12:15 OP **Simona Losio**, ISMAC-CNR, Milano, Italy
Structure-properties relationship of commercial ethylene/1-octene copolymers from chain-shuttling polymerization

12:30 OP **Alessandro Piovano**, University of Turin, Italy
How to exploit the synergy between Ti^{3+} and Lewis acidic Al^{3+} sites on Al_2O_3 -supported Ziegler-Natta catalysts to produce branched polyethylene

12:45 Lunch

Chairperson: Elisa Passaglia, ICCOM-CNR Pisa, Italy

13:45 PL **Vincenzo Busico**, University of Naples, Italy
Molecular olefin polymerization catalysts: fundamentals and industrial outlook

14:25 IL **Piero Sozzani**, University of Milan Bicocca, Italy
In situ polymerization in 3D porous materials

14:45 IL **Fabio Ganazzoli**, Politecnico di Milano, Italy
Effects of the macromolecular architecture on polymer conformations and dynamics

15:05 OP **Nittaya Hansupo**, University of Lille, France
Characterization of intumescent chars by solid state NMR

15:20 OP **Francesca Selmin**, University of Milan, Italy
Exploitation of PLGA conjugates in drug delivery

15:40 OP **Stefania Zappia**, ISMAC-CNR, Milano, Italy
Water-based nanoparticles dispersions of amphiphilic low band gap block copolymers: an alternative eco-friendly approach

15:55 Coffee break

Chairperson: Fabio Ganazzoli, Politecnico di Milano, Italy

16:10 OP **Marco Coletti**, TA Instruments, Milan, Italy
Investigation on the double melting peak of PLLA using modulated DSC

16:25 OP **Günther Arnold**, Anton Paar Germany GmbH, Stuttgart, Germany
Advanced rheometric tools for polymer applications

16:40 Best poster awards

16:55 Closing remarks

PLENARY LECTURES

Playing with the microstructure of polymer systems for self-assembling and application in drug delivery

Julio San Román, Luis García-Fernández, Maria Rosa Aguilar, Blanca Vazquez, Raquel Palao, Sergio M. Saldaña

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Relevant advances in the new concept of “Nanomedicine” are based on the design and preparation of polymeric chains with specific hydrophobic or hydrophilic character by the reversible linking of bioactive compounds to macromolecular systems. This is possible by means of the reaction of functional groups present in the macromolecule, or by copolymerization of functionalized bioactive compounds or drugs, with specific polymerizable functions. This biomimetic approach offers interesting designs by selecting polymerization mechanisms and composition of the active monomers, to give high molecular weight polymers with controlled microstructure, composition and morphology.

Although the preparation of sequenced copolymers has been considered to be result of living polymerization processes by ionic mechanism or novel free radical methodologies, it is also possible to obtain controlled sequenced copolymer by traditional free radical mechanism with the selective election of vinyl or acrylic monomers with very different reactivity. In that case, the average composition of the polymer chains changes with the conversion and at the end result in copolymers with long sequences of the corresponding monomers in a gradient microstructure. If one of them is a functionalized bioactive based monomer, we will have the possibility of the preparation of polymers with specific sequences, structures and morphologies which give rise to self-assembling structures and morphologies in physiological conditions. Examples of systems with specific properties as antioxidants, complexing agents or bioactive polysaccharides will be presented. The self-assembled systems can be applied as low toxicity and high activity “Polymer Drugs” or as nanocarriers of loaded traditional drugs with limited solubility in physiological conditions. Two families of polymer systems will be presented with different behavior and morphologies. All are based on copolymers prepared by the free radical polymerization of functionalized acrylic monomers and vinyl compounds with very different reactivity ratios. The average composition of systems prepared at high conversion gives self-assembling polymers in physiological conditions with specific morphologies and very low toxicity, which allows the application as highly active antitumoral and antiangiogenic or anti-inflammatory compounds that can be applied by local injection in the human body.

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Hyperbranched polymers in coatings and blends

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Hyperbranched (hb) polymers have gained much interest in the recent years due to their special features as result from their highly branched architecture. Prepared in an easy one-pot synthesis by AB_x monomers or a combination of A_x+B_y monomers, their dense globular structure provides, similar as in their perfect but tediously to be prepared analogous, the dendrimers, a very high end group functionality, and special solution and melt properties [1]. The special advantages of the branched structures can be impressively demonstrated when studying hb polymers as blend components or additives in linear thermoplastics like polyesters, polyolefins and polyamides. Here the branching and end groups effects can significantly influence morphology and melt viscosity of the polymeric materials, improving especially processing conditions by reducing e.g. the needed energy input [2].

In addition, early on hb polymers have been considered as highly promising components in coatings as multifunctional polymeric binders and additives [3], allowing to introducing a large number of curable groups combined with a low solution viscosity and a very high compatibility with fillers and other resin components. Examples will be shown that this allowed to preparing environmentally benign solvent-free coating formulation, but also coatings with improved adhesion and low surface energies without the danger of any additive surface migration. Hb polymers also allow to preparing transparent nanocomposite coatings of highly improved mechanical properties and durability. More recently, hb polymers proved to be excellent candidates for various high performance films also for optoelectronic applications [4].

Thus, hb polymers as polymers with a special designed macromolecular architecture help to contribute to a brighter living by reducing energy input in processing, enhancing life time and performance in polymeric products, reducing volatile products and additive migration, but also making new technologies possible to the benefit of the end users.

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3D printing of hydrogel building blocks: going biopolymers or synthetic?

Peter Dubruel, Sandra Van Vlierberghe, Jasper Van Hoorick, Annemie Houben, Nele Pien, Aysu Arslan, Thomas Billiet

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Polymers have found widespread applications in the medical field. Examples range from orthopaedic over ocular and cardiovascular applications to the field of drug delivery. In some more recent cases, materials embracing several functions (mechanical as well as therapeutic) are applied, drug eluting stents being a prominent example.

One of the more novel evolutions in the biomaterial field includes the application of 3D printing with the aim to develop patient specific implants. This research domain has been and is growing exponentially both in terms of the variety of applied materials, applications and 3D printing devices (commercially available and custom-made).

Since 2008, the activities of our research group have focussed on applying 3D printing technologies for the printing of hydrogel building blocks and (biodegradable) polyesters. In this presentation, 3D printing of cross-linkable gelatins and polyethylene oxides, ... will be discussed for applications in the field of orthopaedics, liver regeneration, drug screening, ...

Surface and bulk modification technologies on 3D printed scaffolds being biocompatible while lacking cell-interactive properties will be highlighted. The applicability of indirect printing technologies will be discussed for those hydrogel building blocks that have printing-related limitations (e.g. viscosity, mechanical stability, ...).

In a last part of the presentation, the advantages, drawbacks and emerging opportunities in the field of 3D printing of polymers will be discussed.

Acknowledgments

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Molecular olefin polymerization catalysts: fundamentals and industrial outlook

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Molecular catalysts for olefin polymerization were disclosed almost as early as heterogeneous Ziegler-Natta and Phillips ones. However, for over two decades the lack of understanding of their activation mechanism hampered practical use. The serendipitous discovery of methylalumoxane (MAO) represented the breakthrough that ultimately triggered the dramatic boost of the last 30 years.

Compared with heterogeneous systems, the well-defined nature of the precursor species is unquestionably of great advantage to tailor application, but it is not much more than a convenient starting point; downstream, a smart identification of the target, based on a solid understanding of the chemistry and a clear vision of the market, is mandatory to succeed. In this talk, some case histories will be discussed in order to highlight the concept.

ORAL PRESENTATIONS

Synthesis of functionalized amphiphilic copolymers for the realization of multi-targeted nanoparticles

Mario Malinconico,^a Giovanni Dal Poggetto,^a Alessandra Romanelli,^b Fabiana Quaglia,^b Paola Laurienzo^a

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Nanoparticles (NPs) have attracted significant attention in the field of innovative anticancer therapies. The most common approach to improve selectively their accumulation in tumor tissues remains surface decoration with small targeting moieties recognizing specific receptors that are over-expressed in cancer cells.

Surface-decorated NPs can be prepared by either post-modification of the surface, or by synthesizing tailored all-in-one amphiphilic copolymers. With this approach, the number and nature of molecules on the surface of the resulting NPs can be finely tuned, also avoiding the premature release of drug cargo. Furthermore, NPs made with a charged copolymer can be decorated on the surface with bioresponsive polymers through electrostatic interactions. The lecture will describe two different synthetic approaches: NPs made by self-assembling amphiphilic copolymers bearing the target unit covalently linked on the hydrophilic chain end, and cationic NPs, able to deeply penetrate inside tumors, decorated with hyaluronic acid (HA).

In the first case, copolymers are made up of PEG as hydrophilic block and PCL as hydrophobic one; in this way, methods of synthesis aimed to asymmetrically modify PEG in order to introduce ethero end groups are largely explored in literature. Here, a simple route of synthesis to selectively obtain PCL-PEG- γ Folate (Fol) copolymer, with high yield and purity is described. It is known from literature that only γ -folate conjugates retain affinity towards folate-receptor α , that is overexpressed in the majority of cancer cells. Furthermore, we demonstrate that the extent of specific internalization of targeted nanoparticles can be improved by regulating the length of the PEG chains in PCL-PEG to attain stealth properties (1000 Da) and in PCL-PEG- γ Fol to improve Fol exposition on NPs surface (1500 Da). Formulations of NPs using amphiphilic copolymers with different length of PEG blocks turned to be a good strategy to enhance exposition of Fol on their surface.

In the second case, amino-terminated homopolymer PCL was synthesized to obtain PCL- or PEG-PCL-based NPs with cationic surface. Cationic NPs can be “covered” with anionic molecules, like HA, through non-covalent interaction. HA encourages NPs uptake in cell overexpressing CD44 receptors. We showed how modulation of surface charge density influences cell uptake.

Transition metal complexes of purpose-tailored biocompatible and biodegradable polymers for imaging and therapy

Daniela Maggioni,^a Marco Galli,^a Daniela Donghi,^a Giuseppe D'Alfonso,^a Amedea Manfredi,^a Alessandro Lascialfari,^b Paolo Arosio,^b Laura D'Alfonso,^c Roberta Cavalli,^d Elisabetta Ranucci,^a Paolo Ferruti^a

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Poly(amidoamine)s (PAAs) are a family of synthetic polymers obtained by Michael-type polyaddition of amines to bisacrylamides. Their polymer chain contains *tert*-amino and amido groups in regular succession. In addition, many reactive functional groups can be introduced as side substituents [1]. Several PAAs have been shown to possess a remarkable potential for biomedical applications in that they are biodegradable and biocompatible, and owing to their versatility can be tailored to specific applications. In particular, amphoteric PAAs, which in extra cellular fluids (pH 7.4) are zwitterionic but predominantly anionic, are highly biocompatible and exhibit a “stealth-like” behavior, that is, after intravenous injection in test animals are not captured by the reticulo-endothelial system and have a prolonged permanence in the blood circle. They tend to aggregate in water solutions in the form of small nanoparticles with hydrodynamic diameters in the range of 5–20 nm [2], and in tumor-bearing animals, they are passively concentrated in the tumor tissues by the so-called EPR (enhanced permeation and retention) effect [3]. They are therefore very attractive as carriers for molecular complexes. For this purpose our attention was captured by the possibility to synthesize poly(amidoamine) copolymers bearing in the minor repeating unit a suitable chelating pendant. In this context, the presentation intends to show the most significant results obtained in the last years (Figure 1), which have led to the preparation of rhenium, ruthenium, iridium and gadolinium polymer complexes, as optical imaging probes, γ and β emitter probes (for SPECT imaging and therapy, respectively), photodynamic therapy (PDT) agents, and T₁ and T₂ relaxing agents for magnetic resonance imaging (MRI).

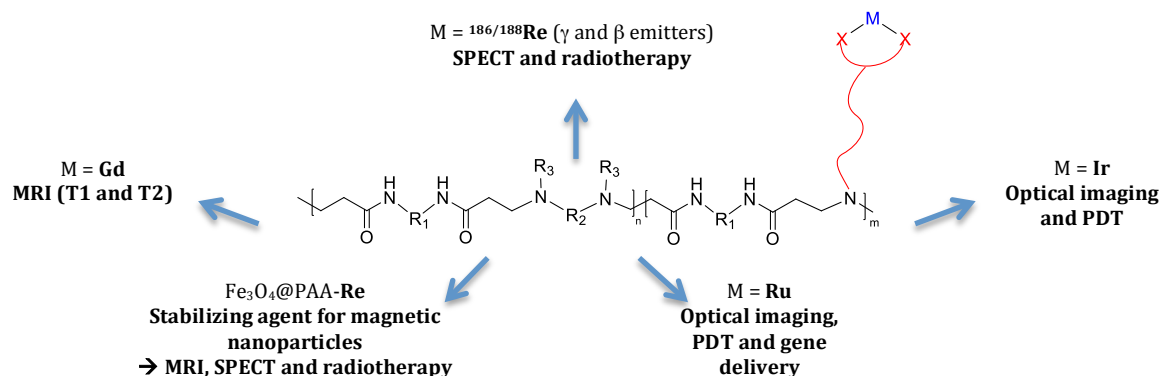


Figure 1.

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Polymer-based core-shell nanoparticles

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Nanoparticle-based drug delivery enables innovative tactics to fight diseases. With their small size and their engineered surfaces, nanoparticles can improve control over drug release, both spatially as well as temporally and can reduce adverse side effects. Furthermore, improved targeting and shielding capabilities allow for more favorable pharmacokinetic and pharmacodynamics profiles. Polymer nanodelivery systems are of special interest for biomedical applications.

A number of nanostructures have been developed and among them core-shell nanoparticles have attracted much research. Their structure consists of an internal core coated with a suitable shell. They represent a feasible way to attain multiple functionalities on a nanoscopic length scale. The shell provides an interface especially designed to tune particle characteristics and interaction with biological environment.

Core-shell nanoparticles have some advantages leading to the improvement of properties such as less cytotoxicity, increase in dispersibility, bio- and cyto-compatibility, better conjugation with other bioactive molecules, increased thermal and chemical stability.

In addition the surface modification can be exploited to obtain smart systems that deliver therapeutic molecules on demand, in the desired site of action, following an external stimulus. The core generally entraps the drug, but it can be encapsulated or attached to the surface of the core/shell NP.

Recently, various polymer core-shell nanoparticles have been designed. Here some liquid-cored system, such as nanocapsules, nanobubbles and nanodroplets, will be described.

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Strategies for utilizing biobased and recycled resources for tailor-making polylactide properties

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Sustainable development requires taking care of and reusing the waste produced. Here, some strategies for valorization of model biopolymer waste to functional chemicals and carbon products [1-3] and further utilization of the derived products as property enhancers in polylactide (PLA) materials are presented. These approaches retain the material value of the biopolymers as well as the degradability and biobased nature of PLA, while broadening of the application areas and properties of PLA is simultaneously achieved. As an example a two-step green and industrially viable process for achieving novel flexible fully biobased PLA with low plasticizer migration rate was demonstrated [4]. The first step included effective recycling of polyhydroxybutyrate (PHB) to functional bioplasticizers. This was achieved by thermal degradation of PHB in an extruder resulting in oligomeric PHB (dPHB) with crotonate end-groups. The second step consisted of covalent anchoring of the obtained oligomeric plasticizer candidates onto polylactide (PLA) chain by reactive extrusion. 20 % (w/w) grafted dPHB increased plain PLA's elongation at break from 7.7% to 538%. Microwave-assisted processes offer another promising approach for rapid and complete degradation of PHB to monomeric degradation products (crotonic acid (CA), 3-hydroxybutanoic acid (3HB) and 3-methoxybutanoic acid (3MB)) in only 20 minutes at 110 °C [5]. The crotonic acid units were further utilized to functionalize PLA main chain and PLA-CA-PBSA was prepared by coupling poly(butylene succinate-co-adipate) (PBSA) to the crotonic acid functionalized PLA [6]. We have also quantitatively degraded cellulose, starch and waste paper to green chemicals and to solid 3D carbon spheres [1-3]. Functional biobased carbon products were created through further oxidation of the obtained carbon spheres to nanosized graphene oxide type carbon dots [7]. These dots were shown to be effective nucleating agents and compatibilizers controlling crystallinity, mechanical and barrier properties of PLA materials and composites [8,9]. The addition of carbon dots could also induce mineralization on the surface of polymer films and scaffolds [10].

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Design and synthesis of complex macromolecular architectures for applications in nanomedicine

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Biocompatible polymers with complex, well-defined macromolecular architectures have recently found promising applications in the field of nanomedicine.

Controlled living polymerisations, including Ring Opening Polymerisation (ROP) and Atom Transfer Polymerisation (ATRP), allow a precise synthesis of macromolecules with predetermined molecular weight [1], controlled topology (linear, multiarm, comb-like, block copolymers) and functionality. Moreover, a combination of these polymerisation techniques with convenient post-functionalisation via click-chemistry (azide-alkyne cycloaddition, thiol-ene conjugation), may be used to produce ultrasmall, amphiphilic and multifunctional polymeric drug nanocarriers, which are able to cross specific biological barriers and target cells, tissues, organs.

ATRP combined with Michael-type addition was investigated for the synthesis of novel immunoactive nanomaterials, based on multifunctional poly(glycerol methacrylate)s which contain dangling immunogenic sugar moieties. By varying polymer composition and architecture, we aimed at developing a new class of bio nanomaterials for antigen-presenting cell targeting and controlled immunostimulation [2].

Ultrasmall polymeric nanocarriers having size distributions below 20nm (5-20nm) were designed to facilitate drug permeation through the glomerular filtration barrier in kidneys, and to target podocytes, cells which are known to play a central role in the progression of proteinuria (loss of proteins in the urine) and chronic kidney diseases(CKD) [3].

These nanomaterials contained multi-arm polyesters, which were obtained from poly (ϵ -caprolactone)-based macromonomers and/or macroinitiators, previously synthesized by ROP. Core-shell nanostructures were achieved by introducing large hydrophilic comb-like coronas, generated by copolymerisation of poly (ethylene glycol)-based macromonomers.

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Cyclodextrin-based nanosponges: a versatile class of cross-linked polymers

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Cyclodextrins (CDs) are cyclic oligosaccharides composed of glucopyranose units placed around a slightly hydrophobic internal cavity, which can host guest molecules, through the formation of an inclusion complex. The addition of suitable bi- or polyfunctional cross-linking agents, capable of reacting with the hydroxyl groups of CDs, can lead to the formation of hyper-cross-linked polymers, commonly named “Nanosponges” (NSs). NSs are characterized by a superior ability to absorb and encapsulate target compounds, owing to the inner cavities of CDs and the interstitial voids around CDs. The properties of a NS and its affinity for specific molecules can be extensively tuned by changing the type of CD and cross-linker.

Over the past few years, different types of CD-based NSs have been successfully employed for several applications. In the pharmaceutical field, molecularly imprinted carbonate CD-NSs have been produced, using L-DOPA as template molecule, for the storage and controlled delivery of L-DOPA in the treatment of Parkinson’s disease [1]. A polyester CD-NS, bearing disulphide bridges, has been developed as a new glutathione-responsive drug delivery system for the targeted release of anticancer drugs [2].

CD-NSs have also been tested for agrochemical applications: a variety of pesticides, insecticides and herbicides have been encapsulated either by addition to a pre-synthesized NS (post-synthesis loading) or addition during the preparation of the NS (molecular imprinting). In general, the complexation of active principles in CD-NSs leads to significant benefits, such as protection from degradation and a more prolonged release kinetics.

An O₂ selective membrane, capable of reducing the entrance of H₂O and CO₂ in Li-air batteries, thus prolonging the charge-discharge life cycle, has been prepared by adding a citric acid-dextrin-CD-based NS to poly(vinylidene fluoride co-hexafluoropropylene) matrix. Thanks to the protective effect of the membrane, the cycling performance of the cell was extended up to 145 cycles [3].

Another potential application of CD-NSs concerns the treatment of wastewaters. Polyester CD-NSs rich in carboxylic moieties have been proven to be able to bind heavy metal cations by ion exchange, while the internal cavities of CDs can absorb unwanted hydrophobic organic molecules, thus helping in the decontamination of polluted waters.

Finally, pyromellitate CD-NSs have been used as precursors for the preparation of microporous carbons. Through a pyrolysis process, performed up to 800 °C under N₂ flow, carbon materials with a peculiar hollow spheres structure and a narrow pore size distribution (5-16 Å) were obtained and fully characterized [4].

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Additive manufacturing of biomedical polymeric scaffolds with dual-scale porosity

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Stemming from the first pioneering works carried out in the late nineties [1], a large body of literature has been published on the employment of various additive manufacturing (AM) techniques (e.g. Fused Deposition Modelling) for the development of polymeric porous scaffolds tailored to different biomedical applications, such as bone tissue engineering and cranioplasty prostheses. In addition, combining the working principles of AM with other polymer processing techniques, such as freeze drying and wet-spinning, has been recently investigated as a successful approach to endow a scaffold with a multilevel pore arrangement. In this context, computer-aided wet-spinning (CAWS) has been developed within our research group as a novel hybrid AM technique, based on the computer-controlled deposition of a coagulating polymeric fibre extruded directly into a coagulation bath, to build up 3D scaffolds with a layer-by-layer process [2]. The resulting porous structure is characterized by a fully interconnected network of pores with a size in the range of tens to hundreds of micrometres, determined by the fibre lay-down pattern, and a local nano/microporous morphology of the polymeric matrix that can be controlled by acting on different parameters of the phase inversion process governing polymer solidification (Figures 1a,b). This manufacturing approach represents a powerful tool to tune key scaffold properties affected by porosity features at different scale levels, such as mechanical behaviour, biodegradation rate and surface roughness. Dual-scale porous scaffolds with a customized external shape, potentially resembling that of a specific anatomical part (Figures 1b,c), and made of different biocompatible polymers, e.g. poly(ϵ -caprolactone) (PCL), poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) and poly(methyl methacrylate), have been developed by CAWS.

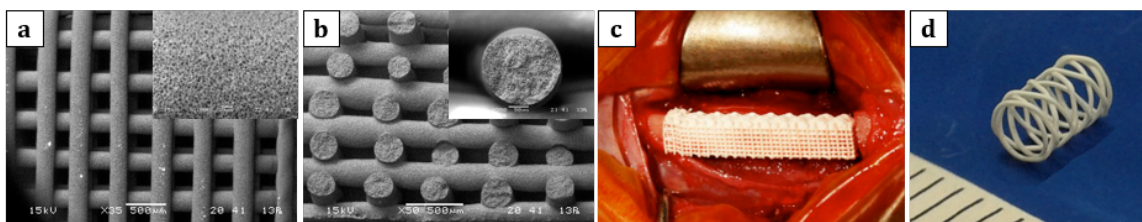


Figure 1. Scanning Electron Microscopy micrographs of poly(ϵ -caprolactone) (PCL) scaffolds by CAWS: (a) top view, (b) cross section [2]. Photographs of (c) an anatomical three-arm star PCL scaffold modelled on a critical size (2 mm) defect in a rabbit radius model [3], and (d) a small calibre intravascular PCL stent (measure unit = 1 mm).

A further advantage of CAWS is the possibility of directly functionalizing the scaffold during its fabrication by processing a polymeric solution containing a bioactive agent as solute or suspension, as recently demonstrated by studies on hydroxyapatite- or levofloxacin-loaded polymeric scaffolds for bone tissue engineering [3,4].

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Aerogels of enzymatically oxidized galactomannans from leguminous plants: versatile delivery systems of antimicrobial compounds and enzymes

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We describe aerogels from laccase-oxidized and lyophilized galactomannans (GM) of the leguminous plants fenugreek, sesbania and guar and suggest their potential practical uses as innovative delivery systems (DS) of active principles. GM are high molecular weight polysaccharides found in the seed endosperms of some *Leguminosae* (belonging to the family *Fabaceae*). They have a branched polymeric structure composed of a backbone of mannose units linked by β -1,4 glycosidic bonds with side units of galactose bound to mannose by a α -1,6 glycosidic bond. The average ratio of galactose to mannose (Gal:Man) is variable, depending on the plant species, and ranges from 1:4.5 in cassia (*Cassia tora*) to 1:1 in fenugreek (*Trigonella foenum-graecum*). The species-dependent monomers ratio makes them, to various extents, soluble in water at different temperatures, chemically/biochemically quite reactive and flexible in application.

GM and their derivatives are used as rheology modifiers, thickening and suspending agents in food, feed and manufacturing industries. They find application as excipients and co-formulants in the biomedical field, such as in pharmaceutical and are also increasingly consumed as dietary fibers with atoxic bioactivities, as texture modifiers and stabilizers in “specialty” foods.

Laccase/TEMPO oxidation of GM in aqueous solution caused a viscosity increase up to fifteen-fold. Structured, elastic, stable hydrogels were generated, due to formation of carbonyl groups from primary OH of galactose side units and subsequent establishment of hemiacetalic bonds with available free hydroxyl groups. Upon lyophilization of these hydrogels, water-insoluble aerogels were obtained, capable of uptaking aqueous or organic solvents several times their own weight. These material were characterized by SEM, FT-IR, elemental analysis and ^{13}C CP-MAS NMR spectroscopy, their mechanical properties were investigated and porosity determined by Hg absorption under high pressure.

To test these new materials as delivery systems, the following model actives were absorbed into GM aerogels from aqueous solutions: the chemical biocides CIT/MIT; the antibiotic polymyxin B (very effective against Gram-negative bacteria); the antimicrobial peptide nisin; the enzymes lysozyme, protease and lipase, followed in all cases by repeated cycles of water rinsing, to eliminate surface-absorbed compounds, dry blotting and re-lyophilization of the hydrogels to generate “loaded” aerogels. The gradual release of the incorporated actives was monitored by measuring enzyme activity in solution or in Petri dish on agar culture medium, seeded with different bacterial strains, by evaluating the inhibition halo of cell growth.

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Complex architecture copolymers and terpolymers: synthesis, characterization and self-assembly

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In this work we report the synthesis, characterization and properties of non-linear block copolymers prepared by anionic and controlled radical polymerization (ATRP) in order to show the well-defined microstructures adopted in bulk when these materials are studied morphologically. Very well ordered morphologies with minor defects and dislocations are evident leading to the conclusion that these copolymers are good candidates for directed self-assembly in thin films for nanolithographic applications.

The synthesis of linear asymmetric triblock copolymers of the ABA' type (A and A':PS, B:PI) and asymmetric miktoarm star-copolymer of the A(BA')_n type (A and A':PS, B:PI) where n = 2 and 3 is reported via anionic polymerization and high vacuum techniques in combination with chlorosilane chemistry [1]. The linear triblock copolymers of the SIS' type were synthesized via sequential addition of the corresponding monomers. Details on the synthesis of all samples are already reported in the literature [2,3]. Blending of these copolymers with homopolymer PS of various molecular weights and weight fraction concluded to the observation of a new thermodynamically stable, aperiodic "bricks and mortar" (B&M) cellular mesophase structure where PS comprises discrete hard "bricks" and PI the continuous soft "mortar" [4,5]. Furthermore, star triblock terpolymers of the (PS-*b*-P2VP-*b*-PEO)₃ type and one dendritic-like terpolymer [PS-*b*-P2VP-*b*-(PEO)₂]₃ of PS: polystyrene, P2VP: poly(2-vinylpyridine) and PEO: poly(ethylene oxide), never reported before, were synthesized by combining atom transfer radical (ATR) and anionic polymerizations. The synthesis involves the transformation of the previously reported Br-terminated 3-arm star copolymers [6] to one or two -OH groups, followed by anionic polymerization of ethylene oxide to afford the star or dendritic structure respectively. The well-defined structure of the terpolymers was confirmed by static light scattering (SLS), size exclusion chromatography (SEC) and NMR spectroscopy. The self-assembly in water, a selective solvent for PEO and the morphology in bulk of the terpolymers, studied by dynamic light scattering (DLS) and transmission electron microscopy (TEM) respectively, revealed new insights in the self-assembly of these complex macromolecular architecture materials [7].

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Stimuli responsive polymers via molecular recognition

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Supramolecular polymers, i.e. non-covalent polymers, represent a novel class of materials that combine many of the attractive features of conventional polymers with the properties that result from the reversibility of the bonds between the monomeric units. This unique feature of self-assembled supramolecular polymers conveys many interesting properties, among which error-checking, responsiveness to specific external stimuli and self-healing are prominent. In the present contribution, supramolecular polymers based on phosphonate cavitands will be presented, in which the polymerization is driven by host-guest complexation [1,2]. In particular, the following examples will be discussed: (i) polymer blending as macroscopic expression of molecular recognition [3] (Figure 1), (ii) electrochemical responsive host-guest polymers in the solid state [4] (Figure 2) and (iii) strain-field self-diagnostic elastomers.

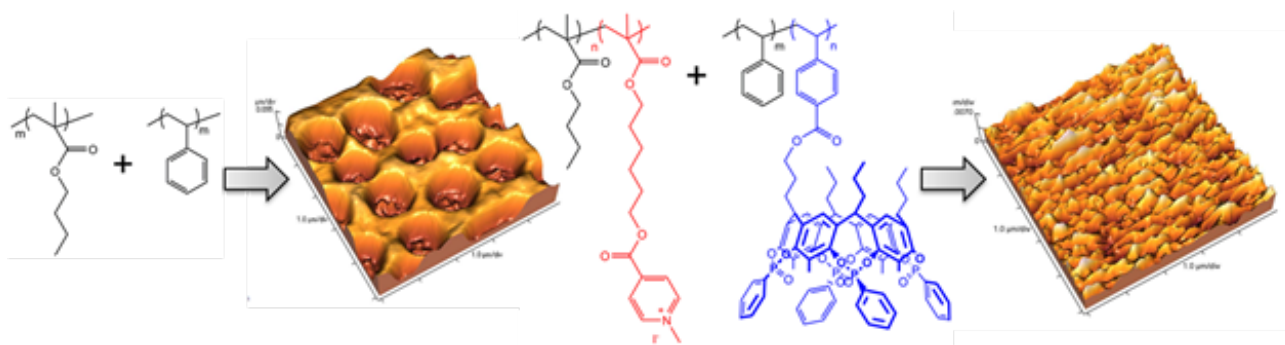


Figure 1. Polymer blending of a polystyrene HOST and a poly(butylmethacrylate) GUEST seen by AFM.

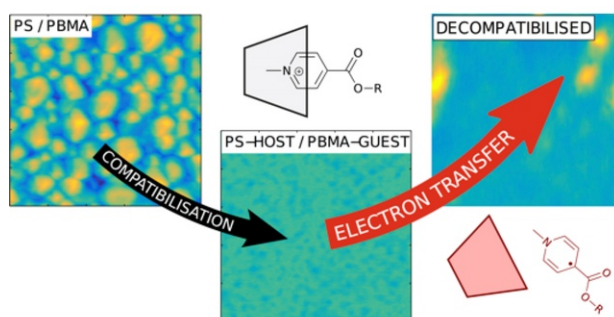


Figure 2. Films of a supramolecularly compatibilised polystyrene/poly(butylmethacrylate) blend show pore opening upon application of an electrochemical stimulus.

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Electrofluidodynamic techniques to design functional polymeric materials for biomedical application

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Electrofluidodynamic techniques apply electrical forces to polymer solutions to gain either microparticles (electrospraying) or continuous fibres with sub-micrometric diameters (electrospinning). Fibers produced by electrospinning can be assembled either into 2D non-woven mats or to develop 3D porous structures [1].

The great potentiality of electrospun polymeric materials is mainly expressed in the biomedical field [2] where they are predominantly applied for tissue engineering applications, drug delivery and filtration of biological fluids. The key features of electrospun materials that make them extremely attractive as biomedical products are: (i) their inherent high surface to volume ratio; (ii) the possibility to engineer morphologically biomimetic scaffolds that resemble the fibrous structure of the natural extracellular matrix; (iii) pore interconnectivity that makes the entire porous structure fully accessible to chemical species and (iv) the possibility to engineer multi-functional hierarchically organized composites designed to fit the structural and chemical requirements of the specific biomedical application [3].

This presentation will give an overview of frontier-research on biomedical applications of electrospun polymeric materials and will provide examples highlighting the possibility to control and modulate material properties thanks to smart combination of both commercial and newly synthesized polymers, surface functionalization techniques and different instrumental setups.

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Graphene oxide surface functionalization of polymeric scaffolds for the recruitment and thermal ablation of tumor cells

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The control of metastatic spread of a primary tumor is related to good probability of eluding extravasation of cancer cells to target organs, thereby containing the progression of disease burden [1]. Circulating tumor cells (CTCs) in the bloodstream have been recently correlated to metastasis outbreak [2], therefore much attention has been focused on the capture of CTCs on functional biomaterials to limit tumor growth. We developed a electrospun microfiber scaffold composed of poly(caprolactone) layered with graphene oxide (GO) sheets at the microfiber surface, named PCL_{MF}-GO, able to simultaneously recruit CTCs and kill them by non-invasive near infrared-assisted photothermal ablation. Here, nitrogen plasma activation was used for scaffold engineering to provide functionalization of the scaffold surface with reactive amines, even if keeping bulk properties of the virgin polymeric material, and to enhance cell adhesion properties of hydrophobic polymers [3]. We investigated the covalent nature of the interactions taking place between GO and amines inserted through plasma exposure by DSC, FT-IR, SEM, AFM and XPS analyses. SEM was employed for the direct morphological study of the PCL_{MF}-GO scaffold. It is evident that microfibers did not display significant damage after the treatment with N₂ plasma (Fig. 2 A-B) and that GO sheets are closely adhered to the microfibers surface, even linking adjacent microfibers (Fig. 2A). AFM analysis shows (Fig. 2C) that PCL_{MF}-GO exhibited a surface characterized by rough and porous areas, typical of polymeric materials, near to highly smooth surface 1 nm thickness that can be credited to the GO monolayers, thus indicating that GO sheets are firmly attached to the mat by the covalent bonds established with amine intermediates provided by N₂ plasma activation. The in vitro preferential recruitment of breast cancer cells (MCF-7) instead of normal fibroblasts (HDFa) was studied as function of non-specific GO-mediated recognition, suggesting a potential pivotal role of GO in recruiting cancer cells in vivo (Fig 2D). We also display that GO deposition, thanks to the high near-infrared (NIR) absorbance, enable the discrete photothermal eradication of the captured cancer cells in situ (\approx 98%). Moreover, this technology can be used to capture circulating cancer cells in patients and, after proper ex vivo propagation, to develop biomarkers and tailor-made anticancer therapies.

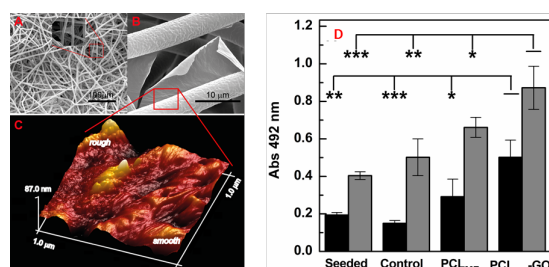


Figure 1. SEM (A and B) and AFM (C) of PCL_{MF}-GO. Cell adhesion properties of PCL_{MF}-GO using MCF-7 cells (D): the cell viability is reported after an incubation time of 6 and 24 h.

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Flame retarded polymers: how to fight against fire?

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The development of science and technology provides the availability of sophisticated products but concurrently, increases the use of combustible materials, in particular polymeric materials. The organic polymers are easily flammable and must be flame retarded to make them safer. To do so, flame retardants (FRs) are very often incorporated into them to limit their flammability. Other methods than FRs can be used: inherently flame retarded polymers (e.g. polyimide, PEEK and polybenzoxazoles) and chemically modified polymers (e.g. grafting of FR function and copolymerization with FR) can also be considered if the cost of the material is not an issue. The talk will review the different methods to make flame retardant polymers with the incorporation of FRs and by the application of FR coatings. The different mechanisms involving the gas phase (e.g. poisoning the flame by radical trapping) and the condensed phase (e.g. formation of a protective ceramic) [1] will be fully commented. A special emphasis will be done on intumescence [2].

Intumescence is a versatile method for providing reaction and resistance to fire to materials. When heated beyond a critical temperature, the intumescent material begins to swell and then to expand forming an insulative coating limiting heat and mass transfer. The talk will consider the use intumescence (coating and flame retardants) to make flame retarded polymeric materials and fire barrier on substrates. Examples are: (i) the resistance to fire of composite (aircraft post-crash fire and flame spread) by an intumescent paint (Figure 1 (a)) and (ii) the use of intumescent flame retardants in thermoplastics (E&E applications) for improving their fire properties (Figure 1 (b)). For all topics mentioned above, it will include a special emphasis on the mechanism of action involved in the fire protection and on the associated experimental method.



Figure 1. a) infrared image of the development of an intumescent coating at the jet fire test (propane burner, heat flux of 200 kW/m²) protecting composite and b) cone calorimeter residue (experiment done at 50 kW/m²) of an intumescent glass fiber reinforced polybutylene terephthalate (PBT).

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Super gas barrier nanocoatings for packaging film from water-based polyelectrolyte solutions

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Layer-by-layer (LbL) assembly is wide-reaching conformal coating “platform” technology capable of imparting a multiplicity of functionalities on nearly any type of surface in an environmentally friendly way. At its core, LbL is a solution deposition technique in which layers of cationic and anionic materials (e.g. clay nanoplatelets, polymers and even biological molecules) are built up via electrostatic attractions in an alternating fashion. Here we are producing nanocomposite multilayers having 10–96 wt% clay that are completely transparent and exhibit oxygen transmission rates (OTR) below $0.005 \text{ cm}^3/\text{m}^2\cdot\text{day}$ (at a film thickness below 100 nm). The oxygen permeability is an order of magnitude below SiO_x coatings and competitive with metalized layers. Unlike those inorganic high barrier layers, these water-based coatings do not suffer from poor adhesion and pinholes. This exceptional oxygen barrier makes these layers interesting for food, pharmaceutical and flexible electronics packaging. Contrary to popular belief, these films can be deposited very quickly (seconds per layer) and maintain near perfect clay platelet orientation. I’ll also describe how these films can also act as a barrier to hydrogen gas, reducing the permeability of a 51 mm polystyrene film 1000X with only a 122 nm thick coating containing five clay layers. All of the coatings described are water-based, transparent, metal-free and processing occurs under ambient conditions. I’ll also describe a “onepot” coating system based upon an aqueous polyelectrolyte complex containing polyethylenimine and polyacrylic acid. A 2 mm coating reduced the OTR of a 127 mm PET film by 100X. Our work has been highlighted in *C&EN*, *ScienceNews*, *Nature*, *Smithsonian Magazine*, *Chemistry World* and various scientific news outlets worldwide (<http://nanocomposites.tamu.edu>).

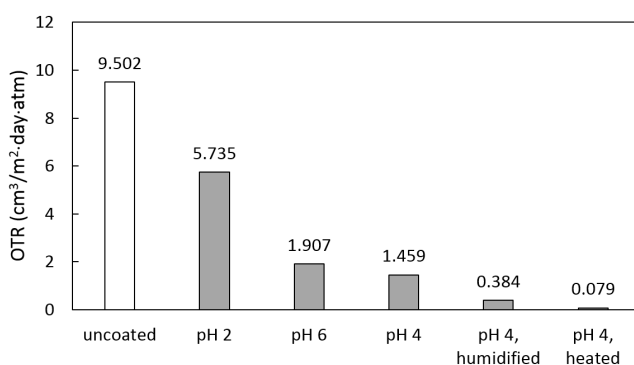


Figure 1. Oxygen transmission rate (measured at 50% relative humidity) of 127 mm PET without a coating and coated with a 2 mm PEI/PAA coacervate, treated with varying pH buffer and/or heat.

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Flame protection of polymers through green step-by-step surface modifications

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Polymer combustion is fuelled by pyrolysis products escaping from its surface due to the heat transferred from the flame to the polymer surface and also radiated from the flame itself [1]. The most significant polymer degradation reactions usually occur in the condensed phase, as they take place mainly within 1 mm of the interphase between the flame and polymer, where the temperature raise is high enough. Therefore, the polymer surface can be considered the critical zone in the polymer combustion scenario because, being the interface between the gas and condensed phases, it controls mass and heat transfers which are the processes responsible for flame fuelling [2]. One of the most valuable fire retardant strategy pursued by bulk addition, proved to be the production or accumulation of a thermally stable surface layer able to act as a barrier to mass and/or heat exchange. Such a layer is built during the early stage of combustion as a consequence of polymer surface layer decomposition. However, the time required for build-up of the surface barrier is straightforwardly connected to the development of the fire in the early stage, consequently adversely affecting the effectiveness of the protective barrier.

Here it is shown how the combination of advancements in polymer surface engineering and development of nanotechnologies supplies an innovative environmentally friendly approach to fire retardance, based on providing polymer material products with a surface barrier, which either reradiates heat and/or slows down heat transmission and volatiles diffusion, without affecting the bulk properties. To this aim, the layer-by-layer (LbL) assembly will be proposed as an alternative and eco-friendly tool for the construction of flame-retardant nanostructured coatings capable of protecting different substrates such as cotton, polyurethane foams, plastic thin films and PET fabrics. Thanks to the versatility of this technique, it is possible to target different surface flame-retardant mechanisms by the appropriate choice of the layer constituents and the deposition parameters. To this purpose, Layer-by-Layer assembly [3], will be thoroughly described through selected examples concerning different types of substrates. In particular, the potentialities of this technique will be discussed in terms of the development of novel and environmentally sustainable flame retardant coatings containing deoxyribonucleic acid (DNA), chitosan and starch [4-6].

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A layer by layer assembled barrier to impart flame retardancy to polypropylene substrate

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The so-called layer by layer (LbL) deposition technique was introduced over fifty years ago but is still little used at industrial scale. The LbL method is an environmental friendly and low-cost approach toward nanoscale multilayers films that allows to modify different kind of substrates.

Our research activity was focused on exploiting the LbL technique to impart flame retardant features to a polypropylene substrate.

This research is part of an industrial project aimed at replace a PVC products with a new halogen free material. The target performance is Euroclass B according to the EN 13823 (Single Burning Item) test. Starting from formulations already investigated at laboratory scale [1-3] several multilayers have been deposited on the polypropylene film through the LbL assembly. Intumescent multilayers based on polycations and phosphorous compounds have been studied; char forming agents selected within the family of water-based starches were included in the coating formulation to improve the formation of a carbonaceous residue during combustion. Furthermore by considering eco-friendliness [4] and the already proved [2] efficiency of clay based flame retardant coating, nanofilled multilayers were investigated. Particularly sodium montmorillonite have been coupled with positive alumina-coated silica nanoparticles to build-up an inorganic coating. In addition the synergism among different flame retardants and different sequence of the layers have been investigated. The combustion tests show that the inorganic coating provides an effective shield that delays the polypropylene melting and reduces the maximum heat release rate.

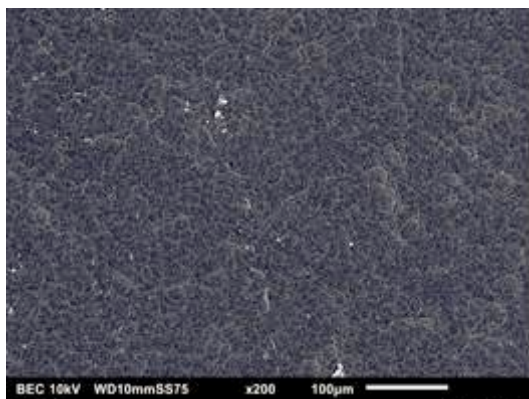


Figure 1. SEM surface of coated PP film



Figure 2. Coated PP film during combustion test

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Biobased nanocomposites combining strength, stiffness and fire-retardant properties

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Research in the field of bio-based materials has received increased attention in the recent years in an attempt to move towards a more sustainable society. In this field, cellulose nanofiber, termed CNF, is of a particular interest due to its intrinsic high strength, stiffness, light weight and abundancy combined with a low cost. However, one of the main drawback of cellulose is its intrinsic flammability, and using halogenated flame-retardant compounds does not suit the concept of environmentally sustainable materials. Phosphorylation of individual cellulose nanoparticles and layer-by-layer approach are some methods developed to improve fire protection of nanocellulosic products, but they both have their limit. Here we suggest the use of montmorillonite clay nanoplatelets in combination with CNF to produce fire-retardant materials. The beneficial effect of nanoclay as a fire-retardant filler is well established and the water-based processing route of CNF accomodates very well the use of clay nanoplatelets.

Inspired from paper-making processes, cellulose/clay thin sheets have been prepared by vacuum filtration and used as a fire protection coating for wood [1] and composites panel [2]. Cellulose/clay porous aerogels have also been produced by freezing a hydrocolloidal CNF/nanoclay co-suspension and subsequent drying under reduced pressure. Both the films and aerogels exhibit some extent of fire-retardancy and other valuable properties such as high stiffness and strength. This unique combination makes these nanocomposites potentially useful in load-bearing applications where fire-retardancy is important, for instance in transport applications.

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Functional polymers through post-reactor modification reactions

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To meet the growing demand of sophisticated technological requirements, polymer-based materials are often complex systems whose preparation combines different methodologies not only typical of macromolecular synthesis, but integrating technologies related to post-polymerization modification approaches ranging from the grafting of specific functionalities to the design of nanostructured composites, and involving skills of physics, materials engineering, biology (depending on final application purposes).

In this scenario the grafting of different functional groups onto polymers is a suitable approach applied to achieve specific properties not naturally intrinsic to the starting macromolecules. Moreover, the classical radical post-polymerization modification of the polymer matrix by using unsaturated monomers does not respond to the requirement of selectivity and does not guarantee the structural preservation of the pristine macromolecular architecture. Indeed, the presence of the propagation and chain transfer steps, increases the amount of free radicals during the functionalization process, causing the occurrence of typical side reactions. Instead, by using a new functionalizing strategy, the nitroxide radical coupling (NRC) reaction, it is possible to insert selected functionalities by a one-step procedure. This process shows a great compatibility with different functional groups and by modulating the feed ratio it is possible to achieve a very good control of the grafting degree and of the macromolecular architecture even though the functionalization is carried out in the melt by using free radical initiators.

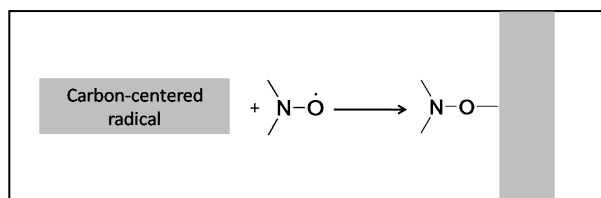


Figure 1. Nitroxide Radical Coupling (NRC) reaction.

In particular the use of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) derivatives as functionalizing agents allows addressing the mechanism toward stoichiometric reactions, by avoiding the macroradical side reactions not producing the target products [1]. Besides, the possibility to synthesize TEMPO derivatives bearing functionalities with specific activity, chromophores [2,3] and antioxidants as for examples, and therefore able to engender properties not inherently owned by basic polymers, renders this approach particularly interesting in both melt and surface radical-initiated functionalization processes.

In this lecture a simplified overview of the work done by our laboratory on this functionalization approach during the last 10 years will be discussed.

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Fiber/matrix interphase engineering in polymer composites with graphene and graphene oxide

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The properties of fiber/matrix interfacial region play a key role in determining the structural and functional properties of polymer composites [1]. In this work a strategy is presented for the electrophoretic deposition of graphene oxide (GO) nanoparticles on the surface of glass fibers (GFs). In a second step, the GO coating was reduced into reduced graphene oxide (rGO) by chemical treatment using hydrazine hydrate. The efficacy of the reduction process was tested by X-ray photoelectron spectroscopy (XPS) surface analysis which indicated a reduction of oxygen content in the coating from 34% in GO to 10% in rGO.

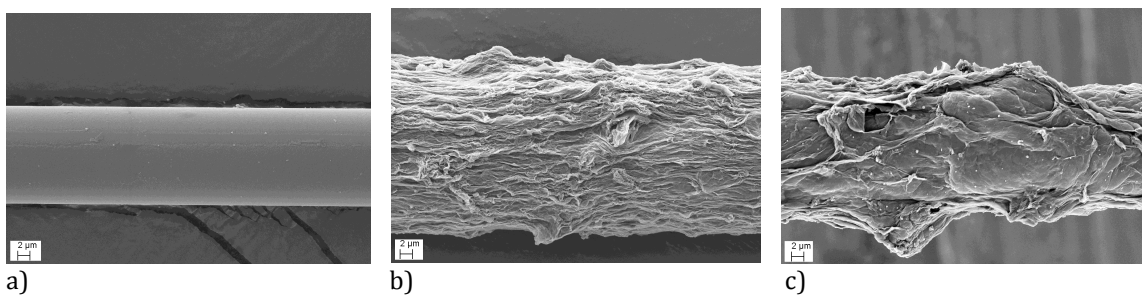


Figure 1. Scanning electron micrographs of bare GF fiber (a), and GF fibers electrophoretically coated with GO deposited at 10 V/cm (b) and subsequently reduced to rGO (c).

Both GO and rGO coated fibers were used for the preparation of epoxy based unidirectional composites. The fiber/matrix interfacial shear strength (ISS) was evaluated by the single fiber fragmentation test.

The adhesion level between GO and GF was evaluated by tribological tests performed at nanoscale by atomic force microscopy. The delamination strength between GO and GF resulted to be much higher than the ISS, thus proving the efficiency of the new GO fiber coating method here proposed for producing advanced graphene based composites [2].

Epoxy/glass unidirectional laminates were obtained by using uncoated, GO- and rGO-coated fibers and were used to test both mechanical and functional properties.

The presence of GO at the fiber/matrix interface resulted in an improvement of ISS values along with an increase of interlaminar shear strength (determined by the short beam shear test) and of the fracture toughness evaluated under the opening mode.

On the other hand, the presence of an rGO coating on the GF surface caused a remarkable increase (by 12 orders of magnitude) of the electrical conductivity of the epoxy/glass composites. Therefore, the strain-monitoring capabilities of composites containing rGO coated fibers were investigated under various (both static and dynamic) mechanical tests in which the strain was monitored (by an axial extensometer) simultaneously to electrical resistance variations along axial direction.

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Novel electrically conductive polymer nanocomposites for industrial applications

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The objective of this work is the investigation of novel electrically conductive polymeric nanocomposites based on polybutylene terephthalate (PBT), filled with commercial carbon black (CB) and carbon nanotubes (CNTs) masterbatches at different concentrations, to be potentially applied as melt blown filters for the automotive field [1,2].

FESEM analysis revealed how a good nanofiller dispersion was obtained both by introducing CB and CNT. Melt flow Index measurements highlighted that the processability of the nanocomposites was heavily compromised at elevated filler amounts, and the viscosity percolation threshold was established at 3 wt% for CNTs and between 6 and 10 wt% for CB nanocomposites. DSC measurements evidenced how the presence of CNT slightly increased the glass transition temperature of the materials, and an increase of 12 °C of the crystallization temperature was obtained with a CNT amount of 6 wt%. Also the crystalline fraction was increased upon CNT addition. Electrical resistivity measurements evidenced that the most interesting results were obtained for nanocomposites with a total filler content of 6 wt% (see Figure 1) and a CNT/CB relative amount equal to 2:1. The synergistic effect obtained with the combination of both nanofillers allowed the achievement of a rapid surface heating through Joule effect even at applied voltages of 2 V.

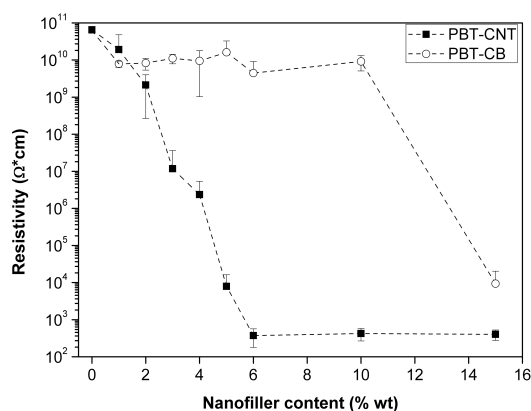


Figure 1. Electrical bulk resistivity of PBT based nanocomposite samples containing different amounts of CNTs and CB (applied voltage = 12 V).

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Acknowledgments

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Polyvinyl alcohol reinforced crystalline nanocellulose in 3D printing application

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Climate change and ecological catastrophes are pushing strongly the research to find solutions to preserve our environment, especially in the field of processing raw materials and in the industrial manufacturing. The widespread of new technologies like 3D printing give us the possibility to produce an object where it is really required. This could lead to a reduction in CO₂ emissions due to the less transportation needed [1]. The development of sustainable and degradable polymers is the natural step to improve the “green” benefits of 3D printing. Poly vinyl alcohol (PVOH) is recognized as one of the very few vinyl polymers soluble in water also susceptible of ultimate biodegradation [2], but for its poor mechanical properties PVOH is used in just few applications.

The aim of this work is to produce biodegradable polyvinyl alcohol reinforced with cellulose nanocrystals (CNC) nanocomposites filaments to improve the thermo-mechanical performance in 3D printing fused deposition modeling (FDM). Cellulose nanocrystals in water solution were prepared from micro-cellulose through a sulfuric acid hydrolysis [3]. Nanocomposites of PVOH containing various amounts of CNC produced by solution mixing and grinded to obtain filaments through a single screw extruder. Dumbbell specimens were printed with the aid of a 3D printer. CNC particles appear homogeneously dispersed without noticeable aggregates and no phase separation had taken place during the extrusion process as we can see from the SEM image (**Figure 2**). The effect of CNC on thermal properties of PVOH and its composites was evaluated with thermogravimetric analysis. The peak in mass loss for neat PVOH is shifted to higher temperatures, with the increase of filler content, enhancing the thermal stability of the composites as compared with the neat PVOH. A progressive enhancement in the storage (E') modulus as the filler loading increases was observed increasing the amount of nanofiller in the filament and in 3D printed specimens (**Figure 3**). An increase of 280% in the value of storage modulus at room temperature was reached in 3D samples with a concentration of 10 wt%. A reduction of the creep compliance with the increase of filler content confirms an improvement of the dimensional stability. The representative stress-strain curves of examined 3D printed nanocomposites, reported in **Figure 4**, underline an interesting increase of the stiffness and the strength of PVOH due to the CNC introduction.

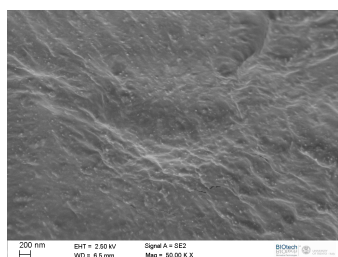


Figure 2. Cryo-fractured surface of PVOH with 10 wt% of CNC.

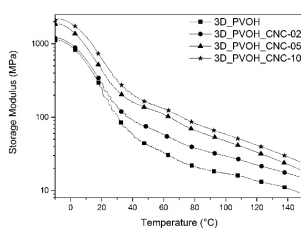


Figure 3. Storage modulus curves for 3D printed samples.

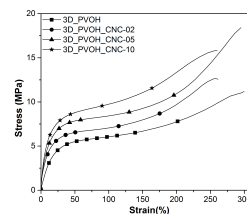


Figure 4. Representative stress – strain curves from tensile test.

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Polymers for art conservation

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There is an increasing attention for the development and applications of polymeric products in the conservation-restoration of works of arts, and cultural assets in general. Practically in all the fundamental conservation phases, i.e. cleaning, consolidation and protection, polymer systems are used which are most often transferred from extraneous sectors like building, cosmetic, or food. The performance requirements and the uncommon variety of problems to be faced make this a stimulating field also from the scientific point of view. Studies which are being carried out in this field at the Polymer Group of the University of Torino are here briefly described. A first subject concerns the development of nanomaterials for conservation of architectural heritage following a tradition of studies initiated many years ago in this group, devoted to polymers for the conservation of stone materials. In the framework of an European funded project we are now investigating the ageing behaviour of polymer films obtained from aqueous dispersions of a series of innovative multifunctional polymer nanoparticles whose synthesis has been developed by partners at the University of Pisa [1]. With the introduction through copolymerization of Hindered Amine Light Stabilizers derivatives, enhanced durability of the polymer structure could be demonstrated. Hybrid and nanocomposite films with inorganic nanoparticles are as well being developed, as they are able to provide additional useful features such as biocidal, self-cleaning or mechanical reinforcement, and the influence of the nanoparticles on the stability of the organic part is being evaluated at the laboratory scale, prior to tests on characteristic lithotypes and on real architectures. Another conservation matter of interest is in damaged or aged paintings, when adhesion treatment is needed at the interface between two paint layers or between a paint layer and the support. The adhesive needs to be applied without compromising the original appearance of the object and must penetrate into a weakened porous material to improve the cohesive bulk properties strength. Within an international collaboration including conservators and museum scientists we have investigated new adhesive formulations which are binary and ternary mixtures based on ethylene copolymers, four classes of tackifier, and a paraffin wax [2]. The formulations have been characterized looking at their miscibility, the rheological transition temperatures, and the adhesion performances. Among the tackifiers, ketone and rosin ester resins showed good miscibility with the selected polymeric components, and it was demonstrated that the wax enhances the mixing properties of the components and affects the adhesion activation point. The final case of polymer compounds for art conservation is that of hydrogels and high viscosity polymeric dispersions, of great interest for cleaning and removal of superficial layers in artworks. These systems allow limitation of unwanted effects such as swelling and extraction of original materials due to direct application of solvents onto the surface of artworks. The preparation and characteristics of synthetic gels with viscoelastic properties apt to obtain workable shapes and complete removal after application are investigated. Gel formulations will be described discussing possible applications and weak points [3].

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Characterization of complex polymer systems by MALDI mass spectrometry

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The introduction of Matrix-Assisted Laser Desorption/ionization (MALDI) has dramatically increased the mass range for molar mass analyses by mass spectrometry allowing the desorption and ionization of very large molecules such as biopolymers and synthetic polymers, even in complex mixtures. The MALDI process produces singly-charged *quasi-molecular* ions with negligible ion fragmentation, by the capture of a proton or a metal ion (usually lithium, sodium, potassium). The polymer is dissolved in the appropriate solvent and mixed with a solution of the matrix to achieve a molar ratio of analyte to matrix of 1:100–1:50,000. In the case of an insoluble polymer it is mixed with the matrix in the solid state.

The high mass accuracy and high mass resolution of MALDI spectra allows the direct structural determination of the species contained in each polymer sample giving information on the mass of individual oligomers, repeat units, end groups, the presence of cyclic, grafted, and branched units. MALDI is also an optimum technique for the determination of Molar Mass (MM) in the case of polymers with narrow molar mass distribution while problems emerge with polydisperse polymers. Alternatively, Gel Permeation Chromatography (GPC) can be combined with MALDI for polymers of broad polydispersity. GPC fractions are collected “*off-line*” and analyzed by MALDI allowing the determination of the average MM of each fraction. These MM data can be used to calibrate the GPC curves, introducing the possibility of using the MALDI as a GPC detector.

The structural information obtained by MALDI was used to determine the structure of the molecules produced in the thermal degradation, thermo and photo-oxidative degradation of several polymers (polyamides, polyesters, polycarbonates...). These data allow the determination of the correct mechanisms involved in the degradation processes of the polymers studied. The determination of sequence and composition in copolymers having large comonomer subunits can be achieved by MALDI-TOF which is often complementary and sometimes alternative to NMR analysis. The intensity of the peaks appearing in the MALDI spectrum of a copolymer is directly bound to the relative abundance of copolymer oligomers and reflects the composition and sequence distributions in the copolymer.

Chain statistics (Bernoullian or first- or second-order Markoffian) allows the characterization of any arrangement of comonomer units along the chain and give us the possibility of building theoretical mass spectra. Composition and sequence distributions for a given copolymer can be obtained by matching theoretical and experimental mass spectra.

This method has been successfully applied to the characterization of several copolymer systems and also to the characterization of the copolymers obtained by reactive melt-mixing of some blends of condensation polymers (polyamides, polyesters, polycarbonates).

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Killing bacteria via ion-complexing insoluble polymers

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New copolymers containing either MMA and 18C6 crown-ether pedants, or PEG, MMA and 18C6 crown-ether pedants were synthesized via uncontrolled radical polymerization or ATRP to test the idea that sequestering structural alkali-earth ions from bacterial Outer Membrane (OM) may lead to bacterial death. ATRP allowed us to produce branched Y-like structures to investigate structural effects. After checking for the capability of complexing Mg(II)/Ca(II) ions, the antimicrobial activity of copolymer plaques was tested placing them in contact with pure water *E. coli* suspensions. All plaques that adsorbed alkali-earth ions also killed bacteria, albeit with different antimicrobial efficiencies (Figure 1).

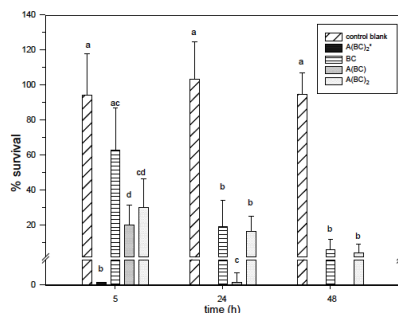


Figure 1. *E. coli* % survival vs time for 18C6-containing polymers (A(BC), A(BC)₂, and BC), the antibacterial A(BC)₂* copolymer containing DMAEMA[1] instead of 18C6, and a linear mPEG-b-PMMA copolymer as control.

Differences in efficiency are attributed to different plaque porosities and surface morphology, as evidenced by both TGA-determined water adsorption and direct visualization with FE-SEM. The role of the 18C6 crown-ether pedants was elucidated by pre-saturating plaques with Mg/Ca ions obtaining a marked reduction in antimicrobial efficiency (Figure 2).

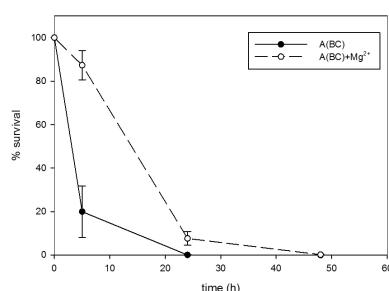


Figure 2. *E. coli* % survival vs time for Mg(II)-saturated and non-saturated 18C6-containing A(BC) polymer.

The latter finding indicates that the plaque complexation ability is a key ingredient in bacterial killing at short (<5h) contact times. At longer times, the mode of action is instead related to the polycationic nature acquired by the plaques due to ion sequestering.

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pH-sensitive nanoaggregates: controlling swelling via copolymer structure and chemical composition

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pH-sensitive vesicles used as drug delivery systems (DDSs) are generally composed of protonable copolymers. The disaggregation of these nanoparticles (NPs) during drug release implies, however, the dispersion of positively charged cytotoxic polyelectrolytes in the human body [1]. To alleviate such issue, A(BC)_n amphiphilic block copolymers with linear (n = 1) and branched (n = 2) architectures [2] were synthesized to obtain pH-sensitive NPs capable of releasing drugs in acidic condition via controlled swelling instead of disaggregation. This feature was obtained finely tuning the relative amount of pH-sensitive and hydrophobic monomers.

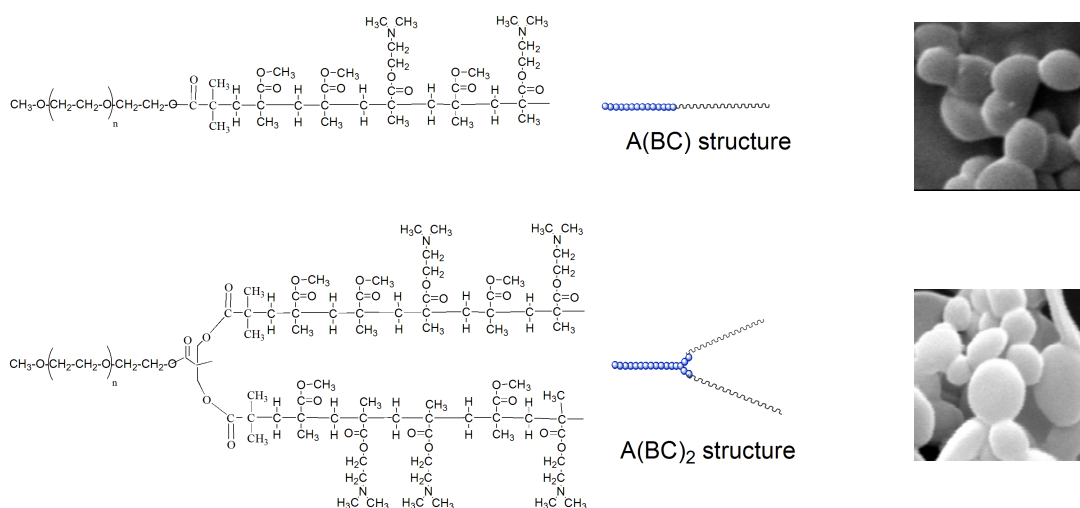


Figure 1. Structures of amphiphilic copolymers and FE-SEM images of NPs in distilled water.

pH-driven swelling was studied by measuring NP size in neutral and acidic conditions, the latter typical of tumors or inflamed tissues (pH ~ 6), and lysosomes (pH ~ 4.5). DLS and zeta potential data provided useful indications about the influence of architecture and chemical composition on NPs swelling, stability and polycation release. Results showed that linear copolymers with 28-30% of protonable monomers in the “BC” block swelled more than other species on going from pH 7.4 to pH 4.5. Moreover, they released no or minimal amounts of polyelectrolytes even in acidic condition. Given such useful traits, the release of PTX from these linear species was tested at various pHs.

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Structure-properties relationship of commercial ethylene/1-octene copolymers from chain-shuttling polymerization

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Several commercial grades of ethylene/1-octene copolymers, INFUSE® by DOW Chemical Company, synthesized by chain-shuttling method, have been studied with different techniques, in order to develop structure–property relationships in the olefin multiblock copolymers.

Commercial copolymers have been fractioned. Unfractioned and fractioned samples were analyzed in order to determine their comonomer content, molecular weight and molecular weight distribution. The structure and mechanical properties of these copolymers have been determined and have been correlated to the mechanical properties and the elastomeric behavior. All unfractioned samples show outstanding mechanical properties at 25 °C. Remarkable differences in the tensile properties of the block copolymers INFUSE occur by stretching at temperatures higher than 25 °C. The elastic performances of ether-insoluble (Et_i) fractions are similar to those of the corresponding unfractioned samples.

The structural analysis for these samples suggests a microphase separated structure which consists of hard domains embedded in the amorphous matrix of soft blocks. Furthermore, the samples that form an interpenetrating network crystallize more slowly (at low temperatures) and show higher mechanical strength and ductility even at high temperatures. The samples with no inter-woven structure instead, form a more heterogeneous morphology, and lose large part of mechanical strength already at 60 °C.

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How to exploit the synergy between Ti^{3+} and Lewis acidic Al^{3+} sites on Al_2O_3 -supported Ziegler-Natta catalysts to produce branched polyethylene

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Heterogeneous Ziegler-Natta (ZN) catalysts are, together with Phillips ones, the main responsible for the wide spread of polyolefin production within the world plastic market. Although their discovery dates back to the 1950s, some fundamental questions about their structure and working are still open, and so far all the advances have been based on a trial and error approach [1]. Achieving a deeper understanding of these intrinsically complex multi-component systems is the first step to rationally design new and more efficient catalysts, in order to finely tune the properties of the final products.

In this work we explore at a molecular scale the properties of alumina-supported ZN catalysts. Alumina was chosen as a support material since it is known in literature to be involved in the acid catalysis of olefin isomerization and oligomerization [2,3]. Two different procedures were investigated for the activation of the pre-catalyst, aiming to exploit the cooperation between the Ti^{3+} centers and the Al^{3+} Lewis acid sites: the typical reaction with the triethylaluminum (TEA) cocatalyst [1], and the reduction in hydrogen at 400 °C [4]. While the former method implies the simultaneous reduction and alkylation of the metal centers, after the latter no alkyl groups are present on the catalyst surface. However, both the catalysts turned out to be very active towards ethylene polymerization, though in a quite different way, as revealed by the FT-IR spectroscopy and the calorimetric analysis shown in Figure 1. The TEA-activated catalyst counts for the production of mainly crystalline HDPE, whereas the polyethylene produced by the H_2 -reduced catalyst has a branched nature. Several spectroscopic and physicochemical techniques were applied to unravel the structure of the different active sites, in order to understand the two different reaction mechanisms and try to rationalize the design of the ethylene polymerization catalysis depending on the desired properties of the final products.

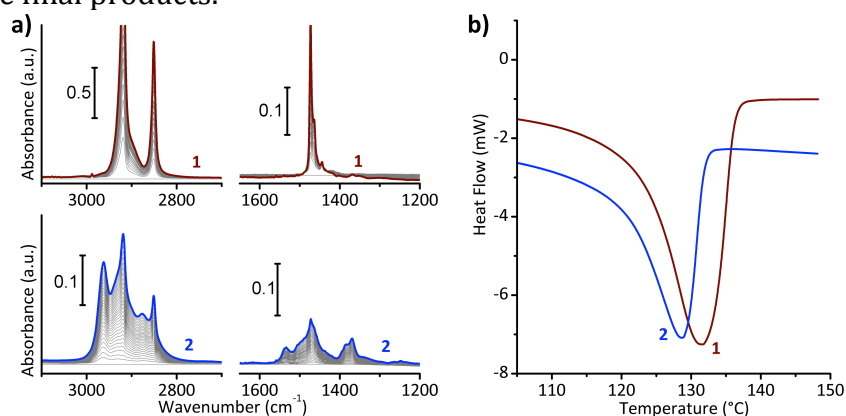


Figure 1. Part a) FT-IR spectra of C_2H_4 reaction over of $\delta-Al_2O_3-600/TiCl_4/TEA$ (1) and $\delta-Al_2O_3-600/TiCl_4/H_2-400$ (2) catalysts, in $\nu(CH_x)$ and $\delta(CH_x)$ regions. Part b) DSC analysis of the polymers produced by $\delta-Al_2O_3-600/TiCl_4/TEA$ (1) and $\delta-Al_2O_3-600/TiCl_4/H_2-400$ (2) catalysts, after dissolving the catalysts in HF.

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In situ polymerization in 3D porous materials

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Porous architectures, thanks to their functional properties, offer great opportunities in several applicative fields. Our scientific activity is devoted to the fabrication of 3D porous materials and spectroscopic observation of polymers obtained in situ within the cavities as well as of host-guest interactions at the interface. The in situ polymerization in the porous covalent framework PAF-1 allowed the synthesis of interpenetrated network in which the robust architecture serves as both the matrix and the reinforcement for the engendered polymer. As a case study, we explored the polymerization of acrylonitrile because the resulting polymer (PAN) thermally transforms into a rigid and conjugated ladder polymer, thus realizing nanocomposites with innovative functional properties.

Confined polymerization was exploited to obtain replica polymers with the same shape and morphology of porous particles at the micrometric and nanometric level. Styrene, was polymerized in 7 Å cross-section channels of a host porous coordination polymer (PCP). The polystyrene chains, that are formed within the PCP channels, crosslink with a minor amount of divinylphthalate ligands inserted in the basic PCP structure. Such ligand bridges together polymer chains of adjacent channels and ensures that, on selective removal of the matrix, the polymer chains remains aligned and periodically ordered in a hexagonal arrangement. This strategy realized a porous polymer by unusual cross-links in the crystalline state. Also, replica effect of micrometric objects from silica to porous polymers was achieved in 30 Å nanochannels by radical polymerization. Moreover, understanding the intrinsic properties of single conducting polymer chains is of interest, for their applications in molecular devices. Interestingly, the isolation of single polysilane chains increased the values of carrier mobility in comparison with that in the bulk state due to the elimination of the slow interchain hole hopping. The main chain conformation of polysilane could be controlled by changing the nanochannel cross-section, as evidenced by Raman spectroscopy and solid-state NMR: indeed, we succeeded in varying the conducting property of single polysilane chains by changing the including matrix nanochannels. Another challenging issue is the dynamics of porous solids and the insertion of molecular rotors in their building blocks. The combination of porosity with ultra-fast rotor dynamics was discovered in porous covalent frameworks, by ²H spin-echo NMR spectroscopy. The rotors, as fast as 10⁶ Hz at 225 K, are exposed to the cavities, which absorb vapors even at low pressure. Interestingly, the rotor dynamics can be switched on and off by vapor absorption, showing a remarkable change of material dynamics. As the temperature is increased, the rotors spin ever faster, approaching free-rotational diffusion at 550 K.

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Effects of the macromolecular architecture on polymer conformations and dynamics

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The conformational and dynamical behavior of polymers, hence also their rheological behavior, strongly depend also on their architecture. In this contribution, we report some theoretical results obtained by statistical mechanical methods about the molecular size and the local and overall dynamics of polymers in dilute solution considering branched polymers such as regular stars and combs, dendrimers and cyclic chains in comparison to linear chains. In these cases, the advantage of considering the statistical symmetry of the individual molecules will be highlighted. The focus will be mainly on the asymptotic, universal properties, but some results accounting also for the specific local behavior of individual macromolecules such as PDMS as obtained within the RIS approach will be considered.

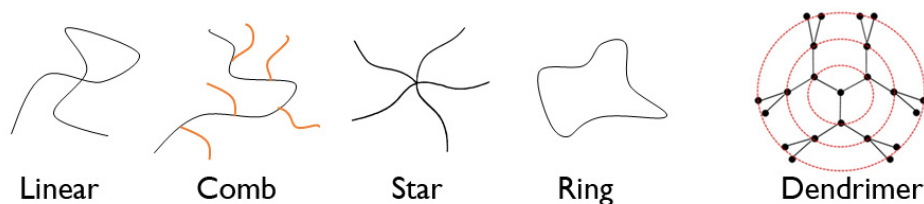


Figure 1. Some polymer topologies.

Acknowledgments

Helpful discussions with prof. Giuseppe Allegra, who introduced me to the statistical mechanical approach to study the conformational and dynamical behavior of polymers, and with prof. Giuseppina Raffaini are gratefully acknowledged.

Characterization of intumescent chars by solid state NMR

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Epoxy resins are widely used as binders for different kinds of coatings and particularly for intumescent coatings. The resins provide high mechanical properties, chemical resistance and corrosion resistance to the coatings. Intumescent coatings contain the conventional triplets for making an efficient system: the acid source, namely borate and/or phosphate, the char former, namely epoxy and isocyanurate, and the blowing agent, namely the evolving ammonia from the phosphate [1]. These intumescent coatings are used to protect steel against fire by forming an expanded multi-cellular insulative barrier. In order to understand the mode of action of intumescent coatings, a number of techniques such as X-ray diffraction (XRD) or one-dimension solid state Nuclear Magnetic Resonance (1D solid state NMR) are useful to analyse the chemical compositions and the structures of intumescent chars. Nevertheless, these methodologies show some limitations when it comes to analyse char of complex chemical compositions involving the formation of numerous species. This work deals with the characterization of fire protective coatings containing a mixture of borate, phosphate, isocyanurate as intumescent ingredients and fibres for reinforcing the char. In addition to XRD and 1D-NMR, the use of two dimensions (2D) Dipolar Heteronuclear Multiple Quantum Correlation (D-HMQC) solid state NMR [2] enables to identify precisely the chemical species formed in the char residue by identifying correlation between heteroatoms through oxygen bridging atom such as borosilicate (B-O-Si) (Figure 1, left) and borophosphate (B-O-P) (Figure 1, right) species. This work thus reports the promising applications of advanced NMR in research and development of polymeric materials for fire protective applications.

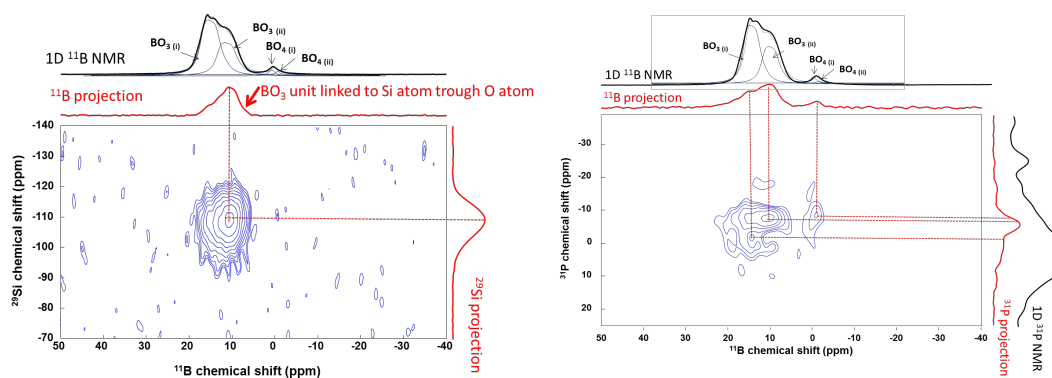


Figure 1. Solid state 2D D-HMQC $^{11}\text{B} \{^{29}\text{Si}\}$ NMR spectra (left) and $^{11}\text{B} \{^{31}\text{P}\}$ NMR spectra (right) of char residue acquired at 18.8 T.

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Exploitation of PLGA conjugates in drug delivery

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Several decades of biomaterials research have led to a progressively heightened interest in the use of biodegradable polymers for drug delivery applications. In particular, poly(lactide-co-glycolide) (PLGA) has been widely used to develop injectable depot formulations or nanoparticles as delivery of various small molecular weight drugs, peptides, and proteins. But PLGA-based carriers have challenges to overcome, such as the low drug loading capacity, low encapsulation efficiency, transformation in a dried final dosage form and terminal sterilization. Whereas for the different applications specific end-use properties are required, the introduction of moieties into the polymer backbone has carried to innumerable PLGA conjugates which can modulate the drug release or polymer degradation rate, and improve the drug loading. A breakthrough in drug delivery research was the link of aliphatic PLGA with a hydrophilic polyethylene glycol (PEG) segment to yield the amphiphilic copolymer structure. Monodispersed nanospheres formed by PLGA-PEG block copolymer were demonstrated to improve the drug encapsulation efficiency and to dramatically increase blood circulation time associated with reduced liver accumulation after injection in mice [1]. It was 1994 and nowadays bi- and tri-blocks polymers are mainly used as thermogelling injectable polymers for various biomedical applications. However, the endless opportunities provided by this example boosted the progress with novel PLGA conjugates addressing specific requirements. The availability of precision synthetic tools has also determined a step change to overcome the low density of reactive groups on PLGA and to improve the possibilities in conjugation. In this context, radical grafting represents one of the most effective and easy methods for polymeric materials modification. This synthetic strategy was successfully used to conjugate some antioxidants to PLGA [2], obtaining novel materials stable to ionizing radiation, which is the method of choice to obtain the final sterilization in overkill conditions for PLGA [2]. Moreover, PLGA grafted to caffeic acid (g-CA-PLGA) improved the encapsulation efficiency of ovalbumin as a model of biological drug, preventing the dimerization process driven by radical pattern [3]. Aiming to overcome the biological barriers, surface properties of PLGA nanoparticles can also be modified both to favour cellular endocytosis [4] and/or achieve active targeting drug delivery. In this respect, the ligands used for the derivatization of PLGA (e.g. peptides or antibodies) can promote the direct interaction with transport systems enabling the nanoparticles to cross biological barriers and/or the selective and specific bind to target cells [5]. PLGA conjugates are also particularly appealing for the design of stimulus-responsive switches to tailor features (i.e. size, surface chemistry and shape) in time so to take control over nanoparticles interactions with cells or subcellular compartments [6]. Lastly, PLGA are currently under evaluation in theragnostic field since this type of polymers present the potentiality to combine passive and active targeting, environmentally-responsive drug release, molecular imaging, and other therapeutic functions into a single platform [7].

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Water-based nanoparticles dispersions of amphiphilic low band gap block copolymers: an alternative eco-friendly approach

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Water-based nanoparticles (NPs) of semiconducting polymers received considerable attention for optoelectronic and biological applications due to their simple preparation method, and their tunable optical properties [1]. NPs are appealing for optoelectronic devices such as organic photovoltaic devices (OPVs) [2], organic light-emitting diodes (OLEDs) [3], and organic field-effect transistors (OFETs) [4] to control the morphology of the active layer that plays a crucial role in the device performance. The NPs dispersion can be obtained through the miniemulsion method, using great amount of surfactants to ensure NPs stability. This approach allows for lowering the chlorinated solvent amount used in the active layer fabrication reducing the environmental payback of the devices, but to achieve good performances the excess of surfactant has to be removed at the end of the process [5].

Amphiphilic block copolymers (BCPs) are a powerful tool to produce nanostructured or supramolecular objects with enhanced properties for electronics, optoelectronics, sensors and biotechnological applications because of their capability to self-assemble, influenced by the physico-chemical differences between the blocks, including the relative block length, block polarity, volume fraction, chain flexibility, etc. [6].

PCPDTBT-*b*-P4VP is an amphiphilic rod-coil BCP constituted by a low band-gap copolymer, PCPDTBT as the rigid segment, and tailored segments of poly-4-vinylpyridine (P4VP). The rod block was studied as donor material in hybrid and organic devices, whilst P4VP is able to interact with acceptor materials, as fullerene derivatives [7].

Taking advantage of hydrophilic behavior of the coil, we studied the capability of PCPDTBT-*b*-P4VP to form NPs dispersion in aqueous medium through miniemulsion method, neat or in blend with fullerene derivatives, without use of surfactants avoiding purification steps.

The NPs were optically, morphologically (AFM, TEM, Synchrotron XRD) and electrically characterized, showing suitable properties for the preparation of active layers and they were tested in eco-friendly NP-based OPVs with efficiency reaching over 2%.

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Investigation on the double melting peak of PLLA using modulated DSC

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Poly(L-lactic acid) (PLLA) is one of the most studied biopolymers nowadays. Due to its good performance, it constitutes an alternative to petrochemical-derived polymers [1–4]. It was largely studied by differential scanning calorimetry (DSC) [5,6] and temperature-modulated DSC [7,8]. Nevertheless, there is an ongoing debate of what happens at the overlapping melting processes [9]. In the present work [10], the experimental setups are discussed. Different modulation conditions are proposed for the study of the glass transition, cold crystallization, and the two reported melting processes. Finally, the experimental results allowed to measure the heat capacity change at the cold crystallization and a correct interpretation of what happens at the reported double melting peak of PLLA, which involves the existence of three crystalline structures.

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Advanced rheometric tools for polymer applications

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Rheological characterization is a powerful tool to determine mechanical properties of polymers in order to estimate the behavior of such materials during processing but also during the whole life cycle. There is a broad range of standard rheological tests which can be used to characterize the rheological behavior of polymers. Nevertheless there are still limitations, or parameters which haven't been considered extensively until now. Aim of the contribution is to highlight several tools which can be of interest for advanced rheological testing and which can broaden the possibilities in order to get profound knowledge of the polymer properties.

A main limitation for characterizing polymer melts and concentrated polymer solutions at large deformations or high shear rates, is known as edge fracture. To limit the impact of edge fracture a cone partitioned plate (CPP) has been recommended on several occasions [1-3]. This contribution will present the concept of a CPP and will show differences in the measuring performance when using a CPP in comparison to cone-and-plate geometries.

While the classical rheology gives information about the macroscopic behavior of a material under certain conditions, this behavior is strongly determined by the underlying microstructure of the material itself. Thus, e.g. the combination of microscopy with rheological measurements is of interest in order to correlate microstructural properties with the rheological behavior. For such tests rheometers with two drive units working in counter-rotating mode can be of advantage due to the possibility to visualize microstructures kept in the stagnation plane. Furthermore rheological testing can be combined with polarized light imaging which allows e.g. the observation of flow induced crystallization processes of polymers or the characterization of the orientation of polymer chains in polymer solutions or melts under shear [4,5]. The presentation will show different examples where the combination of rheological testing and microstructural analysis can help to gain an understanding on the correlations between the samples microstructure and its rheological behavior.

While it is already known that ambient condition can have an impact on the rheological properties of materials mostly only the impact of temperature is taken into account during rheological testing. Nevertheless, for some polymers also relative humidity of the ambient air can influence the rheological properties. Hence using special accessories to control temperature and relative humidity separately during rheological testing can be of advantage. The presentation will highlight some examples where setting temperature and relative humidity helps to get a better understanding on the materials properties at processing and storage conditions.

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POSTER PRESENTATIONS

Dextrin cross-linked polymers as precursors for microporous carbon materials

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Porous carbon materials have received a great attention due to their applications in many industrial fields. Typically, they are produced through the pyrolysis of a carbon precursor, for instance the biomasses [1]. Recently, the synthesis of porous carbon materials using dextrans, i.e. nanosponges, was investigated [2]. The nanosponge is prepared cross-linking the dextrans with pyromellitic dianhydride.

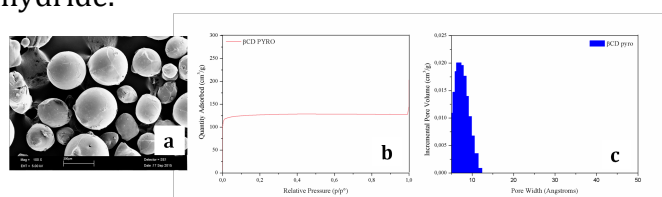


Figure 1. a) SEM picture of the carbon particle obtained by nanosponge pyrolysis; b) N_2 adsorption isotherm; c) DFT pore size distribution plot obtained by N_2 gas-volumetric adsorption at 77K.

Figure 1a reported a SEM image of the material obtained after the nanosponges pyrolysis in a tubular furnace. The carbon residue is almost composed of spherical particles, hollow inside. Using a semi-automatic instrument (ASAP-Micromeritics) the specific surface area and the porosity of the materials were evaluated. The N_2 adsorption isotherm was type 1 (Figure 1b), according to the IUPAC classification. This isotherm shape is typical of microporous materials. The Langmuir equation was applied for evaluating the specific surface area while the DFT method for estimating the porosity. The surface area was about $560 \text{ m}^2/\text{g}$, and the pore size is 5-16 Å (Figure 1c).

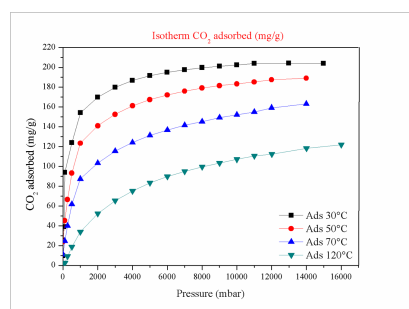


Figure 2. CO_2 adsorption isotherms of the nanosponges at different temperatures.

The material was tested in gas-adsorption (CO_2 , CO , N_2 and O_2) using a microbalance (IGA-Hidenisochema). Surprisingly, the carbon was able to adsorb only the CO_2 . Figure 2 reported the CO_2 adsorption isotherm carried out from 0-20 bar at different temperature. The maximum adsorption at 30 °C is 204 mg/g and it becomes half when the adsorption is led at 120 °C. The sample is selective for the gas adsorption even at high temperature and pressure.

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Dextrin-based nanosponges for the removal of metal contaminants in wastewaters

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Environmental remediation and, in particular, decontamination of polluted water is one of the major challenges of our time and it involves several scientific and technological issues.

In this work, β -cyclodextrin- (β -CD) and dextrin-based hyper-cross-linked polymers, named “Nanosponges” (NSs) have been synthesized and tested for the adsorption and removal of metals from wastewaters. More specifically, eight NSs have been produced for this purpose, by cross-linking β -CD or a maltodextrin (Roquette Kleptose Linecaps[®]) with pyromellitic dianhydride [1], citric acid [2] or 1,2,3,4-butanetetracarboxylic acid; their syntheses were characterized by simple procedures, short reaction times and good yields, especially when the dianhydride was used.

During preliminary investigations, these materials showed the ability of adsorbing metal ions from water solutions, but they also caused acidification of the samples; this phenomenon was particularly remarkable when the NSs were put into NaCl solutions instead of deionized water, because of ion exchange between H^+ of the polymers and dissolved Na^+ . As acidification is an unwanted side effect, the NSs were washed with a saturated NaCl solution for complete substitution of H^+ with Na^+ . The products were still able to remove cations from water, even better than the acid starting materials, without significantly modifying the pH of the solutions. The salified NSs were tested for the adsorption of five metal ions: Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} and Fe^{3+} . The first experiments were performed by adding 10 mg of polymer to 5 mL of aqueous solutions containing 500 ppm of a single metal. In these conditions, the best weight ratios between adsorbed metal and NS were 77 mg/g for Cu^{2+} , 130 mg/g for Zn^{2+} , 272 mg/g for Pb^{2+} , 227 mg/g for Cd^{2+} and 129 mg/g for Fe^{3+} . Some investigations about reaction rate also suggested that the adsorption process is fast, and is completed within 30 minutes.

Subsequently, aqueous solutions of Cu^{2+} or Zn^{2+} with lower initial concentrations, varying from 0.1 to 50 ppm, were taken into account. For these trials, 12 mg of NS were added to 15 mL of every solution. In all the samples, the amount of adsorbed ions was between 70 and 94 % of the whole dissolved metal.

Finally, Cu^{2+} and Zn^{2+} were used to study the adsorption efficacy of the same polymers in artificial sea water, too. In this environment, noticeable differences between the tested materials were observed: the NSs obtained from citric acid provided the best performances, removing up to 89 % of the contaminant from the solutions, while the polymers synthesized from pyromellitic dianhydride never exceeded 63 %.

Given the promising results so far collected, linear dextrin- and cyclodextrin-based NSs rich in carboxylic groups might represent a new effective tool for the treatment and decontamination of metal-polluted wastewaters.

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Glutathione responsive beta-cyclodextrin nanosponges for controlled delivery of strigolactone derivatives for cancer therapy

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Strigolactone analogues are a new class of compounds, belonging from plant hormones, proposed for cancer treatment being able to induce G2/M cell cycle arrest and apoptosis in a variety of human cancer cells [1]. They suffer of low solubility in polar medium associated with instability at pH higher than 8. To improve their therapeutic potential new cyclodextrin-based nanosponges, innovative polymer-based delivery systems consisting of cross-linked cyclodextrin nanostructured within a three-dimensional network, were developed [2]. The aim of this work was the development of nanosponges containing disulfide bridges in their structure, able to incorporate strigolactones and release them 'on demand' as a function of glutathione (GSH) concentration. Indeed, GSH responsive release offers high potential for designing tumor responsive therapeutics, triggering intracellular drug delivery in cancer cells [3,4].

GSH responsive nanosponges were obtained in a one step synthetic route, by reacting cyclodextrin, cross-linking agent and 2-hydroxyethyl disulfide, in order to introduce disulfide bridges in the polymer network. To reduce size of the nanosponges and obtain an almost homogenous nanoparticle distribution, the sample underwent to high pressure homogenization (HPH). Two types of strigolactones, i.e. MEB55 and ST362 were loaded in GSH-responsive nanosponges and *in vitro* characterized. To investigate the pH/redox dual sensitive release from GSH-responsive nanosponges *in vitro* drug release experiments were carried out in the presence of increasing GSH concentrations and at different pH values. *In vitro* biological assays were also performed to evaluate the efficacy of MEB55 and ST362 nanosponge formulations on prostate cancer cell lines, i.e. DU145 and PC-3 cells. The incorporation within the nanosponge structure of the two strigolactones was demonstrated by FTIR and DSC analyses and confirmed by the slow *in vitro* release kinetics, without initial burst effect. The release kinetics were accelerated at acid pH and in the presence of the highest amount of GSH in the external environment. MTT analyses demonstrated that cells with higher GSH concentration were more inhibited by strigolactone-loaded GSH-NS than the free drug. The strigolactone intracellular accumulation was related to GSH content of the two cell lines. Based on these data, GSH responsive nanosponges might be considered a promising nanocarrier for intracellular triggered release of strigolactones.

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New polymer nanobubbles for improving wound healing treatment

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Dermal injury is one of the most prevalent and economically burdensome healthcare issues in the world. Current wound management requires frequent dressing changes and patients are at constant risk of infection until the skin regains its barrier function. The wound-healing process consists in four highly integrated and overlapping phases that need oxygen supply. Oxygen is required for almost every step and it is a prerequisite for successful wound healing due to the increased demand for reparative processes such as cell proliferation, bacterial defense, angiogenesis, and collagen synthesis.

Since chronic ischemic wounds are essentially hypoxic, new systems of topical oxygen delivery were developed in order to ameliorate the healing outcomes. Oxygen-filled polymer-based nanobubbles were formulated using chitosan as shell. Chitosan, a polycationic polysaccharide, was selected for the nanobubble shell because of its low toxicity, low immunogenicity, and excellent biocompatibility, while the core consisted of perfluoropentane.

Moreover the shell composition was modulated in order to tune the oxygen release kinetics. For this purpose, different components were employed to affect the shell thickness of chitosan-shelled nanobubbles, i.e. hyaluronic acid, tripolyphosphate or their combination. All the formulations were characterized measuring the size, the *polydispersity index and the zeta potential by laser light scattering*; transmission electron microscopy (TEM) was used for studying the nanobubbles *morphology*. The formulations stability was assessed in the short and long term and the *in vitro* oxygen release kinetics were investigated through an oximeter.

Thanks to FITC-conjugated to chitosan nanobubbles, their uptake by the cells was measured by confocal analysis. In addition, the potential cytotoxic effects of the nanobubbles were measured on cell lines and a human red blood cells hemolysis assay was used to determine their biocompatibility.

Thus, the use of nanobubbles as oxygen reservoirs is a potentially novel method for improving wound healing treatment.

Fluorinated polymers in photonics

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Fluorinated polymers constitute a special class of materials. They find applications where demanding environmental operating conditions are requested. Among them, there is a peculiar product's family, i.e. that of amorphous materials (Hyflon[®] AD) which show further interesting optical properties. As a matter of fact, they have very high transparency in a wide range of wavelengths (from UV till NIR, [1]). Moreover, they have low values of refractive indexes (1.32-1.33). These characteristics put them in a very special position for photonics applications [2], especially if they are used in combination with "traditional" hydrogenated polymers with higher refractive index values [3]. We realized and studied the optical effects of polystyrene-based opal structures infiltrated with Hyflon[®] AD and Fluorolink[®] PFPE materials. Band gap shifts observed are in accordance with theoretical predicted values [3,4]. 1D Photonic Crystals with valuable optical parameters (Distributed Bragg Reflector, DBR) have also been prepared with a limited number of layers, due to high index contrast provided by these materials. One of the possible applications of such devices is thermal shielding [5], especially if the band gap is wide and targeted to NIR region of electromagnetic spectrum. In Fig. 1 the optical characteristics of one of the devices prepared and the corresponding performances obtained when the DBR was tested as thermal shield device on a glass substrate. The growth and optical characterization of infiltrated opals and DRBs will be reported and discussed.

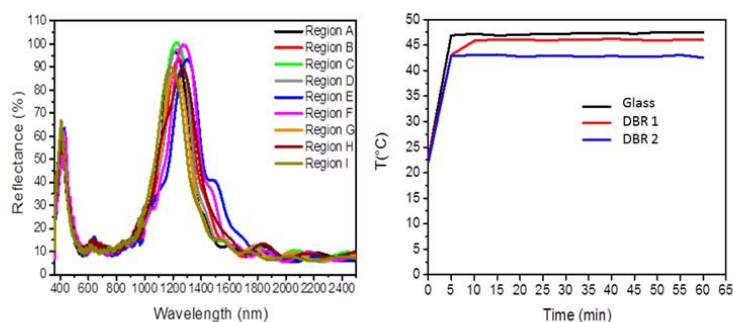


Figure 1. Left: Distributed Bragg Reflector optical properties (materials: Hyflon[®] AD and polyvinylcarbazole). Right: Temperature measured on a glass substrate under sample irradiation without and with a DBR thermal shield.

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Weak polyelectrolytes with strong H-bond interactions: titration and pore adsorption equilibria

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For weak polyelectrolytes, the interplay between pH, solvent properties, and polymer structure affects the amount of charges, their distribution, and hence their conformations via Coulomb repulsion. Attractive interactions can also develop between charged and neutral sites counteracting the expected Coulomb-induced expansion. To gauge how such competition affects polyelectrolyte structure and ionization, the titration of a single polyelectrolyte chain, isolated or close to a charged sphere, mimicked with a novel many-body potential model is simulated with Monte Carlo. Apart from showing a 10-fold higher ionization than isolated monomers at low pH, interacting species contracted forming short-range clusters of charged and neutral ionizable groups. The presence of a charged sphere synergically boosted both effects due to monomer interactions, forcing the chains to condense onto its surface at much lower pH. Structural properties, however, seem to be controlled only by the ionization degree despite the presence of the topological restraint represented by the spherical surface. Using Monte Carlo titration results, the equilibrium ionization of isolated chains is also estimated; the results evidence that even weak interactions can easily lead to a doubling of the total charge.

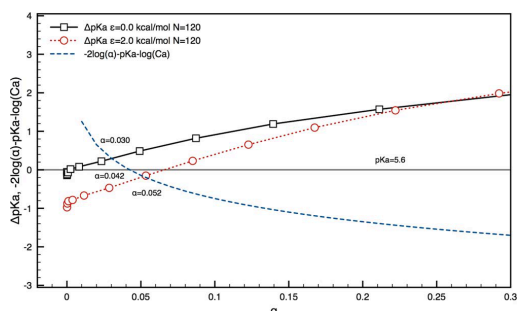


Figure 1. Change in effective pKa versus ionization degree for chains with and without intramolecular interactions [1]. The crossing with the dashed blue line indicates equilibrium ionization in pure water.

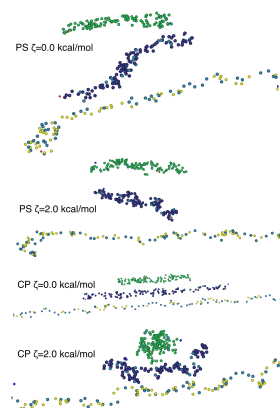


Figure 2. Typical conformations of chains as function of ionization degree in planar slits or cylindrical pores.

The impact of star-like geometries or confinement on the ionization, energetic and structural properties of the same model polymers was also investigated to unravel possible synergies between intramolecular interactions and constraints imposed onto the position of monomers. The effect of background ionic force was estimated introducing explicit ions. In all cases, the presence of intramolecular interactions substantially increases ionization and fosters more compact structures, hence adsorption, at low ionization.

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Theoretical modeling of ethene/propene copolymerization: a quantum mechanical/stochastic approach to the microstructure of block-copolymers

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One among the great challenges in polymer science is the deep understanding of the links between the catalyst features and its catalytic behavior toward monomers. Obviously, such goal has a great industrial and scientific interest for the design of copolymerization catalysts. In this respect, the fundamental role of steric hindrance of catalyst is widely accepted; conversely, the importance of the counter-ion, of the chain-control given by the ultimate or penultimate monomer and the competition between two different coordination sites still remain somewhat unclear [1]. In this work we describe theoretical study of the elementary steps involved in the copolymerization of ethene and propene by two C₂-symmetric metallocene catalysts, *rac*-H₂C-(Ind)₂ZrCl₂ and *rac*-H₂C-(3-*t*Bu-Ind)₂ZrCl₂ [2]. In thus, DFT analysis of reaction pathway gives us the energetics of insertions on the catalyst cation; a kinetic-Monte Carlo model instead, stochastically simulates the kinetic of copolymerization. The results obtained agree well with experimental distributions of triads and for the first time allow us to shed some light on the relative importance of the counter-ion, of the hypothetical penultimate effect and of the presence of two coordination sites.

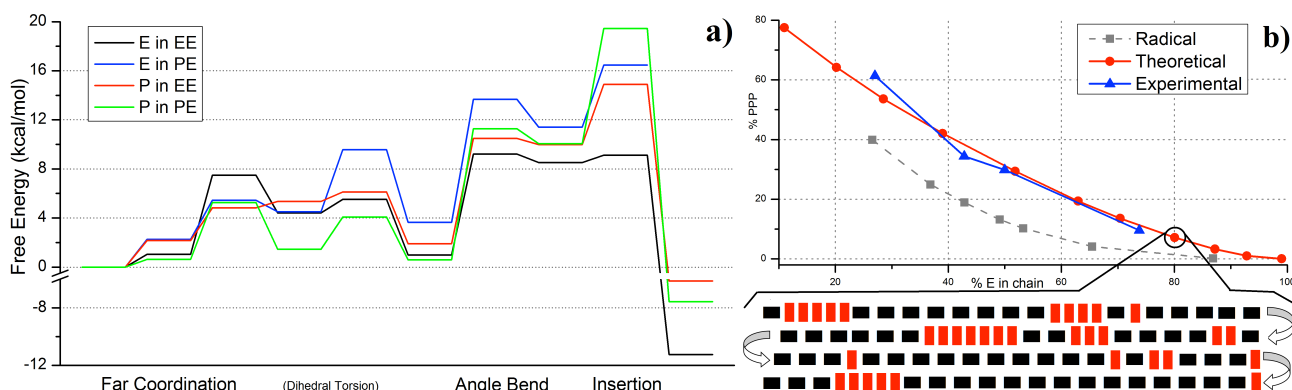


Figure 1. a) A typical insertion reaction pathway; b) PPP triads predicted by our model and experimentally obtained vs. molar fraction of ethene in the chains; on the bottom, a typical sequence of ethene (black blocks) and propene (red blocks) of a simulated chain.

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Carbon nanotubes-ABS nanocomposites for fused deposition modelling

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Development of novel nanocomposites for fused deposition modelling (FDM), one of the most widely diffused additive manufacture technology, offers a challenge for enhancing the properties of 3D-printed components [1,2]. In present work, the thermal-mechanical and electrical behaviour of carbon nanotubes (CNT)/acrylonitrile-butadiene-styrene (ABS) nanocomposites were investigated for FDM application. Various concentration (1 to 8 wt%) of CNT were melt dispersed in ABS by melt compounding, followed by extrusion to produce filaments. Neat ABS and ABS filled 6 wt% of CNT were selected and investigated for the FDM process at different build orientation: perpendicular concentric (PC), horizontal concentric (HC) and horizontal infill 45° (H45). The properties of neat ABS and ABS-CNT nanocomposites were monitored on the filaments to FDM samples including tensile, dynamic mechanic thermal analysis (DMTA), creep test, electrical resistivity, and resistive heating.

The presence of carbon nanotubes in host ABS matrix induced a remarkable enhancement in thermal-mechanical and electrical properties on both filaments and 3D-printed components. Elastic modulus and strength of composites were improved by CNT addition. As a side effect, elongation at break was reduced. Moreover, the presence of CNT also promoted the creep and thermal stability of 3D-printed parts due to the reduction in both creep compliance and coefficient thermal expansion. Conductive 3D-printed samples were achieved, but they exhibited a partial loss in resistivity with respect to filament nanocomposite. Moreover, resistivity of 3D-printed parts are highly dependent on the build orientation, which consequently leads to different surface temperature increment under applied voltages. For future work, the comprehensive understanding for electrical resistivity with respect to build orientation on FDM parts will be investigated.

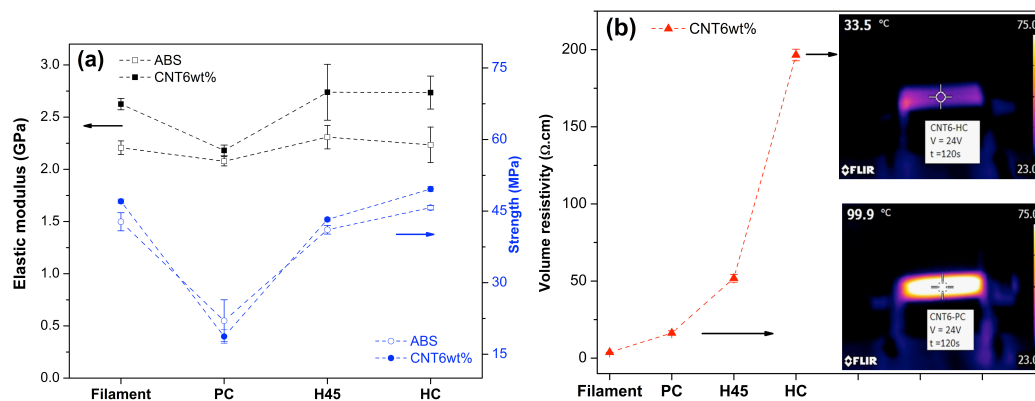


Figure 1. The properties of filaments and 3D-printed samples (HC, H45 and PC): (a) elastic modulus and strength of neat ABS and ABS-CNT nanocomposite, and (b) volume resistivity of ABS-CNT nanocomposites with the temperature increment under resistivity heating.

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From starch to carbon spheres and further oxidation to multifunctional nano-graphene oxide

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Starch represents one of the most abundant and cheap natural plant biomass resources. Graphene (oxide), on the other hand, has attracted tremendous attention due to its excellent thermal, mechanical, and bio-related properties. We have demonstrated [1,2] an efficient/facile route to prepare novel value-added nano-size graphene oxide (nGO) from starch. Microwave was applied firstly to hydrothermally decompose starch to carbon nanospheres (CN) [1]. CN was then transformed to nGO under oxygen-rich acidic conditions [2]. The formation of CN during microwave irradiation was related to the reactions in the soluble phase: starch hydrolyzed to glucose then dehydrated to levulinic acid and formic acid though 5-HMF as an intermediate. Meanwhile, 5-HMF carbonized/polymerized into CN, which was formed as a solid residue (Figure 1). Further oxidation of CN lead to exfoliation of nGO from the spherical CN. The obtained nGO was about 20×30 nm² in the lateral dimension. Due to the unique small and amphiphilic structure, nGO provided unique thermal, crystal, mechanical and barrier properties in PLA/starch biocomposites [2]. It was also proved that nGO is a promising material in bone-related biomedical applications due to its biocompatibility and bioactivity in starch [3] and PCL scaffolds [4]. MTT assay proved that nGO is biocompatible with osteo-MG63 cells under a certain high concentration (1mg/mL). Furthermore, nGO could induce hydroxyapatite in mineralization test, reflecting excellent bioactivity. A delicate closed-loop strategy was thus demonstrated: multifunctional nGO was derived from starch and further utilized as property enhancer in starch based composites.

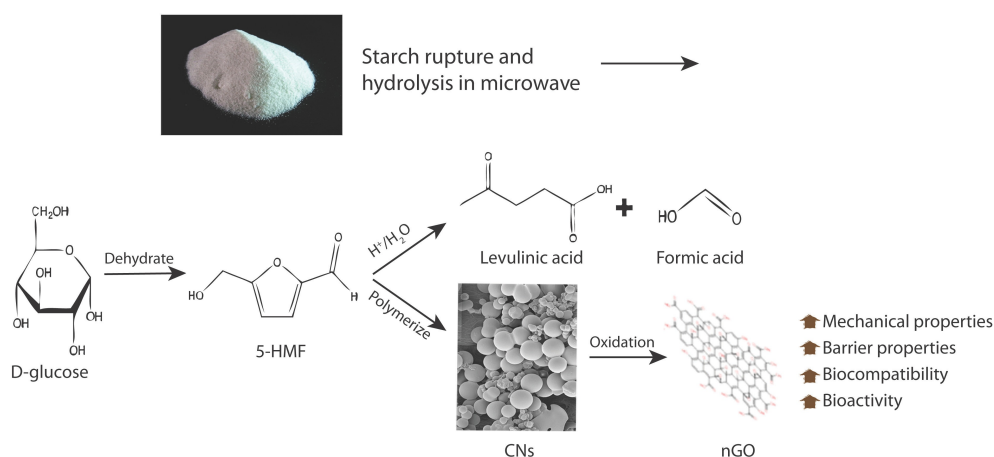


Figure 1. Transformation of starch to nGO.

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Design of polyurethane-based photoresists for two-photon polymerization and depolymerization

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Advanced technologies require the development of materials able to respond to external triggers (temperature, pH, pressure, electrical fields, etc.) by changing their physicochemical properties. Typically, property changes occur over the complete materials volume and cannot be localized. Spatial resolution in the triggering event can be achieved using focused light as stimulus. The most prominent examples are photoresist materials that can irreversibly crosslink or degrade upon light irradiation.

In this work, we present a new strategy to control polymerization and depolymerization using monomers including photocleavable protecting groups (PRPG) (Figure 1). Based on polyurethane chemistry, commercially available isocyanate monomers were crosslinked with caged diamines during light exposure. By including photocleavable groups in the monomer backbone, depolymerization of the network was achieved in a second irradiation step at a different wavelength and the degraded polymer could be washed out with water. Using a scanning laser and two-photon excitation, 3D patterns were fabricated in the polyurethane film.

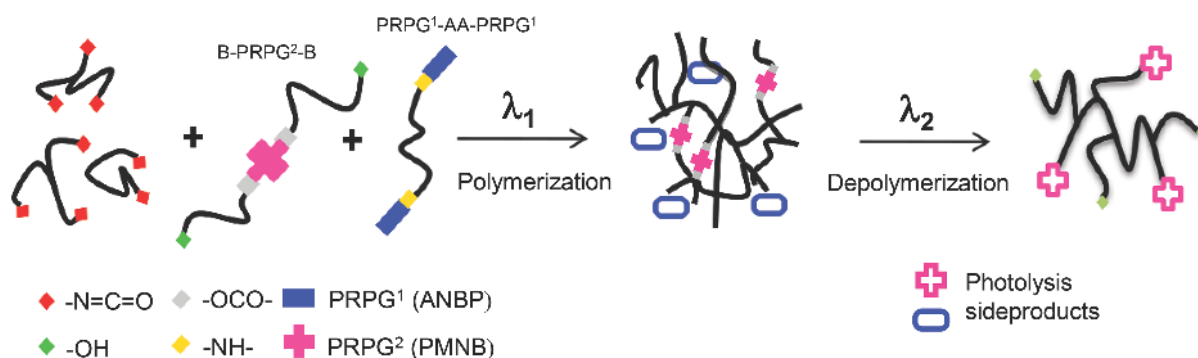


Figure 1. Scheme of a dual photosensitive material.

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New thermally stable Isoidide-derived diols based on Isosorbide for the preparation of thermoplastic polyurethane: microwave-assisted synthesis and optimization

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The synthesis of three new biobased chiral exo-exo configured isoidide-derived diols prepared from isosorbide and three types of diphenols were described. The synthesis conditions were optimized under conventional heating and under microwave irradiations (MW). The efficiency of microwave activation has been proved as an efficient, fast and simple route for the synthesis of the new diols. The results showed a dramatical reduction of the reaction time (more than twenty times faster) and an important improvement of the yield using MW (up to 74%). The thermogravimetric analysis (TGA) showed an excellent thermal stability of the three diols until 320°C compared to the parent isohexide (isosorbide) which has limited thermal stability at high temperatures (>250 °C). These three monomers were successfully polymerized using 4,4'-diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HDI). The resulting polyurethanes, exhibited an excellent thermal stability until 230°C. The new polymers based on the synthesized diols and MDI proved to be semi-crystalline with a high Tg value (between 160 and 177°C), while the polyurethanes which are prepared using HDI, display a Tg between 52 and 79°C. All synthesized polyurethanes exhibit very similar molecular weights since their intrinsic viscosity values differ very slightly between each other (from 0.41 to 0.46 dL/g).

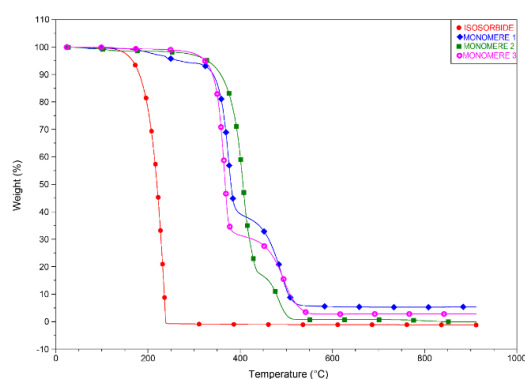


Figure 1. TGA thermogram of the three new monomers based on Isosorbide (heating rate: 10°C·min⁻¹).

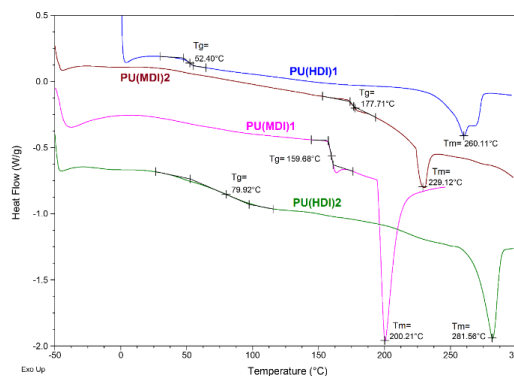


Figure 2. DSC curves of the synthesized thermoplastic polyurethanes from the biobased Isoidide-derived diols (heating rate: 10°C·min⁻¹).

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A comparative study of different winemaking by-products derived additives on oxidation stability, mechanical and thermal properties of polypropylene

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In the last decade, the increasing environmental awareness has led the science community and industry to make an effort in developing new ecological, sustainable and renewable systems. In this scenario, the valorisation of the winemaking by-products has certainly gained an important role because of both the huge amount of waste (millions of tons per years just in Mediterranean area) and the abundant presence of high-valued substance such as organic acids and polyphenols. In this work, solid by-products from winemaking industry are tested, discussed and compared as potential sources of thermal stabilizers for polypropylene (PP). Four different additives are used: three are obtained directly from different parts of solid wine wastes: pomace (Ve), stalks (Re), seeds (B) and a commercial powder tannin extract (T). All the different stabilizers have been added into the PP matrix by melt mixing with the same processing conditions. Firstly, mechanical and thermal properties were analysed and compared in order to understand the influence of the bio-additive on the polymer behaviour. DSC analysis have shown how the presence of the bio-additives does not affect the main characteristic temperatures (T_m , T_c). Creep tests have been conducted at four different temperatures (20, 40, 60 and 80°C) and filled materials have exhibited smaller strain deformation in all cases. The DMA analysis have highlighted an increase of the storage modulus and of the glass transition temperature. Young modulus, tensile strength and yield strain have not been significantly modified, showing similar and comparable values. The efficiency of the stabilizers, due to the polyphenolic component, has been investigated through OIT (Oxidation Induction Time) and OOT (Oxidation Onset Temperature) tests. These tests showed that winemaking by-products derived additives enhanced the thermal stability of PP. These results show that winemaking by-products display promising potentials as possible alternatives to conventional synthetic polymer additives, with an environmentally and cost-effective advantage.

Synthesis, characterization and applicative study of innovative materials for the conservation of cellulosic artefacts

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New biopolymers and nanocomposites were synthesized using saccharides as feedstock and their application in the field of cultural heritage, in particular for the conservation of cellulosic artefacts, was studied. The choice of renewable starting materials was made in accordance to the growing interest of academia and industry for the exploitation of lignocellulosic biomasses. Moreover, focusing on the conservation of cultural heritage, the use of bio-based materials has further advantages like the compatibility, the affinity and the respect for the works of art, especially those made of the same chemical species that constitute the biomass (i.e. wood and paper) [1,2].

Saccharides were chosen as starting materials for the synthesis of bio-based monomers in order to introduce units with a structure similar to that of the cellulosic materials in the new products. Moreover, the synthetic methodologies for the preparation of the new biopolymers and nanocomposites were selected taking into account their future use in the preservation of the cultural heritage.

In particular, allyl saccharide monomers were synthesized using allyl bromide to functionalize α,α' trehalose or methyl α/β -D-glucopyranoside. Copolymers of these allyl monomers were obtained with vinyl acetate through radical copolymerization reactions performed in methanol as a solvent and without additives.

Allyl α,α' trehalose/vinyl alcohol and allyl methyl α/β -D-glucopyranoside/vinyl alcohol copolymers were obtained by hydrolysing the correspondent vinyl acetate copolymers in order to have water soluble products, suitable to be used in the treatment of wood and paper, and to prevent the hydrolysis of the vinyl acetate groups after the application of the products on the degraded material. The copolymers were characterized through FT-IR, NMR, SEC and thermal properties were evaluated by DSC.

The nanocomposites were designed with the aim of obtaining new products with antimicrobial activity for the superficial treatment of cellulosic artefacts. In particular, new nanocomposites between TiO₂ anatase nanoparticles and allyl saccharide/vinyl acetate copolymers were obtained by grafting the copolymers on properly functionalized nanoparticles. The nanocomposites were characterized by FT-IR spectroscopy and SEM.

Finally, some applicative studies on cellulosic substrates, such as wood and paper, were performed to test the properties of the new copolymers and nanocomposites (i.e. consolidating properties, antifungal properties).

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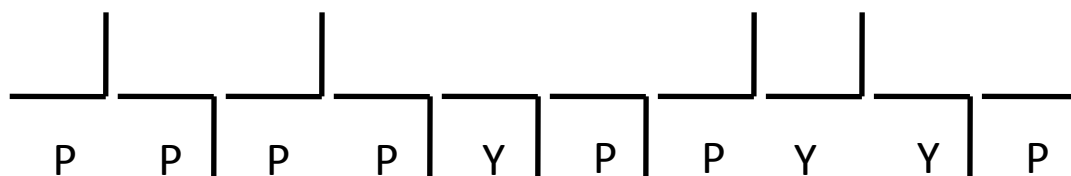
Syndiotactic propene- α -olefin copolymers: analysis of the microstructure by two-dimensional NMR spectroscopy

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Syndiotactic propene- α -olefins copolymers, with the comonomer changing from 1-eicosene to 1-butene, have been synthesized using a single-center metallocene catalytic system of C_s symmetry. Microstructures have been analyzed in details by means of mono- and two-dimensional NMR spectroscopy. Information about the copolymers tacticity has been obtained from the 2D HSQC experiments analyzing the compositional diads, *i.e.* the $S_{...}$ region, (38 - 45 ppm in the spectra). The two homosequences for P and Y, where P = propene and Y = comonomer, showed a syndiotactic microstructure, *rr* as expected, (scheme 1) while each time a PY diad is formed an error can be noticed, associated to the formation of an isotactic sequence, *mm*. This effect could be related to an error in the stereocontrol due to a chain backskip, (chain migration without insertion), due to the presence of bulky comonomer as 1-eicosene. This "error" may be due not to a loss of stereocontrol from the catalytic site and may depend on the length and/or the steric bulkiness of the alkyl substituent of the comonomer. To evaluate the origin of this effect and to understand the copolymerization mechanism, extensive 2D NMR studies were performed on samples with higher comonomer content, changing the length of the alkyl substituent and the bulkiness of the comonomer chain.



Scheme 1. Hypothesis of microstructure for sPP_C20 copolymer

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Water/alcohol soluble conjugated polymers as interfacial layer materials for organic electronics

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Interfacial engineering has been recently identified as fundamental strategy for maximizing efficiency and stability of organic electronic devices. To this aim, a new class of water/alcohol soluble materials comprising a π -conjugated backbone with pendant polar or ionic groups has been recently developed [1]. These polar conjugated polymers have the typical properties of polymeric semiconductors, such as easy processability, chemical tunability, lightness and flexibility, and are suitable for meeting the growing demand for environmentally friendly materials. In fact, the solubility in water and alcohols obtained by the incorporation of polar/ionic side groups can potentially provide increased biocompatibility for sensor applications and more environmentally friendly manufacturing options. Moreover, the possibility for orthogonal solvent processability opens the way to all-solution-processed organic multilayer devices.

In this view, we have designed, synthesized and tested a whole series of polar conjugated polymers featuring a fluorene-based backbone with pendant phosphonate and/or amine groups. We present the synthetic strategies we have followed for their synthesis and a few example of their application as charge regulating layer in optoelectronic devices [2].

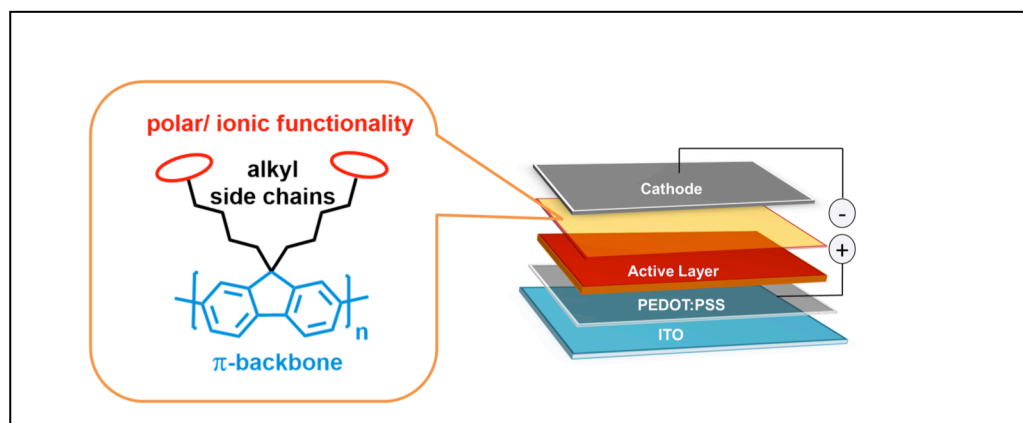


Figure 1. General chemical structure of polar conjugated polymers and OLED design architecture.

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Homo- and co-polymerization of ethylene with norbornene catalyzed by phosphine Vanadium(III) complexes

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The study of phosphine complexes with transition metal halides is an important topic and includes different compounds depending on the metal oxidation state and its position in the periodic table.[1] The preparation of vanadium–phosphine complexes has been the subject of research [2], even if only for $VCl_3(PMePh_2)_2$ has been determined the structure [3], and none of the published complexes has ever been tested as pre-catalyst in processes of interest to the polymer and organic chemistry communities.

In this study, we have synthesized and fully characterized a series of V(III) complexes with alkyl and aryl phosphine ligands such as PMe_xPh_{3-x} ($x = 0, 1, 2$) and PR_3 ($R = tBu, Cyp, Cy$). The complexes were readily prepared in one simple, high-yielding step from commercially available reagents. All the complexes were used, in combination with $AlEt_2Cl$ as cocatalyst, in the homo- and co-polymerization of ethylene (E) with norbornene (NB). The results have been carefully compared with those from the precursor $VCl_3(THF)_3$ and $V(acac)_3$.

The polymerization of ethylene gives linear poly(ethylene)s with T_m s of about 130 °C, while the E/NB copolymerization gives mainly alternating, atactic, amorphous copolymers with a NB content ranging from 35.5 to 39.3 mol%, and T_g s from 81 to 93 °C. The catalysts based on V(III)–phosphine complexes exhibit excellent activities in the E/NB copolymerization, from 10080 to 26424 $kg_{pol}/(mol_V \times h)$. A relationship exists between the phosphine electronic and steric properties and the rate of catalyst initiation (phosphine dissociation), thus indicating that initiation can be tuned by changing the substituents on the phosphorus atom. Overall, catalysts based on V(III) complexes with aryl–phosphine (weaker σ -donor character) are more active than those with alkyl–phosphines (stronger σ -donor character), thus suggesting that the activity increases with decreasing phosphine donor strength. However, steric properties too play an important role on the activity: catalysts based on V-complex with a large size ligand such as $PtBu_3$ ($\theta = 182^\circ$, strong σ -donor) are more active than those with PMe_2Ph ($\theta = 122^\circ$, weak σ -donor). In this case the larger size of $PtBu_3$ likely compensates for its higher donor strength.

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**Ti(IV)-catalyzed polymerization of dicyclopentadiene:
isolation of a crystalline tetramer
having a 2,3-*exo*-disyndiotactic structure**

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Norbornene (NB) and its derivatives vinyl-type polymers possess unique properties, which are advantageous for technical application in microelectronics [1]. In the past years, interesting results were obtained by our group regarding the synthesis of stereoregular crystalline oligomers and polymers from NB with TiCl₄/Et₂AlCl [2]. The crystalline structures of the above polymers and oligomers were determined, being the disyndiotactic polymer structure of particular interest. Indeed, disyndiotactic poly(NB)s adopt a remarkable conformation in the crystalline state: wide helices with relatively compact structures were formed, leaving an empty accessible tubular channel at the core, in which guest molecules like toluene are readily hosted. This feature made the polymer of particular interest, in view of a possible use in sensing and recognition/separation technologies. This application is, however, offset by the poor solubility and hard processability of the polymer. These drawbacks could be improved by using functional NBs such as 5-vinyl-2-norbornene, 5-ethylidene-2-norbornene and dicyclopentadiene (DCPD); in addition to the ready availability of these monomers, the resulting polymers are expected to have double bonds which may be useful for further chemical modification.

We first examined the polymerization of DCPD (the mixture of *endo/exo* isomers) with TiCl₄/Et₂AlCl [3]. A new crystalline DCPD tetramer, having a 2,3-*exo*-disyndiotactic structure, is obtained (Figure 1). By combining global optimization techniques based on configurational sampling in generalized statistical ensembles, with very high quality synchrotron X-ray diffraction data, the molecular mass of the crystallizing oligomer was first singled out, and its structure was then determined with a high degree of accuracy.

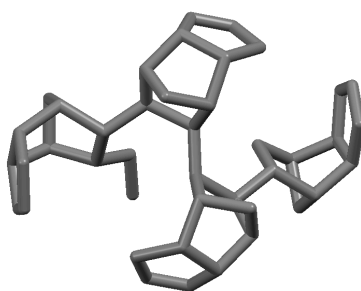


Figure 5. A view of the structure of the crystalline DCPD tetramer.

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1-Octene copolymers with 1-decene and cyclopentene by an α -diimine Ni(II)/AlEt₂Cl catalyst: synthesis, thermal and mechanical behavior

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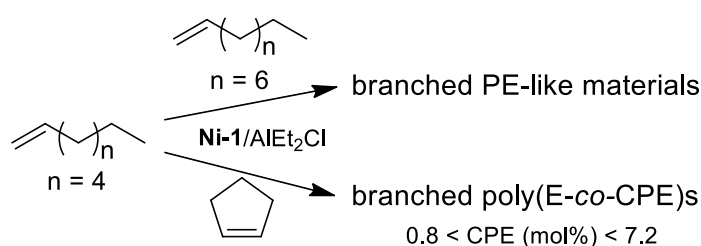
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In our recent work we investigated the polymerization of 1-octene catalyzed by an α -diimine Ni(II) complex [(ArN)C(CH₃)-(CH₃)C(NAr)]NiBr₂ [Ar = 2,6-(*i*Pr)₂C₆H₃] (**Ni-1**) in combination with different aluminum alkyls [1]. Branched poly(ethylene)-like materials with high molecular weight, narrow molecular weight distribution, and low crystallinity were obtained. The tensile tests showed that the resulting polymers behave as thermoplastic elastomers (TPEs) with properties close to those reported for ethylene/1-octene copolymers, and generally outperform the 1-dodecene/ethylene di- and tri-block copolymers in terms of elastic recovery [2]. We found that by suitably choosing the type of aluminum alkyl, monomer concentration, and polymerization temperature it was possible to tune the polymer (micro)structure (*i.e.*, total branching, branch-type, and crystallinity) which in turn strongly affects the polymer thermal and mechanical properties.

We have been searching for alternative routes to easily tune the (micro)structure of the polymers from 1-octene, allowing access to TPEs with improved mechanical properties. In this respect we are now reporting on the copolymerization of 1-octene with 1-decene and cyclopentene catalyzed by **Ni-1** in combination with AlEt₂Cl (Scheme 1). The effect of the type and the feedstock concentration of the comonomer on the microstructure, the total branching and the branch-type distribution was evaluated by ¹H and ¹³C NMR spectroscopy. Moreover, a comprehensive investigation on the mechanical behavior by uniaxial stretching until failure, step-cycle and creep tensile tests was carried out.

The results obtained clearly indicated that this approach can be considered a novel, convenient way to fabricate innovative TPEs from readily accessible starting materials.



Scheme 1. Copolymerization of 1-octene with 1-decene and cyclopentene.

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Cr(II) and Cr(III) complexes with pyridine-imine ligands: synthesis and application in the polymerization of olefins

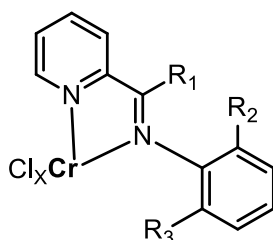
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Chromium complexes have been widely studied in the field of olefin polymerization in both academia and industry, in particular as regards the heterogeneous catalysts for ethylene polymerization {e.g., heterogeneous Phillips catalyst for the production of high-density poly(ethylene)}, and the homogeneous catalysts for the production of linear α -olefins [1], and syndiotactic 1,2 poly(butadiene) [2,3]. Conversely, few reports appeared in the literature concerning the homo- and co-polymerization of cycloolefins with chromium-based catalysts [4,5].



Cr(II) complexes ($X = 2$)

Cr-1 $R_1 = R_2 = R_3 = H$

Cr-2 $R_1 = R_2 = H; R_3 = Me$

Cr-3 $R_1 = H; R_2 = R_3 = Me$

Cr-4 $R_1 = H; R_2 = R_3 = iPr$

Cr-5 $R_1 = Me, R_2 = R_3 = H$

Cr(III) complexes ($X = 3$)

Cr-6 $R_1 = R_2 = R_3 = H$

Cr-7 $R_1 = H; R_2 = R_3 = iPr$

Cr-8 $R_1 = Me; R_2 = R_3 = iPr$

Figure 6. Chromium complexes.

In this communication, the synthesis of Cr(II) and Cr(III) complexes with pyridine-imine ligands having different substituents on the aryl ring is reported (Fig. 1). All the synthesized chromium complexes were fully characterized and then tested, in combination with different Al-alkyls (*i.e.*, MAO, MMAO, Et₂AlCl), in the polymerization of various olefins.

In the polymerization of 1,3-butadiene the complexes showed from modest to good activities, giving amorphous polymers with essentially mixed *cis*-1,4/1,2 structure ($T_g = -85^\circ\text{C}$) or *trans*-1,4/1,2 ($T_g = -58^\circ\text{C}$) in 1:1 ratio, depending on the ligand employed. In contrast, interestingly enough, only the complex **Cr-1**, in combination with MAO, proved to be active for the ethylene polymerization, giving semicrystalline poly(ethylene) ($T_m = 113, 123^\circ\text{C}$, $\Delta H_m = 210 \text{ J/g}$) even at low Al/Cr ratio.

Finally, all the complexes exhibited a rather good activity in the polymerization of norbornene and dicyclopentadiene, giving semicrystalline oligomers through a vinyl-type addition polymerization. In analogy with that previously reported in the literature [4], the low molecular weight polymers obtained were found to have a stereoregular 2,3-*exo*-diheterotactic structure. In particular, the 2,3-*exo*-diheterotactic dicyclopentadiene oligomer is a novel material which was never reported before.

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Effects of diethylaluminium ethoxide on the Cr active sites in the Phillips catalyst

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The Phillips catalyst is among the most important heterogeneous catalysts for ethylene polymerization: it accounts for about 50% of the high density polyethylene (HDPE) world's demand. The active phase is constituted by a highly dispersed chromium oxide supported on silica. Diethylaluminium ethoxide (DEALE) is used in the industrial practice as an alkylating co-catalyst to influence the activity of the Phillips catalyst and the properties of the produced PE. It has been demonstrated that DEALE modifies the active sites distribution, promotes in situ branching, decreases the induction time and enhances the sensitivity to H₂ for MW regulation [1].

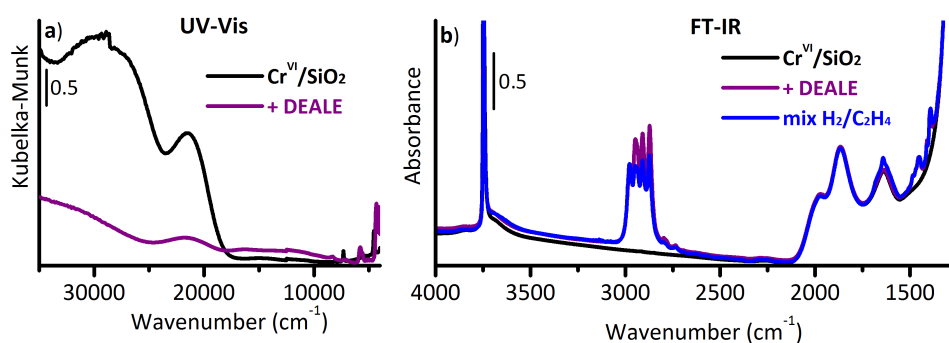


Figure 1 Part a) UV-Vis spectra of the Cr^{VI}/SiO₂ catalyst before (black) and upon treatment with liquid DEALE (purple); Part b) FT-IR spectra of the Cr^{VI}/SiO₂ catalyst collected before (black) and upon treatment with liquid DEALE (purple) and after the reaction with a H₂ + C₂H₄ gas mixture.

The aim of this work is to explore the properties of DEALE-modified Cr sites at a molecular level, in order to understand the reasons behind the improved reactivity at room temperature and at low pressure, considering that the Cr^{VI}/SiO₂ system does not polymerize under the same conditions but only at higher pressure and at 80-110 °C. The DEALE-modified system has been investigated in details by means of in situ FT-IR and UV-Vis spectroscopy, applied also in the presence of probe molecules [2]. Furthermore, the catalyst was tested in the gaseous ethylene polymerization in the absence and in the presence of H₂. Figure 1 summarizes the most relevant spectroscopic results (UV-Vis in part a: partial reduction of the Cr^{VI} sites; FT-IR in part b: effect of H₂ on the modified catalyst). A complete understanding of the molecular modifications occurring on the Cr^{VI}/SiO₂ system upon DEALE reaction will be achieved thanks to the comparison of the same experiments repeated on the CO-reduced Cr^{III}/SiO₂ catalyst, which has been already studied in the literature as a model for the Phillips catalyst [3].

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Recovery and reuse of carbon fibers from composites scraps and production waste by pyrolysis

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Carbon fibers reinforced polymers (CFRPs), due to their extraordinary mechanical properties associated with light weight, are used in a growing number of fields (automotive, aerospace, defence, wind turbines, sport and leisure). This huge development opens the question related to their disposal which, due to their heterogeneous compositions, results very difficult. In particular, in thermoset CFRPs, the high added value carbon fibers cannot be easily recovered and recycled by simply remelting and remoulding the matrix.

Pyrolysis is currently considered to be the only process for recycling CFRPs that is available on an industrial scale and leads to a volatile phase made by gases and oil fractions and to a solid phase mainly composed of carbon fibers covered with char. Curti S.p.A. has recently proposed an innovative static bed batch pilot reactor able to treat directly the whole parts, up to 2 m in diameter, in order to save the energy costs of shredding the feeding wastes and simultaneously recovering energy and materials, in particular CFs. Previous studies [1] highlighted that, in order to reuse such carbon fibers, it is necessary to remove the char layer. Thus the present work aims at demonstrating the potential of the recovered carbon fibers as secondary raw materials, validating a process able to recycle the composite's carbon-fibers fraction and close their Life Cycle in a Cradle-to-Cradle approach. Hence, in this study the solid residue (carbon fibers covered by a carbonaceous layer) obtained upon pyrolysis in the innovative pyrolysis pilot plant by Curti S.p.A. [2] was characterized and subjected to a further oxidative step in different working conditions to provide clean fibers. For the sake of comparison, the same process was applied to virgin fibers, in order to assess the impact of the oxidation step onto their properties, without the bias of the pyrolysis treatment, with the aim of helping to identify the most convenient oxidative conditions. The effects of the process on the recovered fibers, as well as on virgin fibers, were evaluated by SEM and Raman. The characterized post-treated fibers are then used in a lab-scale manufacturing process in order to obtain new Chopped Carbon Fiber Reinforced Polymers (Re-CCFRPs). The Re-CCFRPs mechanical performances are finally compared with composites made using the same process but commercial virgin chopped fibers. Comparable mechanical properties for virgin and recovered chopped fiber composites are achieved, thus paving the way for a reliable approach to the recycling of the carbon fiber reinforced composites.

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Green organogels based on PHB for the cleaning of paintings

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Painted artworks can be seen as complex multi-layer materials, where the layered structure is covered with a protective “sacrificial” coating having the role of preserving the underneath constituents from the environmental ageing. When the protective coating (usually organic in nature) ages too much, however, it degrades and might change the perception of the painting itself, so much that it has to be removed and replaced. This operation has to be carried out without affecting the actual painted layers, in order to prevent micro- and macroscopic damages, causing swelling or leaching of the original paint films. While common organic solvents are usually applied for the task, they might sometimes act too aggressively. In this frame organogels [1] can limit the diffusion of organic solvents towards the painting and, at the same time, can prevent the volatilization of such solvents for the sake of the conservators’ health.

In this work, novel sustainable organogels [2], based on a biopolymer (polyhydroxyalkanoates PHA), bio-based solvent (γ -valerolactone GVL, dimethylcarbonate DMC, ethyl lactate EL) and green plasticizer (triethylcitrate TEC) were produced. Various PHA-based gels were prepared and characterized in terms of molecular weight, thermo-reversibility, morphology and aging behaviour. Their performance in removing aged protective patinas from the surfaces of artworks was then tested, both on mock up surfaces and on real paintings in comparison to traditional solvent-based cleaning protocol with the aim of setting a green and sustainable cleaning approach that could be effective, easily controllable and not dangerous for human health and the environment. The latter aspect is particularly relevant, since in this field no particular attention has been devoted up to now to the environmental impact of the applied cleaning methods. The most effective formulations, after their use, were indeed assessed in term of biodegradability and recyclability. The painting and mock-up surfaces were tested to verify the removal of the protective coatings, and the lack of contamination from gel residues.

The developed PHA-based organogels proved to be highly effective in the removal of varnish layers of different composition (terpenic, acrylic and oily), without affecting the pictorial layers underneath. Moreover, the gels were readily biodegradable in water and non-toxic for humans and aquatic organisms, providing a green tool that can be successfully applied to the cleaning of various works of art.

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Exploring how the architecture of comb-like polycaprolactone-PEG copolymers influences their performances as drug delivery systems

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Poly(ethylene glycol) (PEG) and the polyester poly(ϵ -caprolactone) (PCL) are common substrates for the synthesis of biocompatible and biodegradable nanomaterials [1]. Through a combination of Ring Opening Polymerization (ROP) and Atom Transfer Radical Polymerization (ATRP), we have synthesized well-defined amphiphilic PCL-PEG copolymers. By varying the structure of the initiator used for the ATRP (i.e. linear, 4-armed or hyper-branched), a library of comb-like and multi-branched comb-like polymers, having different morphology and size, was obtained. We have investigated how polymers architecture influences their ability to encapsulate a hydrophobic molecule and behave as efficient drug delivery systems. In particular, the hydrophobic corticosteroid dexamethasone, known as a therapeutic drug for kidney-glomerular diseases [2], was chosen as a model. The ratio between PEG and PCL, as well as the size of the poly(ϵ -caprolactone)-core *versus* the one of the pegylated hydrophilic shell, were also examined.

The synthesis and the characterization of the polymers will be here presented.

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Mannosylated poly(ethylene glycol)-poly(ϵ -caprolactone) copolymers as potential lectin ligands

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Lectins are carbohydrate-binding receptors, whose interactions with saccharides are involved in many biological processes, including cellular infections by viruses and toxins. The possibility to antagonize the pathological interactions between lectins and their natural ligands is at the base of anti-adhesive therapies. Glycopolymers, which are polymers bearing pendant saccharides, are interesting biomaterials because they can easily have high valencies, which confer them the ability to strongly bind to lectins through multivalent interactions. Here we present a library of mannosylated comb-like copolymers based on poly(ethylene glycol) (PEG) and poly(ϵ -caprolactone) (PCL), which have been synthesized by a combination of two controlled radical polymerizations: Ring Opening Polymerization (ROP) and Atom Transfer Radical Polymerization (ATRP). PCL bearing a terminal triple bond was obtained from ϵ -caprolactone by ROP, and subsequently polymerized with different percentages of activated PEG through ATRP. By using a linear or a four-arm initiator, the shape of the final products was varied. Linear or four-armed polymers with a predetermined degree of polymerization and a narrow molecular weight distribution were obtained in high yields, and finally mannosylated through Copper-catalyzed Azide-Alkyne (CuAAC) *click* reaction (Figure 1).

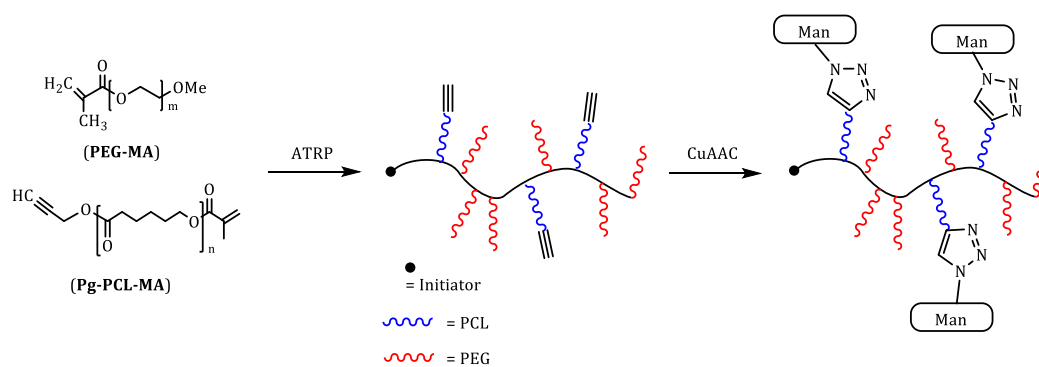


Figure 1. Synthetic pathway towards mannose-functionalized PEG-PCL copolymers.

Finally, glycopolymers activity as ligands for lectins was assessed through *in vitro* biological tests, using Concanavalin A as lectin model.

Potentially edible pectin-based film for a highly water soluble ellagic acid salt release

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Diet and nutrition are fundamental factors in the promotion and maintenance of good health conditions. They occupy a prominent role in the prevention of chronic diseases like obesity, diabetes, cardiovascular diseases, cancer and osteoporosis [1]. Medical research has uncovered the causes of these chronic diseases: virtually, the underlying mechanisms of all of these diseases depend on oxidative processes, which lead to products that display high reactivity and are able to affect specific molecular targets in the body, like cellular DNA [2]. Pectin is an etero-polysaccharide composed by D-Xylose, D-apiose, D-galactose and galacturonic acid as the most abundant. In other terms, pectin could be identified as a multi-block copolymer where monosaccharide units (D-Xylose or D-Apiose) bond blocks of homogalacturonan together, i.e. nearby chains of α -(1-4)-linked D-galacturonic acid. Galacturonic acid is present as free acid moiety or as a methyl ester: the amount of ester units [degree of esterification (DE)] depends on the source of pectin and the method of extraction and affects the properties of pectin itself (i.e. water compatibility, ionic interaction among chains and bivalent cations). Pectins are commonly used for the production of drug release systems; in addition, the possibility to obtain a reversible gel adding bivalent cations, permits to tune the mechanical properties of gels tailoring them for specific aims.

We report the preparation of pectin-based films used as potentially edible ellagic acid (EA) release devices. EA, a natural polyphenol mainly present in pomegranate, berries and grapes, was selected due to its antioxidant effects and apoptosis-inducing activity against certain types of cancer cells ; on the other hand, the poor water solubility of EA ($\approx 10\mu\text{g ml}^{-1}$) dramatically reduces its bioavailability and its applications. We prepared a highly water soluble EA-lysine salt, used to produce pectin-based films, obtained via solvent casting deposition of a solution of pectin, CaCl_2 and EA-lysine salt. Two different types of pectin were used: high and low methoxylated. The release properties were assessed according to calcium concentration, the DE and the amount of EA-lysine salt.

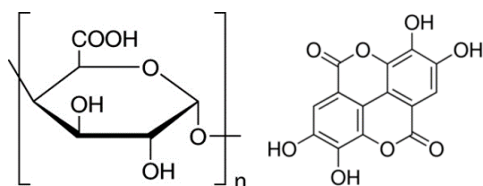


Figure 1. Chemical structure of homogalacturonan and Ellagic acid.

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Polylactide/cellulose nanocrystals: the *in situ* polymerization approach to improved nanocomposites

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Poly(lactic acid), shortly PLA, is one of the most attractive biopolymer, both to researchers and industry, since it proved not only to possess good physical properties, but also appeared to be cost competitive against common packaging plastics (such as PET). In addition, it is biodegradable and its monomer can be extracted from renewable sources. However, alongside with these good properties, PLA still suffers some drawbacks (poor thermal and mechanical resistance, poor barrier properties and low flexibility) which significantly limit its applicability. Among possible alternatives to overcome some of these limitations, the preparation of nanocomposites has emerged as the most promising suitable solution [1]. Aiming to produce fully organic bionanocomposites, we decided to focus our attention onto cellulose nanocrystals (CNCs). CNCs are the crystalline nanometric domains in cellulose fibers and they can be extracted from cellulosic matrices through acidic or oxidative hydrolysis reactions. What is interesting about CNCs comes from their outstanding chemical (many free hydroxyl surface groups that can be functionalized in different ways) and physical (extremely high young modulus, low density and high aspect ratio) properties, and also from the fact that they can be extracted from biomass residues [2].

On the basis of our related experience on preparation of PLA nanocomposites containing nanosilica (NS) [3] or modified montmorillonite (MMT) [4] fillers, we looked at PLA-CNCs nanocomposites via the *in situ* polymerization of L-lactide in the presence of various amounts of CNCs. It is well established that *in situ* polymerization in the presence of fillers provides distinct advantages when compared to other nanocomposite synthesis techniques, appearing more appropriate in providing excellent dispersion of the nanoparticles, which should have a greater impact on achievable properties. To the best of our knowledge, no *in situ* polymerization strategies employing CNCs have been described for the preparation of PLA nanocomposites.

In this study, the *in situ* polyaddition of L-lactide was performed with different loading ratios of CNCs, prepared by acidic hydrolysis of cotton linters. The protocol exploits the alcoholic moieties of CNCs as initiators in ring opening polymerization reaction of L-lactide. Molecular weight, morphology, thermal, mechanical and crystallization properties of the obtained nanocomposites were evaluated. Some of them exhibited enhanced thermal stability compared with pure PLA and with conventional PLA-CNCs blends, introducing for the first time the *in situ* polymerization strategy as a valuable approach for the preparation of improved PLA-CNCs nanocomposites.

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Conductive inks based on methacrylate end-capped poly (3,4-ethylenedioxythiophene) for printed, flexible and wearable electronics

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A new synthesis of methacrylate end-capped Poly (3,4-ethylenedioxythiophene) (PEDOT) was performed: it is soluble in common organic solvents, thus overcoming the well-known technical problems related to the use of commercial PEDOT in different printing technologies, such as screen printing, due to its poor processability and compatibility in formulations with other resins and polymers [1]. The new synthetic method developed is based on the direct oxidative polycondensation of 3,4-ethylenedioxythiophene (EDOT) in the presence of an oxidant species and a cross-linkable end-capper, i.e. methacrylate end-capped EDOT (mEDOT), prepared via Friedel Crafts acylation with methacryloyl chloride. The oxidative polycondensation between EDOT and mEDOT monomers in the presence of a new kind of doping agent, Sulfonated Polyarylethersulfone (SPAES) [2,3] - characterized by different degree of sulfonation (DS) - was conducted, leading to functional end-capped conducting PEDOT, with conductivity of 210 S/cm, 50 S/cm higher than the one of commercial PEDOT. Thanks to the enhancement of solubility, leading to better processability, end-capped PEDOTs were formulated with a thermoplastic ink, Plastisol[®], and electronic circuits were successfully screen printed on flexible textile substrates [4,5], in order to obtain wearable electronic circuits [6] (Figure 1).

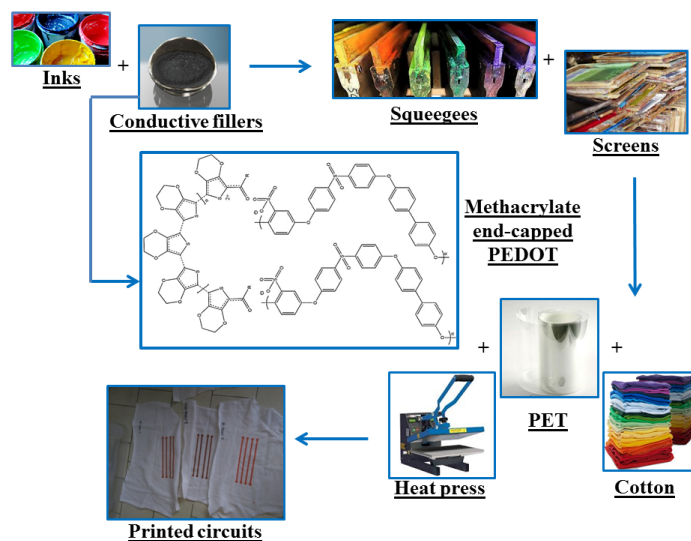


Figure 1. Printed, flexible and wearable electronic circuits.

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Poly- L-lactic acid nanofiber–polyamidoamine hydrogel composites: preparation, properties, and preliminary evaluation as scaffolds for human pluripotent stem cell culturing

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Human Pluripotent Stem Cells (hPSCs) hold great promise for cell therapy and tissue engineering, as well as drug screening [1,2]. For a clinically valid development of stem cell-based therapies some biological and engineering challenges still need to be overcome, such as the design of engineered cell culture microenvironment that support hPSCs proliferation while maintaining their pluripotency.

In this study a novel composite synthetic scaffold was designed, inspired by the overall structure of tissue extracellular matrix (ECM), and the short-time expansion and self-renewal of human Embryonic Stem Cells (hESCs) and human Induced Pluripotent Stem Cells (hiPSCs) was investigated in view of potential application of the materials as scaffolds for stem cell-mediated tissue engineering applications. The scaffold was composed by an *arg-gly-asp* (RGD)-mimic polyamidoamine hydrogel [3] with embedded poly-L-lactic acid (PLLA) mat of continuous electrospun nanofibers with average diameter 570 ± 170 nm, mimicking the gel and fibrous components of ECM, respectively. The biomimetic properties and the softness of the hydrogel component were therefore combined with the strength of the nanofibrous PLLA mat. Strong matrix-fiber adhesion was achieved by N₂ atmospheric pressure non-equilibrium plasma treatment of the PLLA mat. The scaffolds were characterized for their swelling and degradation behavior and their mechanical properties were investigated. Biological studies demonstrated that the scaffolds supported short term self-renewal of Human Pluripotent Stem cells in feeder-free conditions and that the cells fully retained stemness for at least 7 days. The novel composites developed in this work are entirely synthetic and they can be obtained by standardized procedures [4]. Moreover, their mechanical properties, swelling and degradation behavior in aqueous media can be easily tuned by tailoring hydrogel crosslinking degree. Prospectively, their chemical structure is suitable to covalently incorporate bioactive molecules in order to specifically modulate the signaling pathways of hiPSCs.

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Amphoteric polyamidoamines as innovative tools to selectively direct antimalarial drugs towards *Plasmodium*-infected red blood cells

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In 2015 malaria, an infectious disease caused by the protist *Plasmodium spp.*, registered 212 million cases and claimed the lives of 429,000 people, mainly young African children in developing regions. Despite a significant reduction in the number of malaria-related deaths, there is still a need for new therapeutic strategies such as finding new antimalarial drugs or substantially improving old ones, through decreasing side effects and avoiding resistance evolution. Because malaria pathophysiology is so complex and the disease is so widespread, it is generally accepted that to achieve eradication a combination of tools targeting the parasite and/or mosquito will be needed. These include the improvement of existing approaches and the development of new ones, with drug therapy remaining the mainstay of treatment and prevention to target the parasite reservoir, and nanotechnology being able to provide innovative useful strategies. Encapsulation of drugs in targeted nanovectors (NVs) is a rapidly growing area with a clear applicability to infectious disease treatment, and pharmaceutical nanotechnology has been identified as a potentially essential tool in the future fight against malaria. With the advent of nanoscience, renewed hopes have appeared of finally obtaining the long sought-after *magic bullet* against malaria in the form of a NV for the targeted delivery of antimalarial compounds exclusively to *Plasmodium*-infected red blood cells (pRBCs), thus increasing drug efficacy and minimizing the induction of resistance to newly developed therapeutic agents. We have engineered polyamidoamine (PAA)-derived NVs combining into a single chemical structure drug encapsulating capacity, antimalarial activity, low unspecific toxicity, specific pRBC targeting, optimal *in vivo* activity, and affordable synthesis cost. Recent data suggest that the antiparasitic mechanism of PAAs consists on a coating of *Plasmodium* that has the effect of blocking the erythrocyte invasion of egressed parasites. The ensuing prolonged exposure of *Plasmodium* to the immune system might be applied to the design of new malaria prophylactic approaches where PAAs could play a dual role as carriers of antimalarial drugs, and as boosters of immunity. In addition to binding egressed merozoites, PAA-based nanoparticles are capable of penetrating late-stage pRBCs, and of adsorbing on intracellular merozoites of both human and murine malarias. Affinity chromatography assays indicate that the specific targeting of PAAs to pRBCs results from the presence of adhesive proteins exported by the parasite to parasitized erythrocyte membranes. The mechanism of pRBC entry by PAAs has not been elucidated yet but it seems to be related to the known increased permeability of parasitized cells to small nanostructures. Preliminary experiments where fluorescently labeled PAAs were administered to living *Anopheles atroparvus* mosquitoes revealed the presence of the polymers in the circulatory fluids of the insect, thus opening new possibilities for the application of PAAs to malaria therapeutics.

Acknowledgments

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One-step synthesis of poly(lactic-co-glycolic acid)-*g*-poly-1-vinylpyrrolidin-2-one copolymers

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In this work we present a one-pot synthetic process leading to poly(lactide-co-glycolide)-*g*-poly(1-vinyl-2-pyrrolidone) (PLGA-*g*-PVP) copolymers consisting of high molecular weight PLGA carrying oligomeric PVP side chains (Fig. 1). PLGA is a lipophilic biodegradable polymer, whereas PVP is hydrophilic, biocompatible and bioeliminable for molecular mass < 40,000 [1,2]. Both polymers have been approved for human use by the US Food and Drug Administration, therefore PLGA-*g*-PVP copolymers are eligible for medical applications. The water-soluble PVP portion imparts amphiphilic properties to the otherwise hydrophobic PLGA, thus modifying its behaviour in aqueous systems. The title copolymers were prepared by bulk radical polymerization of 1-vinyl-2-pyrrolidone in the presence of PLGA 50:50 acting as polymeric chain transfer agent, and characterized by ¹H-NMR, FT-IR, DSC, TGA.

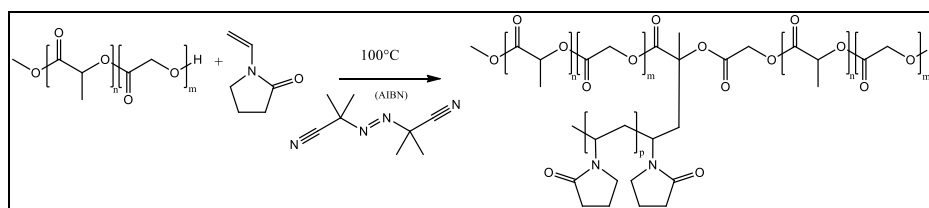


Figure 1. Synthesis of poly(lactide-co-glycolide)-*g*-poly(vinylpyrrolidone) (PLGA-*g*-PVP) copolymers. Multiple PVP grafts are present on a single PLGA chain.

They were also saponified giving PLGA degradation products and PVP with molecular mass in the range 2.7K-28K, lower than the renal filtration threshold. The MALDI-TOF spectra of the PVP obtained after PLGA-*g*-PVP saponification were consistent with low molecular weight PVP chains bearing at one end a hydrogen atom and at the other end monomeric, dimeric or, to a minor extent, trimeric residues of lactic- and glycolic acid or their combinations. These data unambiguously confirmed that the PVP chains had been covalently grafted onto the PLGA backbone. The orthogonal solvent pair ethyl-acetate/methanol was used to fractionate PLGA-*g*-PVP. Preliminarily, the effectiveness of this pair was tested on PLGA/PVP intimate blends obtained by co-precipitation of PLGA/PVP co-solutions. In this case, the complete separation of the two components was achieved. However, in the case of PLGA-*g*-PVP only PLGA- and PVP-rich fractions with widely different compositions, but not pure homopolymers could be separated. All un-fractionated PLGA-*g*-PVP samples and their fractions gave stable nanodispersions in water by the solvent evaporation technique, irrespective of the PVP content. Similar results were obtained with PLGA/PLGA-*g*-PVP blends, but not with PLGA/PVP blends, which gave unstable nanodispersions in water. These data suggest that the PLGA-*g*-PVP copolymers have a potential as components of bioeliminable and nanodispersed drug delivery systems [3].

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PLGA-*g*-PVP-based nanocarriers for the controlled delivery of antimalarial and antitumour drugs

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Purpose of this piece of work was to establish the best formulation technologies to transform PLGA-*g*-PVP copolymers [1] into nanosized carriers, namely nanoparticles (NPs) and lipid nanocapsules (NCaps), for the delivery of antitumour and antimalarial drugs, respectively. PLGA-PVP copolymers were used to prepare stable NPs loaded with doxorubicin [2] in base (Dox_B) and salt (Dox) forms, using the solvent displacement technique. Nanoparticles were characterized in terms of average diameter; polydispersity, zeta potential, morphology pH and osmolarity were also evaluated. The effect of the drug incorporation on their properties was also studied. *In vitro* release studies showed that after 24 h drugs were retained by PLGA-PVP NPs in blood physiological condition (pH= 7.4). In contrast, initial burst followed by a sustained drug releases were typical at pH 5.5 (tumour cytoplasmic pH). Antitumoural efficiency was evaluated by MTT test on mice (4T1) and human (MDA-MB231 and CRL-2335) breast cancer cell lines. Dox-loaded PLGA-PVP_{10:2} NPs highly affected cancer cell proliferation, allowed an inhibition activity of about 65-95 % at 0.02 M, instead of 25 % of free Dox. Simultaneously, PLGA-*g*-PVP copolymers were used as coatings of lipid nanocapsules for the delivery of curcumin [3] and artemisinin [4] as antimalarials. Drug loaded-lipid microdispersions were first prepared by oil in water emulsion. The lipid drops were converted into nanometric ones by high-pressure homogenization and finally surface coated. The physicochemical properties of nanoparticles were evaluated. *In vitro* cytotoxicity studies were performed on *Plasmodium Falciparum* infected red blood cell (p-RBC) (3D7 culture lines). From preliminary growth inhibition assays, a significant parasitemia reduction was observed in the case of curcumin-loaded PLGA-PVP NCaps treatments (IC₅₀ = 0.4-0.5 μM) with respect to free curcumin (IC₅₀ = 8.0 μM). Artemisinin-loaded PLGA-PVP NCaps presented similar activities of free artesimin, thus they were not further analysed. No haemolytic activity was detected after 24 h for PLGA-PVP NCaps at concentrations used for parasitemia inhibition assay.

In conclusion, PLGA-PVP nanocarriers were demonstrated to be effective as drug carriers for both antimalarial and antitumour applications.

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Amino acid-deriving chiral polymers with potential for biotechnological applications

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Polyamidoamines (PAAs) represent a well-known family of soluble synthetic functional polymers with a recognized potential for biotechnological applications. PAAs are obtained by stepwise Michael-type polyaddition of *prim*-monoamines or *sec*-diamines with bisacrylamides. The reaction occurs in aqueous solution at pH = 8–9 and at room temperature. The amine groups involved in the polyaddition pass from primary or secondary to tertiary preserving their amine character. By using α -amino acids as monomers, poly(amidoaminoacid)s (PAACs) are obtained. PAACs maintain the configurations and the amphoteric properties of the starting amino acids. These properties may affect their interaction with biological structures as proteins and living cells.

A PAAC named L-ARGO7 was synthesized from L-arginine and N,N'-methylenebisacrylamide [1]. The acid/base properties of L-ARGO7 show an isoelectric point of ≈ 10 and positive net average charges per repeating unit of +0.25 at pH 7.4. In vitro tests with mouse embryo fibroblasts balb/3T3 clone A31 show that L-ARGO7 polymers are endowed with effective cell internalization ability combined with minimal cytotoxicity.

PAACs can be also obtained from D-enantiomers of amino acids, as in the case of D-arginine. The secondary structure of D-, L-, and D,L-ARGO7 in aqueous solution was studied by recording their circular dichroism (CD) spectra at different pH values. The spectra showed characteristic peaks at well-defined wavelengths. In particular, L-ARGO7 shows broad signals in the 250–340 nm region, indicating structuring. At pH = 5, these peculiar signals are minimized, clearly demonstrating that structuring in solution is pH-dependent. Comparison between D- and L-ARGO7 polymers is being performed in order to determine their differences in cell internalization.

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Arginine-deriving polyamidoamine stereoisomers: synthetic chiral macromolecules showing self-organization in solution

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Linear polyamidoamines (PAA) are synthetic polymers obtained by polyaddition of *prim*-amines or bis-*sec*-amines with bisacrylamides. The PAAs obtained by polyaddition of D-, L-, and (D,L)-arginine with N,N'-methylenebisacrylamide gave the corresponding PAA stereoisomers named as D-, L- and (D,L)-ARGO7, whose repeating unit is depicted in Figure 1. In aqueous solution, the CD spectra of D- and L-ARGO7, but not those of (D,L)-ARGO7, suggested pH-dependent self-organization [1].

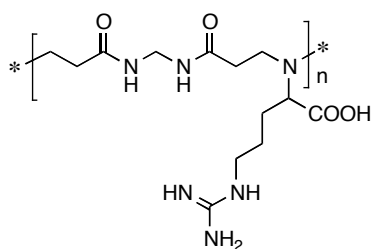


Figure 1. Structure of the ARGO7 repeating unit.

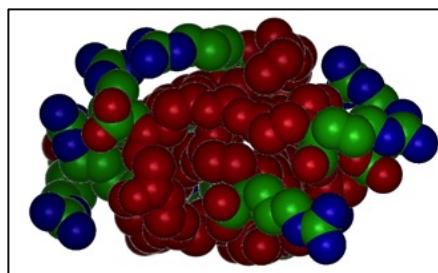


Figure 2. Conformation of oligomeric D-ARGO7 chain at pH = 7.4. The main chain is coloured in red; in the side chain the nitrogen atoms are blu, oxygen atoms are in red. Hydrogen atoms have been omitted for clarity.

A theoretical study based on Molecular Mechanics and Molecular Dynamics methods [2-5] was performed to study the conformational properties of ARGO7 isomers. Here we show through atomistic molecular dynamics simulations that, in aqueous solution, these PAAs with chiral-substituted *ter*-amine groups in the main chain adopt a relatively compact conformation with elongated parallel strands in a sort of “hairpin arrangement” of the backbone. Such self-organization is attributed to the conformational properties of the main chain as well as to the dipolar and/or electrostatic interactions, including also a few H-bonds, involving both the side chains among themselves and the main chain.

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β -Cyclodextrin-end-capped oligo(4-acryloylmorpholine) as amphiphilic drug carrier

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β -Cyclodextrin-oligo(4-acryloylmorpholine) mono-conjugate (β -CD-PACM) is a tadpole-shaped drug carrier in which the β -CD ring is the hydrophilic head and the PACM chain the amphiphilic tail. The β -CD-PACM is biocompatible, non-cytotoxic and non-hemolytic. One of its most interesting features is the ability to complex lipophilic drugs and to improve their bioavailability and stability through the non-covalent interaction with the β -CD. The oligomeric chain might cooperate with the β -CD moieties in stabilizing the complexes via secondary interactions with the guest molecule. The synthesis of β -CD-PACM of controlled molecular weight consists in the radical polymerization of 4-acryloylmorpholine (ACM) in the presence of 6-deoxy-6-mercapto- β -cyclodextrin (β -CD-SH) as chain-transfer agent [2]. Their average molecular weight is in the order of 10^4 . The chain-transfer constant (C_T) of β -CD-SH in ACM radical polymerization is about 1.30, therefore the molecular weight of the β -CD-PACM does not appreciably vary on conversion. The chain transfer (β -CD-SH) is obtained by saponification of 6-deoxy-6-thioacetic- β -cyclodextrin, in turn prepared by exchange reaction between β -CD-tosylate and potassium thioacetate. Finally, the monotosylation reaction of β -CD is performed in aqueous alkaline medium at room temperature. The product, that is much less soluble than virgin β -CD was recovered by neutralizing with a cationic exchange resin [1]. Different formulations were prepared and biological studies performed using β -CD-PACM as drug carrier. For example, 4-hydroxynonenal (HNE) [3], which is a promising new molecule in anticancer therapy, but is poorly bioavailable being scarcely water soluble, exceedingly reactive and rapidly degraded by specific enzymes was successfully formulated by complexing with β -CD-PACM. Complexation enhances HNE stability and significantly increases its antitumor activity towards several tumor cell lines. Moreover, it proved active on melanoma tumor cells grown on human reconstructed skin.

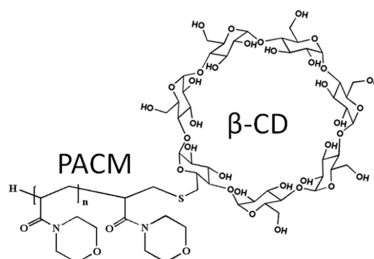


Figure 1. Chemical structure of β -CD-PACM.

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Linear biocompatible mannosylated PAAs as potential broad-spectrum microbicides for sexually transmitted diseases

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Interactions between viral proteins and cellular receptors mediate the initial steps of viral infections. Blocking the host receptors with high-affinity ligands may prevent viral adhesion and stop the infection process. We already demonstrated that mannosylated glycodendrimers are able to specifically block DC-SIGN, a C-type lectin receptor that mediates human immunodeficiency virus (HIV) infection [1]. In addition, an amphoteric, but prevalingly cationic polyamidoamine (PAA), named AGMA1, proved effective as infection inhibitor for several heparan sulfate proteoglycan-dependent viruses, such as human papilloma virus HPV-16 and herpes simplex virus HSV-2 [2], whilst an amphoteric, but prevalingly anionic PAA, named ISA23, proved inactive [2].

Here we show that the substitution of mannosylated units for a limited percentage of AGMA1 repeating units, while imparting anti-HIV activity, preserves the fundamentals of its HPV-16 and HSV-2 infection inhibitory activity, thus providing broad-spectrum, dual action mode, viral infection inhibitors [3].

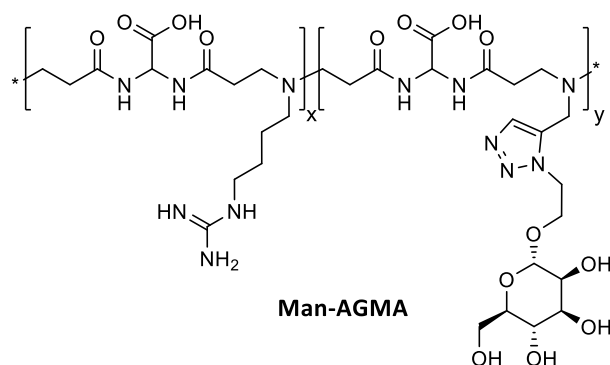


Figure 1. General structure of the mannosylated AGMA polymers.

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A new catechol-functionalized poly(amidoamine) as an effective nanoparticle stabilizer

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Superparamagnetic iron oxide nanoparticles (SPIONs) have been in the spotlight in the last years as promising candidates for a plethora of different biomedical applications, for both imaging (magnetic resonance imaging, MRI) and therapeutic purposes (e.g. magnetofluidic hyperthermia, MFH). However, in order to impart the SPIONs the necessary stability and solubility, a coating of the iron oxide surface is needed. In this work we aimed at functionalizing SPIONs with a previously developed amphoteric poly(amidoamine), nicknamed ISA23: this polymer is synthesized by a stepwise Michael addition of 2-methylpiperazine onto bis(acryloamido)acetic acid, and was previously found to be biocompatible and to exhibit “stealth-like” properties once injected into animals, avoiding immediate identification and disposal after intravenous injection [1]. These important characteristics would be imparted to the core/shell SPION@ISA23, improving this way their blood circulation times and, consequently, their potential usefulness for biomedical applications.

Effective binding to the iron oxide surface was achieved functionalizing the polymer with catechol moieties, whose high affinity towards iron is already exploited in a variety of natural siderophores [2].

In order to introduce this functional group, nitrodopamine was chosen over dopamine thanks to its higher stability towards oxygen- and metal-catalyzed oxidation. Coupling of nitrodopamine to the free carboxylic group of the polymer, employing EDC-coupling chemistry, resulted in the functionalization of ca 15% of the repeating units (see Figure 1).

This polymer was then successfully employed for SPIONs coating, affording stable and water-dispersible nanoparticles, whose characterization is currently in progress.

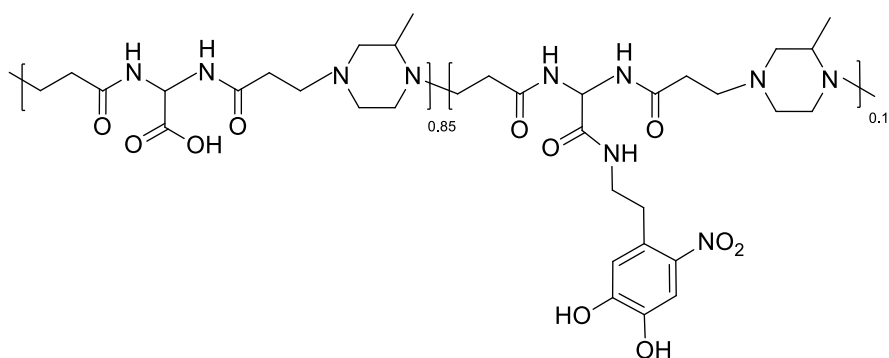


Figure 7. Structure of the new ISA23-nitrodopamine polymer.

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Synthesis of gold nanoparticles with polyamidoamines as new biocompatible stabilizing agents for the delivery of anticancer drugs

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The use of nanotechnology in medicine and more specifically drug delivery, is set to spread rapidly. Currently many substances are under investigation for drug delivery and more specifically for cancer therapy. Specifically, gold nanoparticles (AuNPs) exhibit physical properties that make them suitable for several biomedical applications. The nature of coatings present in the AuNPs affects their stability and plays a key role to determine their cytotoxicity, since AuNPs' aggregation induces cells death. In addition, different coatings can make AuNPs "stealth" with respect to the reticulum endothelial system and allow them evading clearance by the body and thus remaining in circulation for extended periods of time. For these reasons, a new class of stabilizing agents was used to improve the colloidal stability and the biocompatibility: polyamidoamines (PAAs), a family of synthetic polymers obtained by stepwise polyaddition of *prim*- or *sec*-amines to bisacrylamides. PAAs are degradable in aqueous media and offer a variety of advantageous properties, as biocompatibility, biodegradability and very low cytotoxicity [1]. In this study, a new synthetic route leading to stable colloidal AuNPs with two different PAAs as coatings of the inorganic core with diameters in the range 4 - 20 nm was investigated (Fig. 1). Their colloidal stability was monitored with X-ray diffraction, ultraviolet-visible spectroscopy and dynamic light scattering. AuNPs proved stable at least for 8 months. AuNPs were subsequently conjugated with Herceptin, a chemotherapeutic agent used to treat breast cancer, and their efficacy was estimated in vitro. In particular, two breast cancer cell lines were used (SK-BR-3 and MCF-7) and compared with fibroblast-like cell line (NIH3T3). AuNPs functionalized with Herceptin showed increased efficacy and specificity for target cells in comparison with free drug. Noteworthy, the AuNP chemical modification procedure is a "green" one since it is carried out in water.

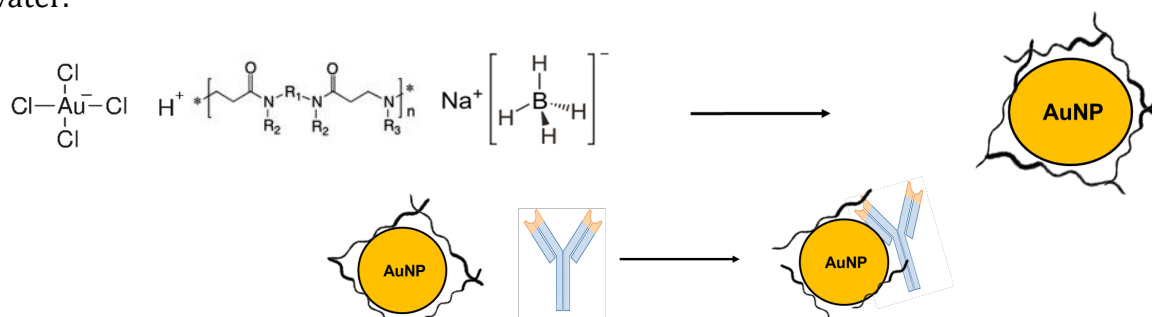


Figure 1. Scheme of AuNPs synthesis with a generic PAA and its functionalization with the Herceptin.

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