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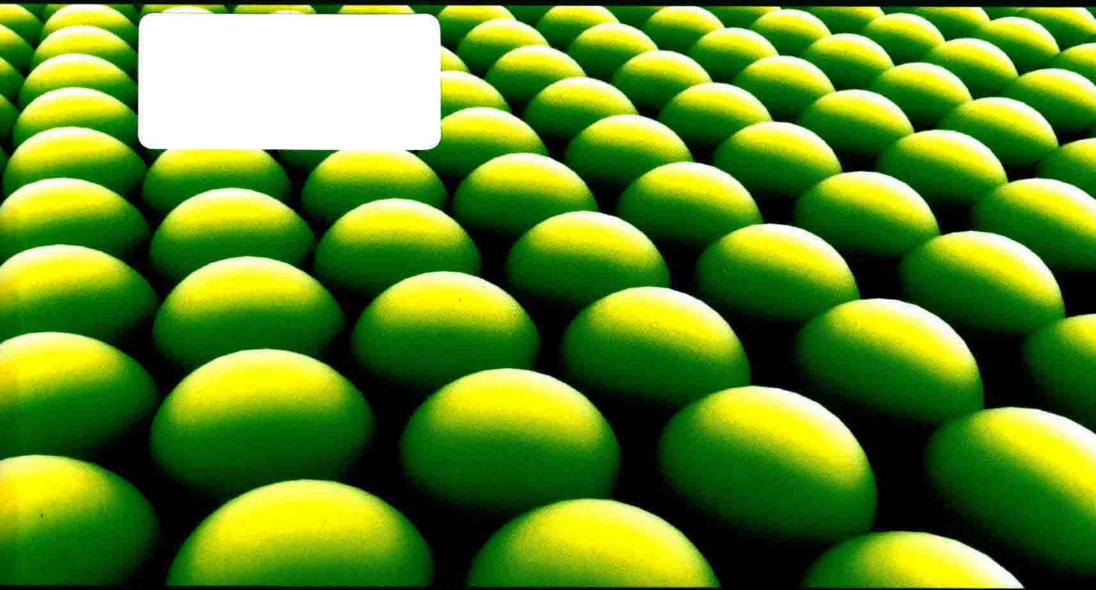

Environmental Impact of Polymers

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Preface

Better known by its acronym GFP, the French group for the study and applications of polymers (www.gfp.asso.fr) is a non-profit organization established in November 1970. Its mission, recognized as a public utility in 1990, is to promote the development of polymers, not only in universities and research centers but also in industry.

The GFP Commission focuses on promoting all aspects of the teaching of "polymer science", both in France and abroad. A significant part of its activity is devoted to the periodic organization of educational internships for teachers willing to update their knowledge in all the areas specific to polymers. Following each of these courses a textbook is published, which is available to all members of the GFP. The list of available titles can be found on the Website of the GFP (www.gfp.asso.fr).

The Education Commission therefore organized several meetings between teachers, researchers and industrialists on the theme of *Polymers and the environment: the impact of polymers on society and the eco-design of plastic materials. What solutions can be proposed for the societal impacts of polymeric materials*?

The main objective of these meetings was to go beyond the traditional analysis of the lifecycle of polymers and to provide for everyone willing to acquire the basic concepts of the environmental, and therefore societal, impacts of polymers and the means to reduce their effects, in order to update their knowledge and to be able to integrate it optimally into their lecturing. They wanted to share the solutions already in existence and implemented by industry and the prospects for the short and medium term. This book collates several contributions originating during these periods. It provides solutions already in existence, as well as predictable or desirable developments. It concludes with reflections upon the role of education and training in order to ensure and guide the future.

Thierry HAMAIDE

President of the Education Commission of the GFP

June 2014

Introduction: The Societal Impact of Polymers and Plastic Materials: Solutions and Perspectives

I.1. Polymers, an ever young science in step with the economy and employment

Whatever their origin, natural or synthetic, polymers involve chemistry and/or process engineering at one time or another in their lifecycle. Chemistry and process engineering are fundamental sciences for sustainable development; they are fundamental disciplines for understanding the world around us, at all scales, and for mastering its transformations. They are able to strongly interact with other disciplines – physics, biology, mathematics. Moreover, they are in a huge number of fields of application in our daily life: energy, materials, information and the living world.

If organic chemistry is essential to describe the majority of molecules around us, it is analytical chemistry that helps us identify them and catalysis is at the heart of transformation of materials and of energy savings; inorganic chemistry is strongly involved in the issues of production and energy storage. Process engineering – which includes different levels of physical chemistry – is essential for the feasibility, economics and environmental performance of production.

Finally, the interaction of humans with chemistry encourages a better understanding of our reading of the world, our opinions, beliefs, historical creations, representations and evolution.

Introduction written by Bernard SILLION, Thierry HAMAIDE, Gérard PIGNAULT and Jean-Charles MOUGENEL.

This crossroads of science, economics and human values constitutes precisely the zone of overlap which is described by the term sustainable development. The evolution of how people view polymers, more commonly called plastics, is exemplary in many respects [BER 95] and illustrates this concept.

Polymers are used in more than 90% of materials, and their cohesion and properties depend closely on the chemical structure and the organization of chains which can be governed by the methods of production. Thus, polymer science consists essentially of three scientific disciplines, which are chemistry, physics and mechanics. Chemistry is involved in the transformation of raw materials and also in the production processes, which becomes possible due to chemical engineering [FON 08, FON 10, MER 96, ODI 04, ETI 12]. Physics leads to the development of analytical tools that make available the characterization of these macromolecules of different sizes, unveiling their organization. Finally, because of mechanics, properties of application of polymeric materials can be explored [OUD 94, FON 08, FON 10].

Polymer science is a relative young science, and the concept of macromolecules for understanding the properties of polymeric materials was introduced by H. Staudinger in 1919 and developed in the 1920s, in particular on cellulosic materials. The industry had certainly previously produced vulcanized rubber, a process invented by Goodyear in 1839, celluloid in 1865 with the Hayatt brothers, bakelite in 1910 developed by Baekeland, but the true nature of the chemical species was at that time not yet revealed. From 1930, a better understanding of the macromolecular structure led to the fast development of different chemical families: low-density polyethylene by radical polymerization synthesized in 1933, and the works of Carothers on polycondensation led to polyamides in 1938.

The period following the Second World War saw the emergence, with an accelerated speed, of new polymerization methods: in 1953–1954, polymerization catalysis by coordination was developed by K. Ziegler and G. Natta (Nobel Prize, 1963), which led to for high-density polyethylene (PEHD) and polypropylene (PP). Anionic polymerization and the concept of living polymerization proposed by M. Szwarc in 1956 led to the design of blocks copolymers and the first macromolecular architectures. We then saw the emergence of catalysis by metallocene in 1980 by W. Kaminski. Radical polymerization controlled by M. Sawamoto and K. Matyjaszewski in 1994 combined the benefits of radical and ionic polymerization without the drawbacks of the former.

Meanwhile, analytical physical chemistry made progress at the same speed. Significant evolution in chromatographic methods and the study of interactions between matter and radiation helped in analysis with higher precision of the polymer microstructure, and to revisit the intimate mechanisms of polymerization [TAN 00].

As in all areas, fundamental discoveries have often been generated by industrial developments which tackle global problems of the planet such as energy and water resources as well as those experienced at the level of individuals in everyday life such as health and hygiene, nutrition, comfort, communication, recreation and so on, and therefore we can claim that society has entered the "age of polymers", which is explained in the first section of introduction.

At the same time, this entry into the age of polymers goes hand in hand with an overall negative societal impact [LEM 10]: polymers in general suffer from double penalties, namely the image of plastic materials in addition to those of chemistry. For society, the chemical aspect is the one that generates questions or concerns, because it highlights the impacts on the environment of waste which does not easily degrade biologically or leads by combustion to hazardous materials such as dioxins. We are also concerned about health risks caused by the release of toxic materials during use.

All of these concerns should be taken into account, but the requested analysis of risks should also be carried out in terms of risk-benefit assessments. It is thus important for society to recognize the developments in science and in industry in the field of polymers. It is not generally known that plastics consume only 4% of global oil production and that their widespread use makes it possible to save a much larger quantity. In addition to this, at the end of their life they produce less waste, because they are lighter (less than 1% of the total weight of waste in Europe). The study by Claude Duval (see Chapter 2) allows us to address the intimate link between plastic waste and the environment. Thus, despite appearances, plastics undoubtedly contribute to sustainable development, and are beneficial for the future, as Michel Loubry attempts to demonstrate (see Chapter 4).

The industrial world in close collaboration with academic research strives to develop new methods of developing plastic materials. We are therefore moving to an eco-design approach which consists in integrating the environment into the fabrication phase of products, requiring us to take into account the whole steps of the lifecycle of products [ADE]. In other words, the lifecycle analysis must integrate to the maximum extent possible the use of new sources of raw materials (and wisely) and of new methods of production, and no longer be limited to issues concerning the end of life related to recycling and valorization of waste.

Eco-design is not really a new profession or an established university discipline but a new approach, acquired through specialization by individuals already owning the skills needed in the different core disciplines, especially in chemistry related to polymers. The training needs are clearly identified. As a result, this approach must also now enter into the world of education, through a course suited for all ages. The essential role of the teacher is discussed at the end of this chapter.

However, to go further in this reflection, we should write Education with a capital E, because while the vast majority of people have little, or no, impact on the eco-design, the whole society has a major role in the gathering and recycling of plastic waste. Are the "plastic continents" attributable to industrial plastics or to the consumers of these plastics? In this regard, the study by François Galgani (see Chapter 3) allows us to judge the effect of polymers and litter on the environment and the societal assessment. Another example from everyday life concerns carrier bags. Are bags which are displayed as biodegradable (but are they really?) designed to deal with the incivility of some of our citizens or to follow a fashion?

I.2. The polymer industry: its role in the economy and the workforce

The production of plastics, which was 1.5 million tons in 1950, rose to 230 million tons in 2009, going through a record production of 260 million tons in 2007. This increase is much larger than what is observed for other materials. Europe is well positioned in the world with a production of 55 million tons in 2009.

With regard to employment, taking into account the whole sector, that is to say production, construction of machines dedicated to processing and the processing industry, the sector employed 1.6 million people, which places this industry at the top of those who contribute to the economy of Europe [PLA 10]. For example, the chemical industry in 2011 generated only 1.19 million jobs in the European Union [CEF].

French plasturgy is a growing business which embraces all industrial sectors. Today it ranks fourth in the world and second in Europe with 4,500 thousand tons of products, representing a turnover of 29 billion euros, with a quarter for export. It employs more than 140,000 employees in 3,850 companies, of which more than 90% being small and medium businesses [LAPa].

However, the crisis has affected more, in terms of production, the polymers and specialty chemicals than the basic chemistry, as shown in Figure I.1 where growths in different domains are compared [CEF]. It reveals the clear reduction in the growth in 2012.

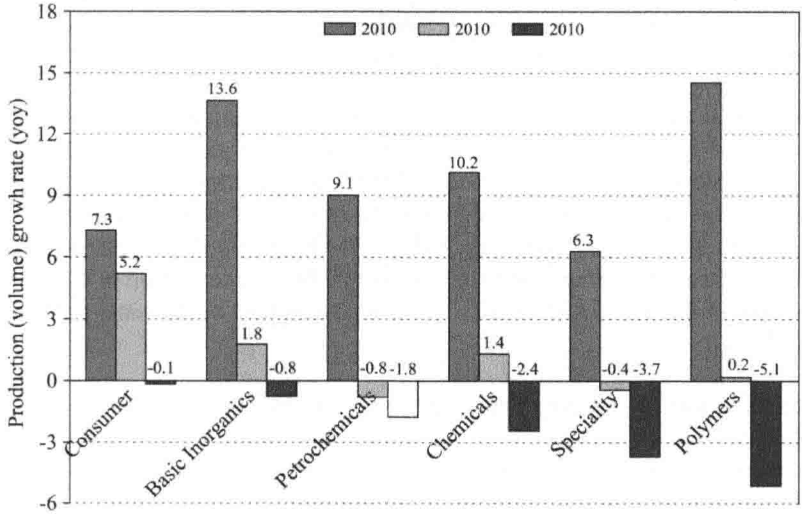

Figure I.1. *Growth reduction in 2012*

I.3. Polymeric materials to assist society in addressing the big problems facing the planet: water and energy

I.3.1. *Polymers for water*

The world's population is currently 7.2 billion. The curent issue of food supply, already happening today, will be particularly important in 2050 for a world population around 9.6 billion. 2013 was the international year of cooperation in the domain of water for UNESCO [UNE]. Water is abundant on Earth, but 97.2% (sea water) is unsuitable for human consumption and the rest (fresh water) is very poorly distributed in the world since 2.5% is in the form of polar ice. The water available for use, 0.3% (river, groundwater, lakes), is itself distributed very unevenly across the world: 800 million people are deprived of drinking water; 2.4 million have no sanitation and 450 million experience periods of shortage (according to UNESCO [AQU]). The need for water is rising twice as fast as the population, which leads to a mobilization to save and recycle consumed water, but also requires the development of processes for producing fresh water and drinking water. The use of polymers has become essential for the production of drinking water and for the management of water in agriculture.

For the production of drinking water from saltwater, techniques of membrane treatment have been developed. Different methods of membrane separation help in separating water from objects in suspension or solution according to their sizes

[MAU 10], ranging from conventional filtration with dimensions greater than 10 µm to nanofiltration with dimensions of the order of the nm.

Osmosis is the phenomenon that occurs when two solutions of different salinities are separated by a membrane permeable to water. For example, the desalination plant of Ashkelon in Israel produces 320,000 m^3 of drinking water per day, or 108 million m^3 per year (the consumption of a city of 1.4 million inhabitants). After a pre-treatment (bilayer filtration and microfiltration), the water is gradually desalinated through 32 stages of reverse osmosis. The concentration of dissolved salt coming out of the plant is 30 $mg.L^{-1}$, 1,000 times less than in the water pumped from the sea [LIN].

Several families of polymers may be used for this application, including cellulose acetates, aromatic polyamides and polysulfones, but progress remains to be made regarding the nature of membranes and their implementation to control the morphologies of the interface.

For water management in agriculture, cross-linked polyacrylamides are used for water retention and for soil moisture [HOL 05]. In contrast, polymers and copolymers of ethylene glycol are used to promote infiltration of water. The recycling of wastewater uses for the step of clarification (flocculation and sludge conditioning) polymers derived from polyamines or acrylamide.

I.3.2. *Polymers for energy management*

The energy consumption of the world in 2009 was 8.4×10^9 toe (ton of oil equivalent; 1 toe = 11,628 kWh), but for this final consumption of energy, it was necessary to actually produce 12.3×10^9 toe, the difference of 3.9×10^9 toe being used for transformation, transport, etc. The needs for energy throughout the world are not the same in all parts of the world, as shown in Figure I.2 from International Energy Agency (IEA) documents [BRO 11].

For 40 years, energy consumption has increased by more than 40%, and the development of emerging countries accelerates this trend, which raises two main problems: the scarcity of raw materials: oil, coal and gas; and the production of carbon dioxide, which contributes to climate change. The production of primary energy is at the beginning of this century based on fossil fuels, as shown in Figure I.3, extracted from IEA statistics for 2008.

We see from this figure that more than 80% of primary energy is fossil fuels. In 2010, the amount of CO_2 released into the atmosphere was more than 30 gigatons, which leads to a concentration in the atmosphere of the order of 385 ppm; these releases are due in part to the transformation of fossil energy.

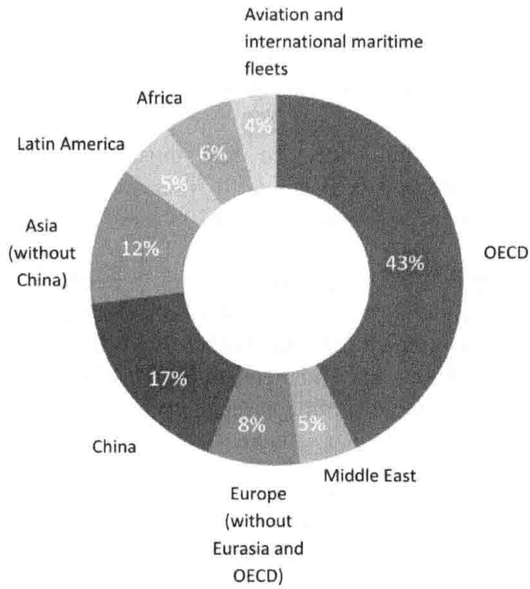

Figure I.2. *Distribution of the total consumption of final energy (8,353 Mtoe) in 2009 [BRO 11]*

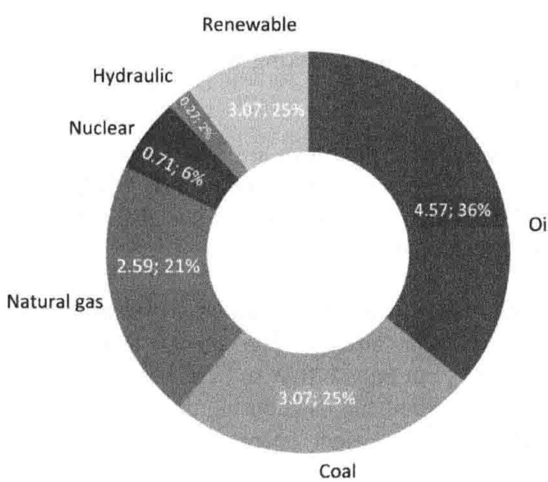

Figure I.3. *Primary energy sources (in Gtoe) at the beginning of the 21st Century (12.27 Gtoe in total)*

The thinking behind the evolution of primary energy consumption in the world is the subject of several hypotheses that take into account not only the evolution of populations and the evolution of GDP in different countries, but also the establishment of policies to fight against global warming, that is to say, the control of emissions of carbon dioxide [BRO 11, BOU 09]. In 2050, fossil fuels will still hold an important role in primary energy because resources are still significant: oil between 180 and 200 gigatons, gas 150 Tm^3 ($T = 10^{12}$) or about 150 Gtoe and coal between 700 and 900 Gtoe. To this must be added the reserves of unconventional gas (shale and coal gas with reserves of around 380 Tm^3) which could ensure production for between 120 and 150 years [TOTAL].

Among the scenarios used to predict the supply needs in 2050, a hypothesis based on the control of global warming involves a reduction in rich countries so as not to exceed a consumption of 20 Gtoe [BOU 09, WIE 05], or 2.4 times that in 2009. However, it is likely that this consumption will be exceeded given the difficulties in signing and implementing agreements against global warming.

I.3.2.1. *The role of polymers in the production of energy*

If we examine the role that polymers play and can play in the field of energy, we can distinguish improvements which focus on the production of fossil fuels and others which allow the saving of energy.

It is known that the efficiency of oil recovery from a field is only about 30% and it was found that the injection of water made more viscous by the dissolution of polymers, including biopolymers obtained by fermentation, helps to increase the production of the reservoir. The injection of biodegradable biopolymers for fracturing would contribute toward making the exploitation of shale gas less risky for the environment.

Beyond saving fossil fuels, polymers are key materials for the development of new energies such as composites for wind turbine blades by the resin transfer molding process. The development of composites is also a determining factor for the transport sector, as shown below.

Another renewable energy, which can be described as permanent and which is rapidly developing, is solar energy. The power available above the Earth's atmosphere is 340 $W.m^{-2}$, but only 170 $W.m^{-2}$ can be recovered at ground level, the rest being reflected or absorbed and used during the water cycle. The transformation of solar light energy into electrical energy occurs in inorganic semiconductor materials based on silicon (made of silicon doped with phosphorus, which provides negative charges and boron, which creates a deficiency of electrons within the silicon). Two types of polymers are involved in protecting the doped silicon: a film of ethylene vinyl acetate on the front of the plate and a film of polyvinyl fluoride

(Tedlar ®) at the back [WIE 05]. Research seeks to develop totally organic photovoltaic cells with the help of semiconducting polymers. The power available from photovoltaic cells in 2011 was 63.3 GW, which is still very low.

I.3.2.2. *The role of polymers in the storage of energy*

The development of more efficient batteries is crucial for the development of hybrid cars or cars running with electric motors. In 1978, the team of Michel Armand [ARM 87] studied the complex between polyether glycol and lithium to produce solid electrolytes. The batteries of polymer electrolytes derived from poly(ethylene oxide) offer many advantages, including non-volatility, and the possibility of using Li metal, but they require an operating temperature of 80°C. A lot of work to improve the conductivity of the polymer was undertaken and led to the use of fluorinated copolymers doped with electrolyte [COL]. The Bolloré Group and Renault in 2011 announced the launch of an electric car based on lithium polymer technology. In aviation, the problems with the 787 batteries now seem to have been resolved.

I.3.2.3. *The role of polymers in the saving of energy*

Housing and transportation are the most important areas in which to achieve energy savings. With regard to housing, 40% of primary energy is used for heating and cooling, and the question of building insulation is paramount. Polymers provide a surface thermal resistance (heat resistance R per unit area in $m^2.KW^{-1}$) greater than that of mineral insulators. Expanded polystyrene would probably be used more often, given its low price, if it did not have a flammable nature.

In transport, polymers have definitely brought the greatest energy savings, i.e. the lightening of motor vehicles and aircraft.

In the 1990s and 2000s, the weight of automobiles increased by about 25 kg per year in order to improve comfort by increasing the size and also to increase safety. It is known that reducing weight by 100 kg results in the reduction of consumption by 0.6 liters/100 km and, more generally, decreasing the weight by 10% leads to a decrease in consumption of the vehicle of 5–6%. Any decrease in consumption correlatively reduces the CO_2 emissions. In 2012, the European Parliament deliberated that the average new car should not emit more than 130 $g.km^{-1}$ in 2015 and no more than 95 $g.km^{-1}$ in 2020 [ADE]. The strategy for lowering the weight of vehicles relies on the decrease in the thickness of steel plate (decreasing the thickness by 1/10th brings a weight benefit of 10%), and on the use of polymer materials; the weight of the vehicle can therefore be decreased by 10–15%. Some examples are reported:

– wings of the C4 are a polyamide/poly(phenyl oxide) alloy, which provides a gain of 1.5 to 2 kg and a resistance to small impacts, because this mixture has a shape memory. In the same spirit, we can cite the low-support bumpers which prevent injury to pedestrians. Tanks (fuel, washer fluid) use PE, the dashboard is made of ABS, the floor mat is of PVC, the bumpers of PP, which is more easily recyclable than the ABS resins. The two studies on the recycling of PP by Frédéric Viot (see Chapter 11) and Valérie Massardier (see Chapter 12) concretely illustrate these aspects;

– with a view to reducing CO_2 emissions from transport, the electric car (*vide supra*) offers the most efficient solution, but there is a factor of 15 between the energy contained in 1 kg of battery and 1 liter of petrol (180 $Wh.kg^{-1}$ and 3000 $Wh.kg^{-1}$) [TAR 10] and the issues of the autonomy of the vehicle and the recharge time have not yet been resolved;

– the fuel cell is based on the principle of the combination of oxygen and hydrogen with the formation of water [FOU 02]. The cell consists of two compartments separated by a membrane of Nafion, a fluoropolymer produced by Dupont de Nemours. The hydrogen oxidized into a proton in the anodic compartment crosses the membrane to reduce the oxygen at the cathode. This membrane is effective for hydrogen but not suitable for methanol which has greater ease of storage in a conventional tank of an automobile because it is a liquid;

– in the field of air transport, polymers were introduced into aircraft construction in order to reduce weight and to provide more seats and/or consume less kerosene. The most recent examples are the *dreamliner*, the Boeing 787, of which 50% of the mass is due to composites; the replacement of aluminum leads to a weight reduction of 20% and a saving in kerosene of around 20% during operation. In Europe, Airbus built the A350 with 52% composites, thereby reducing the weight by 10–15 t. For these applications, scientists are developing new high-performance composite materials based on carbon fibers and polymers.

I.4. Polymers in daily life

It would be too long and too tedious to make an exhaustive list of all the applications for which polymers play a fundamental role in everyday life. The most important is packaging which uses more than 40% of the production of plastics, we shall simply mention three domains less well known to the public: food, health, clothing, sports and leisure.

I.4.1. *Polymers and food*

Plastic materials in contact with food, and the duration of contact, are constantly increasing. The more lively debates on the real safety of food in contact with materials, popularized by magazines more or less able to master the concepts used to protect the consumer (low toxicity, low migration of the substance, low exposure of the consumers, etc.), do not promote consumer confidence in plastic materials used for packaging. Successive regulations on polycarbonate materials, on residual bisphenol A, illustrate this idea perfectly. This controversy and the accompanying media coverage are analyzed in the study by Laura Maxim (see Chapter 1).

There is less emphasis on the fact that polymers have experienced a strong growth in the field of food packaging, as the barrier effect to oxygen indeed provides good conservation of oxidizable products and avoids contamination of meat and vegetables, with more transparency of the packaging allowing examination of the product. In their study (see Chapter 13), Olivier Vitrac and Audrey Goujon emphasize the universal character of the diffusion of the constituents of materials. This risk, as with many risks involving chronic chemical contaminants, requires specific attention and a proper consideration going beyond regulatory requirements alone, helped by a reliable prediction using simulations and modeling.

I.4.2. *Polymers and health: diagnosis, treatment and surgery, vectorization*

Polymers have become essential in all areas of health, from the solid materials used, for example, for prostheses, catheters and blood bags to the nanosystems developed for the vectorization of active substances and for diagnostics [GAU 03]. Among all these devices, some are single use (syringes, infusion sets, etc.), while others are introduced into the body for a period which is *a priori* indefinite (articular prostheses, vascular substitutes, artificial crystalline lenses, stitches thread, etc.).

I.4.2.1. *Surgery*

For hip surgeries, the protection of the acetabulum is provided by a deposit on the metal of the prosthesis of a layer of polyethylene with a very high cross-linked mass using γ radiation. Inguinal hernias are treated by the introduction of a polypropylene membrane. Cataracts are treated by the extraction of the natural crystalline lens, and replacing it with a substitute in polymethylmethacrylate.

In the cardiovascular area, PET has a dominant position with heart valves. Expanded polytetrafluoroethylene, known for its chemical inertia and its high-thermal stability, possesses other advantages compared with PET, especially its biostability and the possibility of sterilization by heat. Finally, substitutes based on synthetic textiles now open up an alternative therapy for the replacement of injured arterial segments. Plastic surgery utilizes silicones but with the risks that have come to light during recent cases.

I.4.2.2. *Vectorization and the controlled release of active ingredients*

Vectorization consists of encapsulating substances of interest (solid or liquid) within a carrier material and transporting them to their area of action, where they will then be released. Vectorization techniques principally use materials based on natural or synthetic polymers. In parallel with conjugated polymers – the active ingredient – the galenic form of the polymer is involved in the activity of the active ingredient. We can distinguish the self-assembled polymers (for example, micelles) and the nanoparticles such as nanoshells, wherein the active ingredient is scattered in a polymer matrix or in nanocapsules consisting of a heart and a polymer membrane [SHA 12, VIL 12]. The concept of "polymer therapy" has emerged from this synergy.

The choice of which type of particle and polymer to use depends on the desired effect. The support material helps in changing the layout to control the immediate or delayed release of the active ingredients. For example, it has been shown that for certain leukemias, the drug treatment (gemcitabine) alone was less effective than when the drug was administered by nanoparticles [DEL 03].

In this particular field, it is noted that polymers are not used as structural materials, strictly speaking, but as a tool for formulation (polymer formulation as opposed to the formulation of polymers commonly used). They are found here ranging from the micrometric scale as a component of nanoparticles to the micelle, or even the macromolecule in the case of nonionic polymer surfactants for the stabilization of particles [HAM 11, TAD 01]. A self-association leads to particle sizes from 50 to 80 nm in water in the presence of poly(ethylene glycol). Nanoparticles can also be obtained with associative polymers which spontaneously self-assemble [GRE 11].

I.4.2.3. *The diagnosis*

The principle is to use physicochemical interactions between a complex molecule (hormones, antigen antibodies, etc.) contained in a biological fluid and a specific reagent bound to a polymer. The target molecule binds to the site of the polymer and is then recognized by the same reagent fixed on a specific enzyme which causes a color reaction, facilitating the measurement [DEL 03]. This technique is used for pregnancy tests, for example.