

Glycerol-Derived Renewable Polyglycerols: A Class of Versatile Chemicals of Wide Potential Application

Rosaria Ciriminna,[†] Benjamin Katryniok,^{‡,§} Sébastien Paul,^{‡,§} Franck Dumeignil,^{*,§,||,⊥} and Mario Pagliaro^{*,†}

[†]Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy

[‡]Unité de Catalyse et de Chimie du Solide, UCCS UMR CNRS 8181, F-59650, Villeneuve d'Ascq, France

[§]Ecole Centrale de Lille, ECLille, F-59655 Villeneuve d'Ascq, France

^{||}Université de Lille, Sciences et Technologies, F-59652 Villeneuve d'Ascq, France

[⊥]Institut Universitaire de France, Maison des Universités, 103 Boulevard Saint-Michel, 75005 Paris, France

ABSTRACT: Glycerol-derived polyglycerols are a versatile class of biocompatible oligomers whose wide potential application is translating into rapidly increasing levels of utilization across many industries.

■ INTRODUCTION

Linear polyglycerols (PGs), from diglycerol (PG-2) up to decaglycerol (PG-10), obtained via catalytic oligomerization of glycerol,¹ are biocompatible polyols of high thermal and chemical stability which find growing utilization in cosmetic and food preparations as well as in technical applications. As already emphasized by Martin and Richter in an excellent recent review,¹ calling “polyglycerols” oligomers obtained via condensation of 2, 4, or 6 glycerol molecules inherently leads to confusion with truly polymeric polyglycerol formed by hyperbranched polymerization of glycidol. This language confusion originates from prolonged use (for decades) of the term “polyglycerol” in the chemical industry to indicate manufacture of short chain polymers (oligomers). In the following, therefore, we use the word “polyglycerol” to refer to the oligomers.

Known since the early 1900s, these versatile molecules found their first practical applications two decades ago, first manufactured starting from glycidol (and hence from epichlorohydrin; see below) and then, since the early 2000s, directly from glycerol (Figure 1) when low cost glycerol eventually became available.

The highly biocompatible nature of these oligomers has been fully assessed in the mid 2000s by *in vitro* as well as *in vivo* experiments.² Results showed even higher biocompatibility when compared with some of the common biocompatible polymers already in human use.

Having considerably higher thermal stability compared to glycerol, PGs used as plasticizers allow higher polymer processing temperatures, for example in starch-based biodegradable thermoplastic compositions.³

The hydroxyl groups of the polyglycerol molecule are easily esterified with carboxylic acids of a different nature and in different PG:acid ratios to produce a wide variety of amphiphilic polyglycerol esters (PGEs) characterized by the desired HLB (hydrophilic–lipophilic balance) used across many industries due to their unique properties, such as, for example, high viscosity retained also at high temperatures.

Hence, a decade ago, a brief study⁴ of a leading manufacturer of polyglycerols reviewing the first industrial applications concluded that the primary application of PGs was as PG esters incorporated in polymers as antifogging and antistatic agents, or lubricants. The emerging use of PGEs as emulsifiers and stabilizers was also reported and related with the increasing need for safer and more ecological additives. Four years later, industry's practitioners at another leading chemical company described the use of polyglycerol and its esters as versatile materials for making sustainable cosmetic products.⁵

The applicative potential of this versatile family of biocompatible and renewable products, we argue in this account, largely exceeds their existing utilization. In the following we describe selected new applications that, showing the benefits of polyglycerols and polyglycerol esters utilization, highlight their wide potential application. Further insight in the Conclusions points to a forthcoming dramatic increase in PG manufacturing and utilization across many industries.

■ SYNTHESIS

The homogeneously or heterogeneously catalyzed synthetic routes affording PGs have recently been described in detail.¹ As mentioned above, before the biodiesel and fatty alcohols boom, thanks to which about 2 million tons of renewable glycerol accumulate annually,⁶ the industrial synthesis of PGs started from epichlorohydrin undergoing basic hydrolysis to afford glycidol, which then reacts with glycerol or with nonconverted epichlorohydrin to afford diglycerol. The reaction is neither selective nor quantitative. Following removal of unreacted glycerol and water, the product is distilled, affording a mixture comprising 90% linear diglycerol with some residual glycerol and triglycerol.⁷

Special Issue: Sustainable Chemistry

Received: October 3, 2014

Published: November 6, 2014

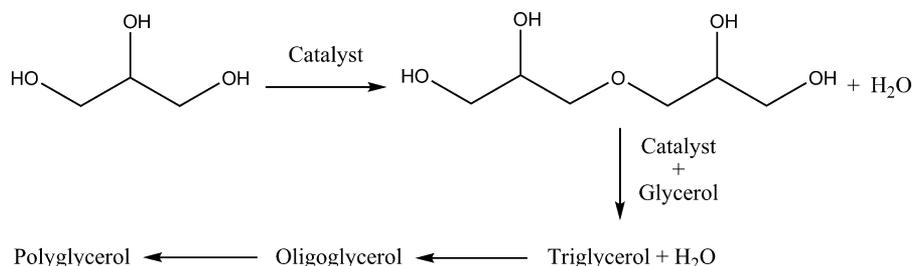


Figure 1. Schematic representation of the etherification of glycerol to linear polyglycerol. [Reproduced from ref 11, with kind permission.]

Precisely defined linear polyglycerols of high molecular weights can be obtained by using suitably protected glycidol, followed by removal of the protective group in a postpolymerization step.⁸ Yet, glycidol is a costly and highly toxic monomer whose utilization in the ROMBP (Ring Opening Multibranching Polymerization) synthesis of hyperbranched PG (HPG) leads to high cost of the final product (8,000 EUR/kg),⁹ which so far has limited wider utilization of HPG.

A lower cost catalytic route to PGs, including high molecular weight PG, starting from glycerol, makes use of acid-¹⁰ or alkali-catalyzed polycondensation of n glycerol molecules with elimination of $n - 1$ water molecules. We remind here that biodiesel glycerol used to make PGs, being heavily contaminated with base (sodium or potassium methoxide) and methanol, is purified via high temperature vacuum distillation so as to obtain glycerol of the high purity required for cosmetic and food applications (USP or kosher/halal grade).⁶

Condensation may be intermolecular to produce linear oligomers, or intramolecular to give cyclic species. Lower reaction temperatures and lower pH favor the formation of cyclic isomers, whereas at higher temperatures side reactions produce dark colors and flavors of strong smell.¹¹ In general, acid-catalyzed condensation is carried out at lower temperatures, when compared to the base-catalyzed process.

The influences of the reaction temperature, catalyst nature, catalyst amount, and reaction time on base-catalyzed glycerol polymerization were identified already in 1981 by Garti and co-workers in Israel.¹² The reaction is typically carried out at 260 °C with 2.5 mol % catalyst (K_2CO_3 , Li_2CO_3 , KOH, NaOH) under nitrogen so as to exclude air to avoid acrolein formation for 1 to 4 h, depending on the desired polyglycerol.

The step-growth polymerization of glycerol using acid and basic catalysts has been studied and modelled by Dubé and co-workers in 2011:¹⁰ namely 30 years later the first comprehensive study on alkali-catalyzed polymerization.¹²

The reaction mechanism of the base-catalyzed polycondensation involves coordination of the primary hydroxyls of glycerol to the calcium ions with formation of a favored 6-membered ring (Figure 2), and easier attack of incoming deprotonated glycerol on the coordinated carbon of $-CH_2OH$ whose lengthened carbon oxygen bond lowers the energy of the transition state complex.

Alkaline catalysis is used in industry, as it reduces the formation of cyclic oligomers, with carbonates normally used in place of hydroxides due to better solubility of carbonates in the glycerol and in the polymeric product at high temperature.¹³ Today's chemical separation technology, for example, allows us to obtain diglycerol with less than 1% cyclic compound, or colorless PGs up to PG-6 with less than 5% cyclic compounds.¹⁴

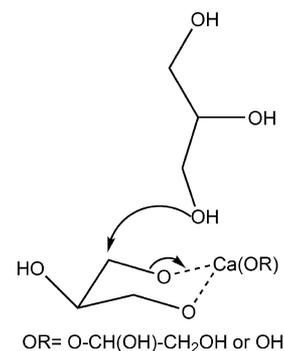


Figure 2. Participation of calcium in polymerization reaction. [Reproduced from ref 10, with kind permission.]

MARKET, RESEARCH, AND REGULATORY ASPECTS

In 2007, Pérez Pariente and co-workers published¹³ a chart (Figure 3) comparing scientific and technological publications on fatty acid polyglycerol esters. The statistics clearly showed strong and increasing innovation activities on PGEs, with strong leadership of Japanese companies. However, the team noticed how these materials remained “virtually unexplored outside the industrial R&D departments”.¹³

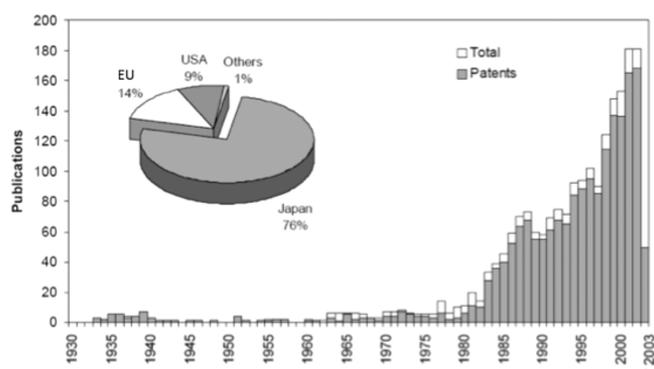


Figure 3. Scientific and technological publications on the synthesis, processing, and use of fatty acid polyglycerol esters. The inset shows the distribution of patent applicant nationalities. Data on 2003 correspond to the period from January to April. [Reproduced from ref 13, with kind permission.]

A decade later the fall in price of once too costly glycerol coupled to the excellent performance of both PGs and PGEs in many applications has led to a dramatic increase of the market size, as well as of research activities. Driven by the rapidly increasing demand for PGEs in the cosmetic and food industries alike, the global market for polyglycerols, estimated at 10,000 tonnes in 2011,¹⁵ is now more realistically at 20,000 tonnes.

The original manufacturers of PGs, including Sakamoto in Japan and Solvay Chemicals and Lonza in Europe, saw the entrance of a number of new companies manufacturing PGs and PGEs from refined glycerol originating from the biodiesel and oleochemicals industries.

In Europe, Spiga NORD and Evonik started to manufacture, respectively, PGs and PGEs. In China a recent market research report¹⁶ on the polyglycerol-3 industry alone included ten different suppliers of “polyglycerol (CAS 25618-55-7)” (namely a mixture of mostly di-, tri-, and tetraglycerol with low amounts of cyclic byproducts) led by Hangzhou J&H Chemical, while other companies such as Silver-Un Chemical Technology manufacture other PGs, such as polyglycerol-10.

In India, companies such as Fine Organics, Parry Enterprises, and Estelle Chemicals polymerize glycerol and manufacture large amounts of PGEs of fatty acids as emulsifiers and surfactants for value added applications in food and cosmetics.

As it happened with many other segments of the fine and specialty chemicals market, the entrance of Chinese and Indian manufacturers has led to a rapid increase of supply and price fall. Companies on the global market compete on quality, price, and time of delivery. Quality valued by customers in the food and cosmetic industries here translates into purity of the PG mixture, particularly in the lack of cyclic compounds and low coloration. With ever increasing levels of quality enabled by advanced chemical technology, highly pure PGs will shortly enter the pharmaceutical and biotechnology markets.

Polyglycerols are nontoxic and can be applied directly in cosmetic formulations as a solvent for fragrances, thanks to their nonvolatile nature or as mild skin moisturizer. They are widely approved for use in contact with food.

It is interesting to notice how different regulations dictate product manufacturing in different regions of the world. For example, the EU law requires that the “polyglycerol” approved for use in contact with food should not contain polymers comprising more than 7 condensed glycerol molecules (PG-7), with the main oligomers in the approved “polyglycerol” with a maximum of 100 g of polyglycerols per kg of product being di-, tri-, and tetraglycerols.

In the US, on the other hand, the Food and Drug Administration (FDA) approves the use of PGEs as food and pharmaceutical additives starting from PGs with a polymerization degree up to ten (PG-10) and with considerable polydispersity in both molecular weight and structure.

■ POLYGLYCEROL ESTERS

Polyglycerol esters of fatty acids are widely used in a number of food products,¹⁷ and in cosmetics and toiletries, where they outperform homologous polyol esters, including glycerol esters, in reducing the interfacial tension (Figure 4).¹⁸ Accordingly, PGEs are powerful defoaming agents and are widely used in foods as emulsifiers, fat-substitutes, and active agents for the maintenance of rheology and humectants.

In the EU the manufacture of PGEs must comply with the specifications in Regulation 231/2012 and in 21 CFR 172.854 for the Food Additive “E475 Polyglycerol Esters of Fatty Acids” formed via reaction between polyglycerols and edible oils, fats, or fatty acids.

A specific reference number E476 is ascribed to “Polyglycerol Polyricinoleate”. Polyglycerol polyricinoleate (PGPR, Figure 5) formed via esterification of condensed castor oil fatty acids with polyglycerol gives a powerful water-in-oil emulsifier which is used by the food industry as an emulsifier in making chocolate,

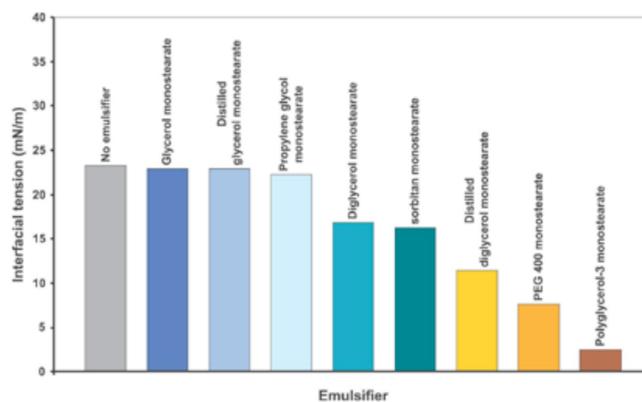


Figure 4. Interfacial tension against distilled water at 20 °C obtained using a 0.1% ester solution in caprylic/capric triglyceride. [Reproduced from ref 18, with kind permission.]

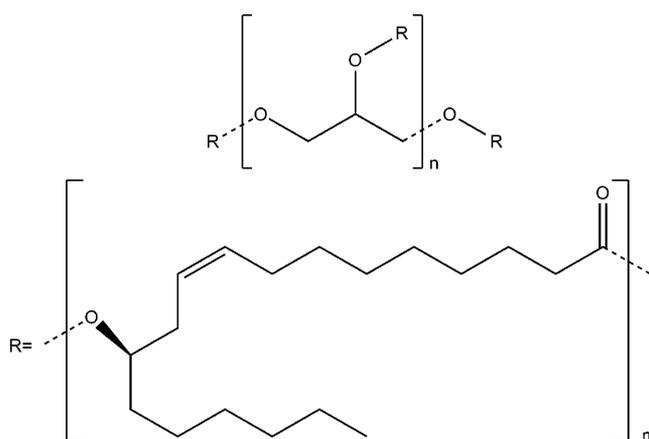


Figure 5. Polyglycerol polyricinoleate: An ester widely employed as emulsifier by the chocolate industry.

enabling the industry to remove cocoa butter, which is then sold to the cosmetic industry at a higher price.

A broad safety evaluation programme undertaken in the late 1950s and early 1960s to determine whether this food emulsifier presented any health implications for consumers showed no adverse effects on tolerance, liver and kidney function, and fat balance at levels up to 10 g/day PGPR, leading to the conclusion that its use in foodstuff does not constitute a human health hazard,¹⁹ even though its use in chocolate in place of cocoa butter, containing most of the antioxidants contained in a quality chocolate, eventually reduces the health benefits of that chocolate.

The chemistry of PGEs offers unprecedented versatility to develop surface active agents that may vary considerably in composition, owing to differences in the extent of polymerization of the glycerol, in the nature of the hydrophilic part, and in the degree of esterification. Coupled to excellent biocompatibility, this has opened the route to their use as emulsifiers, dispersants, emollients, wetting agents, or thickeners in personal care formulations in cosmetic and personal care products, where they are increasingly replacing fatty acid and fatty alcohol ethoxylates.²⁰

In personal care applications, there is an increasing trend, especially driven by consumers in Europe, to replace cleaning, personal care, and cosmetic ethoxylated ingredients such as ethoxylated polyethylene glycol (PEG), which often contain toxic 1,4-dioxane as a byproduct of the industrial process used to

make PEG,²¹ with naturally derived alternatives.²² In detail, the majority of the synthetic polymeric emulsifiers in use today are esterified polyethoxylated polymers, such as PEG-100 stearate. However, health concerns surround these PEG-containing ingredients, since it became known that ethoxylated materials can generate the highly toxic 1,4-dioxane in their manufacture.

PG is an ideal candidate to replace PEG in emulsifiers and solubilizers due to the flexibility to tailor molecular weight, polydispersity, and degree of substitution. The multifunctionality due to multiple hydroxyl groups per molecule allows for functionalization with more than one type of hydrophobic group per molecule towards various application profiles.

In addition, the physicochemical properties of polyglycerols are less sensitive to temperature and salts than those of PEGs. These properties have led the industry to develop new cosmetic ingredients based on polyglycerol, which are differentiated from PEG derivatives not only by their natural origin but also by their unique performance.⁴

For example, emulsifiers for water-in-oil (W/O) and water-in-oil (O/W) emulsions can be designed based on polyglycerol backbones. One example is Evonik's emulsifier ISOLAN GPS (International Nomenclature of Cosmetic Ingredients or INCI: Polyglyceryl-4 Diisostearate/Polyhydroxystearate/Sebacate), which provides good emulsion stabilization and additionally enables the formulation of fluid emulsions with very low oil phase ratios. This characteristic allows the realization of cost-efficient W/O emulsions with a pleasant and light skin feel.²³

Another, using higher molecular weight polyglycerols, is the O/W emulsifier TEGO Care PSC 3 (INCI: Polyglyceryl-3 Dicitrate/Stearate), namely a mixed ester of polyglycerol with stearic acid and a substoichiometric, optimized amount of citric acid, suitable for formulations at a pH of 4.0 to 5.5 such as those using natural preservatives, such as organic acids, in contrast to former products such as Glyceryl Stearate or Glyceryl Stearate Citrate.²⁴ Moreover, the structure and composition of Polyglyceryl-3 Stearate/Citrate were optimized to support the formation of liquid crystalline structures in emulsions to form O/W creams and lotions with an excellent stability profile without using polyacrylate-based thickeners.

In contrast, the O/W emulsifier with the trade name Evonik TEGO Care PBS 6 (INCI: Polyglyceryl-6 Stearate and Polyglyceryl-6 Behenate) is a tailor-made solution for stabilization of low-viscous O/W emulsions even in combination with ingredients such as water-soluble UV filters.²⁵ The emulsifier indeed has a high hydrophilic–lipophilic balance (HLB = 13), which stabilizes O/W emulsions with high water content, namely low-viscous emulsions such as those used in formulate sunscreen, skin care, and body lotion as sprays, which are increasingly demanded by customers, showing at the same time excellent moisturization properties.

Not only does the new product of full vegetable origin replace the ethoxylated derivatives questioned for health and environmental reasons, but also it does so by providing enhanced performance.

Several other companies, including Lonza, Brenntag, Danisco, Estelle, and many others, manufacture PGEs worldwide. Advances in controlling the molecular weight and structure of polyglycerols, while improving the economics of manufacturing tailored compositions, will be an active field of development and will further broaden the use of this new class of renewable ingredients.

PERSPECTIVES AND CONCLUSIONS

In 1981 the team led by Garti published the results of an economic analysis for the alkali-catalyzed production of PG-3, PG-6, and PG-10.¹² The production cost of the PGs amounted to ca. \$3/kg and was substantially independent of the degree of polymerization. As of November 1980, when glycerol was commercialized at \$1490/ton, 60% of the production cost was due to the cost of glycerol. For comparison, as of November 2014, the price of readily available 80% pure glycerol was \$292/t.²⁶ This fact, even taking into account the 0.15 \$/kg cost of refining, explains why PGs are increasingly manufactured and marketed as a “sustainable” solution worldwide.

However, sustainability is not a fashionable concept through which companies can conduct “greenwashing” advertising campaigns.²⁷ In brief, it is customer demand which increasingly requires that cosmetic and food products be derived from nontoxic ingredients, preferably of natural origin. The very issue of bioglycerol as chemical raw material derived from biodiesel and oleochemicals manufacturing is a consequence of this global trend. In this broader context, glycerol-derived polyglycerols are a versatile class of biocompatible polymers whose large applicative potential remains largely unfulfilled.

Reviewing the pharmaceutical (potential) applications of linear polyglycerols, Frey and co-workers recently concluded⁸ that PG is not suitable to replace PEG for large-scale applications (such as for cosmetics and for pharmaceuticals) but that it may be considered as a promising highly functional building block in specialty applications. However, today glycerol has become ubiquitously available at low cost and a number of routes to low cost PGs and PGEs have become available.

Hence, we argue herein that polyglycerols and polyglycerol esters are good candidates to replace not only PEGs but also a number of surface active agents, including antifouling coatings, especially when the polyglycerol backbone is coupled to other renewably sourced chemicals.

For example, researchers in the US have recently developed esterified polyglycerylated alkyl glucosides (Figure 6) which are excellent emulsifiers suitable for use in personal care, home care, and industrial and health care applications.²⁸

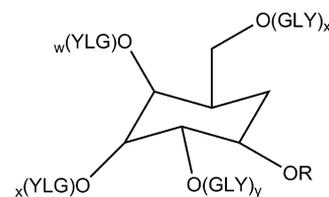


Figure 6. Esterified polyglyceryl alkyl glucoside. R represents an alkyl group containing 1 to 22 carbon atoms; and GLY is a polyglyceryl residue. [Reproduced from ref 28, with kind permission].

Environmentally benign glycerol carbonate, today readily accessible via nanocatalysis,²⁹ can be employed as polyglycerol starting material. Again, these emulsifiers can be successfully used in stabilizing O/W emulsions of natural oils, such as vegetable-derived oils that, being composed of triglycerides, are notoriously difficult to emulsify, requiring the use of undesirable ethoxylated surfactants that now can be replaced with naturally derived surfactants.

Put simply, covering a broad range of hydrophilicities and molecular weights, and by allowing modification with hydrophobic groups of different size and structure, versatile

polyglycerol linear polymers satisfy numerous application criteria that other polymers cannot meet. Reinforcing this viewpoint, one large chemical company (Evonik) in the past few years has introduced a number of surfactant products suitable for practically all types of existing cosmetic formulations.

The biocompatible nature of these materials, and the ease of derivatisation (including bioconjugation with peptides) suggests that their pharmaceutical, biomedical, and biotechnological potential remains largely unexpressed. For example, temperature and pH-responsive polyglycerol-based hydrogels are easily made by cross-linking polyglycerol with epoxide-containing glycidyl ethers.³⁰

Chemical applications that so far were limited by the high cost of both polyglycerol and its esters will start to replace petrochemical polyols at an even faster pace than what happened with glycerol replacing sorbitol and propylene glycol. Biobased PG, for example, is an excellent polyol to manufacture polyurethanes as reactive polyols, with higher hydroxyl numbers affording polyurethanes with better thermal and mechanical properties. It is sufficient to alkoxyate the as-synthesized PG and react the resulting PG-based polyether polyols with MDI (4,4'-methylene diphenyl diisocyanate) to obtain rigid polyurethane foams with excellent dimensional stability and good physical and mechanical properties.³¹ Accounting for about 5% of all plastics produced worldwide, polyurethanes are among the most widespread polymer technologies.³²

Manufacturing polyglycerol and polyglycerol derivatives is straightforward and the raw material is readily available. After India and China, countries where large amounts of bioglycerol streams exist, such as Malaysia, the Philippines, and Indonesia, are likely to invest soon in PG manufacturing plants. This will lead to further market expansion until PG will replace PEG. Polyglycerols are a safe bet for the future.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: mario.pagliaro@cnr.it. Mailing address: Istituto per lo Studio dei Materiali Nanostrutturati, CNR, via U. La Malfa 153, 90146 Palermo, Italy.

*E-mail: franck.dumeignil@univ-lille1.fr. Mailing address: UCCS UMR CNRS 8181, Université Lille 1, Cité Scientifique Bâtiment C3, 59655 Villeneuve d'Ascq Cedex, France.

Notes

The authors declare no competing financial interest.

Biographies



Rosaria Ciriminna is a chemistry scholar based at Palermo's Institute of Nanostructured Materials of Italy's Research Council. Developed in

cooperation with numerous research groups worldwide, her research in the field of green and nano- and photochemistry is aimed at developing solutions for relevant sustainability issues. She has published over 120 research papers and is in the top 1% of most cited chemists. Rosaria is also a frequent mentor of graduate and undergraduate students and is a member of doctoral committees abroad.



Originally from Germany, Benjamin Katryniok performed his undergraduate and graduate studies in Marburg and RWTH Aachen, before he moved in 2007 to Lille (France) for his Ph.D. in the Laboratory for Catalysis and Solid State Chemistry (UCCS). After his Ph.D. he was given a lecturer position at Ecole Centrale de Lille, one of the leading engineering schools in France. In 2012, he became Assistant Professor. His main research area is heterogeneous catalysis for the upgrading of biomass to high-value intermediates for the chemical industry. He is author and co-author of more than 20 articles and 5 international patents.



Sébastien Paul is Professor at the Ecole Centrale de Lille, where he has been the head of the Sciences of the Matter department since 2009. After his obtaining Ph.D. in Chemical Engineering at the University of Technology of Compiègne, France (1996), he was hired by the Ecole Centrale de Lille as Assistant Professor (1998). From 2004 to 2009 he was the head of the "Chemical Engineering" Department, which then became the "Sciences of the Matter" Department. In 2009 he was nominated Associate Professor and in 2011 Full Professor. His research work is carried out in the Unité de Catalyse et de Chimie du Solide (UCCS - UMR CNRS 8181), France, which comprises more than 200 persons. More particularly, he is a member of the VALBIO group (standing for Valorization of the ALkanes and of compounds issued from the BIOMass), led by Prof. Franck Dumeignil. He is the scientific leader and the user committee chairman of the REALCAT project (Advanced High-Throughput Technologies Platform for Biorefineries Catalysts Design; 9.4 M€), and he is deputy-director of the Franco-Japanese International Associate CNRS Laboratory CAT&P4BIO

(Innovative Catalysts for Oxidation Reactions and Processes, Biomass Conversion). He is involved in the frame of academic and industrial collaborations in the development of a large variety of catalytic processes using raw materials, such as compounds issued from biomass or hydrocarbons. Finally, he has supervised or co-supervised 17 Ph.D. candidates and 12 post-docs and is co-author of 50 scientific articles, 10 patents, and more than 80 communications in international congresses.



After obtaining his Ph.D. in 1998 from Lille 1 University, Franck Dumeignil spent more than six years in Japan: a post-doctoral stay of 2 years at the NIMC in Tsukuba before obtaining a 2-year postdoctoral contract at the Tokyo University of Agriculture and Technology (TUAT), following which he became Associate Professor at a Centre of Excellence (Scientific Cluster). He returned to France as a Full Professor at Lille 1 University, Sciences and Technologies, where he piloted several research projects. In January 2010, he was appointed Deputy Director of UCCS, UMR CNRS 8181, which employs more than 200 people. He coordinated the PCR07 European EuroBioRef Programme “EUROpean Multilevel Integrated BIOREFinery Design for Sustainable Biomass Processing” (www.eurobioref.org), gathering 29 partners from 15 countries for a global budget of €38 million (€23 million of European subvention) during 4 years (01/03/2010 to 28/02/2014). As part of that project, his research team was, in particular, involved in the development of a wide variety of catalytic reactions. Recently, he was awarded the ANR EQUIPEX REALCAT project (“Advanced high throughput technologies platform for biorefineries catalysts design”; €8.3 million) and created the Franco-Japanese International Associate CNRS Laboratory CAT&P4BIO (“Innovative Catalysts for Oxidation Reactions and Processes, Biomass Conversion”), of which he is Director. Finally, he is piloting the SP3 “Catalysis and Biocatalysis” of the “Genesys of Lipids Biorefinery” GENESYS program in the framework of the ANR ITE P.I.V.E.R.T. “Picardy Plant Innovations, Teaching and Technological Research” (2011–2020; €247 million). He was also named a Junior Member of the Institut Universitaire de France (University Institute of France, IUF) on October 1st, 2010. The mission of the IUF is to promote the development of high-level academic research and encourage interdisciplinary projects. He has co-authored over 80 scientific articles, 20 patents, and ca. 287 presentations (oral and poster) in national and international conferences



Mario Pagliaro is a chemistry and solar energy scholar based at Italy's CNR, where he leads a research group whose achievements are reflected in over 130 research papers, 19 books, and several book chapters and patents. A Fellow of the Royal Society of Chemistry, he is the co-founder of Sicily's Solar Pole. His research interests are in the broad area of nanochemistry and span from sol-gel materials to biorefineries and solar energy. He has a prolonged interest also in sustainability and management topics. His research, which has been extensively covered by the press, is developed in co-operation with researchers based in 11 countries, including Israel, Portugal, China, France, the UK, Canada, and the US. In 2009, he chaired the 10th FIGIPAS Meeting in Inorganic Chemistry. Since 2011, he has been presiding over the “SuNEC—Sun New Energy Energy Conference” and the “FineCat—Symposium on heterogeneous catalysis for fine chemicals”, a series of premier scientific meetings held annually in Sicily. Currently he is co-editing (along with Paolo Fornasiero) the “Pd Catalysis” thematic issue of ChemCatChem. Since 2004 he has been organizing the prestigious Seminar “Marcello Carapezza”, whose 2011 edition was hosted by Italy's Parliament.

■ ACKNOWLEDGMENTS

This article is dedicated to Dr Giovanni Duro (IBIM, CNR) for all he has done to advance the standing of the CNR in Sicily. We thank Dr Henning Wenke, Evonik, for kindly providing updated industrial information on polyglycerol esters.

■ REFERENCES

- (1) Martin, A.; Richter, M. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 100.
- (2) Kainthan, R. K.; Janzen, J.; Levin, E.; Devine, D. V.; Brooks, D. E. *Biomacromolecules* **2006**, *7*, 703–709.
- (3) Taghizadeh, A.; Sarazin, P.; Favis, B. D. *J. Mater. Sci.* **2013**, *48*, 1799.
- (4) Solvay Chemicals. *Polyglycerols in Industrial Applications*; 2005; http://www.solvaychemicals.com/EN/products/Chemicals%20Literature%20Documents/Polyglycerols/APP-2800_industrial_applications_x3.pdf (accessed, October 28, 2014).
- (5) Wenk, H. H.; Meyer, J. *SOFW-J.* **2009**, *135* (8), 25–30.
- (6) Ciriminna, R.; della Pina, C.; Rossi, M.; Pagliaro, M. Understanding the Glycerol Market. *Eur. J. Lipid Sci. Technol.* **2014**, *116*, 1432.
- (7) See at the URL: <http://www.solvaychemicals.com/EN/products/Polyglycerols/Diglycerol.aspx> (last time accessed, October 28, 2014).
- (8) Thomas, A.; Müller, S. S.; Frey, H. *Biomacromolecules* **2014**, *15*, 1935.
- (9) See for example at the URL: www.nanopartica.com (last time accessed, October 2, 2014).
- (10) Salehpour, S.; Dubé, M. A. *Macromol. Chem. Phys.* **2011**, *212*, 1284.
- (11) Hasenhuettl, G. L., Synthesis and Commercial Preparation of Food Emulsifiers. In *Food Emulsifiers and Their Applications*; Hasenhuettl, G. L., Hartel, R. W., Eds.; Springer Science + Business Media: New York, 2008; pp 11–37.

- (12) Garti, N.; Aserin, A.; Zaidman, B. *J. Am. Oil Chem. Soc.* **1981**, *58*, 878.
- (13) Marquez-Alvarez, C.; Sastre, E.; Pérez Pariente, J. *Top. Catal.* **2004**, *27*, 105.
- (14) See at the URL: www.spiganord.com/en/spiga-nord-polyglycerols-polyglycerine-products.php (last time accessed, October 28, 2014).
- (15) Personal communication of leading industry's practitioner to M.P. (2012).
- (16) Prof Research. *Global and Chinese Polyglycerin-3 (CAS 25618-55-7) Industry, 2009–2019 Market Research Report*, Shanghai, China; August 2014.
- (17) Krog, N. J. Food emulsifiers and their chemical and physical properties. In *Food Emulsions*; Friberg, S. E., Larsson, K., Eds.; Marcel Dekker: New York, 1997; pp 141–188.
- (18) Solvay Chemicals. *Polyglycerols for Ester Production. Application Data Sheet*; 2008; http://www.solvaychemicals.com/Chemicals%20Literature%20Documents/Polyglycerols/APP-2800_for_ester_production_x3.pdf (accessed, October 28, 2014).
- (19) Wilson, R.; Van Schie, B. J.; Howes, D. *Food Chem. Toxicol.* **1998**, *36*, 711.
- (20) Szeląg, H.; Sadecka, E.; Pawłowicz, R.; Kuziemska, A. *Polym. J. Chem. Technol.* **2013**, *15*, 128.
- (21) Juhász, M. L. W. Marmur, E. S. A review of selected chemical additives in cosmetic products, *Dermatol. Ther.* DOI: 10.1111/dth.12146.
- (22) McCoy, M. *Chem. Eng. News* **2007**, *85* (5), 13–19.
- (23) Meyer, J.; Allef, P.; Foetsch, H. *SOFW J.* **2005**, *131* (11), 20.
- (24) Jha, B.; Meyer, J.; Polak, G. *SOFW J.* **2010**, *136* (9), 36.
- (25) Friedrich, A.; Biehl, P.; Unger, F.; Marian von Hof, J.; Meyer, J. Easy Formulation, Demanding Ingredients. *Personal Care Eur.* **2014**, *March*, 33–37.
- (26) Gan, A. China crude glycerine falling on weak demand, rising supply. *ICIS News* **2014**, *14 July*, 04:25.
- (27) Bowen, F. *After Greenwashing Symbolic Corporate Environmentalism and Society*; Cambridge University Press: Cambridge (UK), 2014.
- (28) Wu, A.; Barr, D. M.; Marchant, N. S.; Sengupta, A. K.; Gorden, F.-I. Lubrizol Advanced Materials. WO 2014031353 A2; 2014.
- (29) Sonnati, M. O.; Amigoni, S.; Taffin de Givenchy, E. P.; Darmanin, T.; Choulet, O.; Guittard, F. *Green Chem.* **2013**, *15*, 283.
- (30) Salehpour, S.; Zuliani, C. J.; Dubé, M. A. *Eur. J. Lip. Sci. Technol.* **2012**, *114*, 92.
- (31) Ionescu, M.; Petrović, Z. S. *J. Cell. Plast.* **2010**, *46* (3), 223–237.
- (32) Sonnenschein, M. F.; Koonce, W. Polyurethanes. *Encyclopedia Of Polymer Science and Technology*; Wiley: New York, 2011.