

» you're gonna take control of the chemistry
and you're gonna manifest the mystery
you got a magic wheel in your memory
I'm wasted in time and I'm looking everywhere «¹

1. Introduction

1.1. The Ways of Science

The beaker on the cover of this thesis is more than the obvious indicator of the experimental and chemical content of this work. Hopefully, you – as the reader of this booklet – will find that the technical quality of the scientific content gathered between the two covers matches that of this image, but its meaning goes deeper than this superficial reference. More subtly, it attempts to expose the problem of observation.

How can a piece of colorless transparent glass leave such a clear and detailed picture on one's retina, other than by the elucidating action of projection, shadow and reflection? Where direct perception is impossible, the underlying reality is reconstructed from these secondary observations.

In this way this simple beaker, or rather the image of the beaker, or even more accurately: the image of the projections of this beaker, symbolize the scientists' dilemma: how to gain knowledge on reality? How to unravel the truth when it goes under-cover among mirages, illusions and delusions and only manifests itself indirectly?

The problem was already described allegorically by Plato in his *Politeia*.² The Greek philosopher composed a parable about a group of captives that were forced to look at the dead end of a cave. On this wall they observed shadows. Projections of objects and people moving behind their backs, their shadows cast on the blind wall by a fire lit in the caves' entrance. These people had never seen anything else than their own shadows and those of the objects that were carried around behind them. They were chained such that they could not look around. How were they to know that a reality existed other than that of the shadows they observed? In the eye of the beholder these captives possess only a very limited view on reality while they are unaware of this restraint. Plato acknowledged the difficulty of this problem but

did not consider it impossible to know reality. For Plato it was enough to realize this situation and to attempt to gain deeper knowledge; somehow finding enlightenment, rising above the world of observation, realizing the existence of reality.

Nietzsche was one of the first to explicitly classify this pursuit as a vial attempt to do the impossible.³ Science is unable to truly comprehend things but only allows the description of phenomena. All progress in science can be designated as improvements and refinements in this describing capability, devoid of any advance in understanding things, as he describes on several occasions in *the gay science*. Paragraph 112 in the third book, for instance, starts with the following:

»Erklärung« nennen wir's: aber »Beschreibung« ist es, was uns vor älteren Stufen der Erkenntnis und Wissenschaft auszeichnet. Wir beschreiben besser – wir erklären ebensowenig wie alle Früheren...

According to Nietzsche, truth and reality are no longer universal and objectivity is non-existent.

In our post-modern era, even the existence of something more real than the original shadows is disputed.^{4,5} Surely something would cause this shadow, but why would this object be more representative of reality than the projection it produces? Why would it be something else than a mere reflection itself? Why would there be something deeper, or more meaningful than this chaotic ensemble of mirror images, projections and reflections?

This may not be the most optimistic way to start a thesis; declining thorough understanding of matters. It pinpoints, however, what science is really aimed at: describing observations, recording measurements in the hope to be able to generalize and extrapolate, to model and predict, resulting in simulations and calculations being able to replace experimental procedures, rendering a comprehensive picture. In this respect, this thesis is aimed at the addition of yet another small fragment to this immense jigsaw. Though only of small size, the author sincerely hopes that it will be one of those valuable pieces that allow a whole new corner of this puzzle, representing this mouldable flexible shapable, and above all, *plastic* reality, to be actively explored.

1.2. Polymers

Plastic, derived from the Greek *'plassein'* meaning *'to mold'* or *'to shape'*, is often used as a *pars pro toto* for the class of polymer materials as a whole. Polymers or plastics have been wrestling with the image of pollution, environmental-unfriendliness and non-biodegradability like, for instance, in Coupland's *Generation X*,⁶ acclaimed for its strong portrayal of the *Zeitgeist*:⁷

DUMPSTER CLOCKING: The tendency when looking at objects to guesstimate the amount of time they will take to eventually decompose: "Ski boots are the worst. Solid plastic. They'll be around till the sun goes supernova."

Nothing could be further from the truth, however. Most polymers can be recycled and even when they are not, they form a most useful intermediate between fossil organic fuel and the power station's incinerator, not adding much to the environmental burdening intrinsic to the generation of energy. In fact, a full cradle-to-grave analysis depicts plastic packaging products as the preferred alternative to paper or wood.^{8,9} Recycling is the key factor in this case and not so much the biodegradability. The fact that most polymers disintegrate slowly does not mean that polymers are unnatural. Polymers belong to nature's most sophisticated molecules. Life itself stores its variables, parameters and other software components in this genetic polymer database called DNA. Completely biocompatible by nature. Proteins, copolymers of amino acids, are deployed as enzymes; nanobots regulating all of the fine organic chemistry taking place in our body, maintaining delicate equilibria.

While these may be appealing examples to show the high-tech aspects of polymers, it must be said that DNA and proteins are exceptional and specialized polymers. Right now, we can only marvel at their functional complexity although the application of polymers in high-tech man-made systems like electronic components is coming on. Display panels, memory chips and other semiconductor technologies based entirely on polymers are on the verge of replacing the old metal & sand based units.¹¹ Polymeric drug delivery systems are able to generate a long lasting supply of medication at 'just the right dose'.¹² Smart clothing is being developed with properties that adapt to the temperature and humidity of both the body and environment.¹³

Also when it comes to mere mechanical properties, polymers are among nature's topflight picks. Trees for instance owe their strength to the stretched cellulose fibres that are aligned with their trunk and embedded in lignine. The effectiveness of this reinforced composite architecture can regularly be witnessed in news reports. When tornados rage over picturesque little tropical islands, more often than not the houses and other artificial constructions, build from isotropic materials like stone, are restored to their state of highest entropy while trees, relying on the flexibility and toughness of their polymeric cellulose skeleton, are still erect if the ground has held them.

While in nature polymers appear to be the material of choice for a wide variety of applications, to us human beings, polymers for a long time have been the poor man's cheap replacement for natural fibres like silk and wool, an easily applicable material for the production of bulk commodity goods and a convenient source for packaging materials.^{14,15} Only during the last few decades of the past millennium we have passed a turning point when it was recognized that polymers can form truly unique and intelligent substances possessing properties beyond the scope of traditional materials like metals and ceramics. In some fields this knowledge has lead to superior products, while for many other areas we still lack the appropriate techniques to translate ideas into materials with sufficient precision. For advances in this field first rely on more precise construction methods of these polymer chains and not as much on the use of more exotic starting materials. Just 'making long molecules' no longer suffices and the design aspect is gaining importance. Starting from the same type and amount of monomer(s) one can create polymer architectures with highly different macroscopic properties by tailoring the chain length distribution, monomer sequence distribution, tacticity, functionality type distribution and the degree of branching, for instance.

1.3. Free-Radical Polymerization

Free-radical polymerization is one of the most convenient ways to prepare polymers on a large industrial scale. In fact, more than 70% of vinyl polymers – more than 50% of all plastics – is produced in this way.¹⁶ The versatility of the technique stems from its tolerance towards all kinds of impurities like stabilizers, trace amounts of oxygen and water.¹⁷ The facile polymerization in an aqueous medium is truly unique and offers many benefits as evidenced by the large proportion (40–50%) of free-radical polymerizations that are conducted in this way, in the

form of emulsion polymerizations.¹⁸ Moreover, the range of monomers that can be polymerized by radical means is considerably larger than those compatible with other techniques.¹⁹ Unfortunately, however, control over the polymer architecture is difficult to attain in free radical polymerization. Molar mass distributions are generally broad and can only be influenced to some extent by the use of chain transfer agents and variations in the initiator concentration. Continuous or semi-batch processes may reduce the variations in macroscopic conditions that typically occur during a batch reaction, but on a microscopic scale, statistical variations in the environment of the growing chains will give a polymer product with a large variation in *e.g.* chain length, composition, composition distribution and degree of branching. This lack of control confines the versatility of the free radical process, because of the intimate relationship that exists between the polymer chain architecture and the macroscopic behavior of the polymer material. The absence of control over the incorporation of monomer into the polymeric chain implies that many macroscopic properties cannot be influenced sufficiently.

Block copolymers with amphiphilic properties, star-shaped specimens and hyperbranched structures have become more important in recent years. To comply with these ever growing demands, polymer chemistry has resorted to the application of living polymerization techniques, such as anionic polymerization, group-transfer polymerization, and several others. Despite the structural control that these techniques offer, major drawbacks exist. For instance, their requirement of ultra-pure reagents and, more importantly, the fact that they allow only a small fraction of the commercially interesting monomers to be polymerized. This renders these living polymerization techniques less interesting from a commercial point of view. Clearly, techniques are desired that combine structural control with the robustness and versatility of radical polymerization.

1.4. Objective and Outline of this Thesis

This thesis is meant to present a sturdy polymerization technique, which allows the construction of some types of polymer with a much higher level of microstructural ‘user-input’ than was possible before, while retaining the advantages of free-radical techniques. This is the realm of controlled or *living* radical polymerizations, a more sophisticated variety of conventional free-radical polymerization. More specifically, this thesis aims to investigate Reversible Addition–Fragmentation chain Transfer (RAFT) polymerization thereby focussing on its application in dispersed

media. The prospects of RAFT are appealing, for the addition of RAFT agent to a system should in principle not influence the radical concentration and polymerization rate. Therefore, existing recipes and technology can be used to which RAFT agent can be added as the *magic* ingredient, much in the same way in which appropriate spices transform a mishmash of nutriments into a delicious dish. The fact that only a handful of publications have appeared after its invention, however, might serve as an indicator that the application of RAFT is more complicated than is to be expected at first sight. The investigations in this thesis are aimed at gaining a more thorough understanding of the RAFT system and the prevailing mechanisms, especially those that are important in heterogeneous media.

Chapter 2, presents a short overview of living radical techniques, highlighting differences and similarities with other established approaches like ATRP and nitroxide-mediated polymerizations. Several characteristic kinetic and mechanistic aspects of RAFT polymerizations are indicated and investigated using simulations and experiments in homogeneous media.

Chapter 3 is dedicated to the preparation of the type of RAFT agents applied in this thesis, namely dithioesters. The first part of this chapter presents a range of different synthetic pathways leading to these compounds, while the second part gives the experimental details of the syntheses of the dithiobenzoate derivatives that are used as RAFT agents for this research.

Chapter 4 is concerned with the controlled copolymerization of styrene and maleic anhydride. Whereas other living radical polymerizations have produced a very large gamut of controlled architectures of various monomers over the years, a particular class of vinylic monomers was found to cause problems, namely those with a carboxylic acid or anhydride group. The versatility of RAFT polymerizations is exemplified by copolymerizing maleic anhydride and styrene and illustrated further in a particular application in which the controlled polymerization of maleic anhydride can yield unique materials, namely functionalized polyolefin block copolymers.

Chapter 5 describes the application of RAFT in emulsion polymerization. The effect of the presence of RAFT agent on the rate is investigated by elimination of the complex nucleation stage through the use of seed latices. Seeded experiments are performed both in the presence and in the absence of monomer droplets. Fur-

thermore, the effect of RAFT on the nucleation process is studied in *ab initio* reactions. Stability issues are partly eliminated by the application of nonionic surfactants.

Chapter 6 continues with the study of miniemulsion polymerizations in the presence of RAFT. The stability of the miniemulsion polymerizations is shown to be affected by RAFT, much in the same way as in the macroemulsions in Chapter 5, when ionic surfactants are used. Nonionic surfactants give stable systems and consequently allow living radical polymerizations to be conducted in a dispersed medium in a straightforward fashion. This is demonstrated by the preparation of low polydispersity homopolymer and block copolymer dispersions.

1.5. References

1. Sonic Youth, fragment from *Cotton Crown* on the album *Sister* © Cesstone Music, **1987**
2. Plato, *Politeia* (Dutch translation: Gerard Koolschijn, Impressum Amsterdam Athenaeum-Polak & Van Gennep, 3th revised edition, **1991**)
3. Friedrich Nietzsche, *Die fröhliche Wissenschaft*, 2nd edition, **1887**, Insel Verlag Frankfurt am Main, **1982**
4. Jean Baudrillard, *La Guerre du Golfe n'a pas en lieu*, Éditions Galilée, **1991** (English translation by Paul Patton, Indiana University Press, Bloomington & Indianapolis, **1995**)
5. Jean Baudrillard, *Simulacres et simulation*, Éditions Galilée, **1981** (English translation by Sheila Faria Glaser, The University of Michigan Press **1994**)
6. Douglas Coupland, *Generation X*, St. Martin's Press, **1991**
7. e.g. Jay McInerney's book review in The New York Times (June 11, **1995**)
8. www.plasticsresources.com
9. Hocking, M. B. *Science* **1991**, 251, 504
10. Fukuda, Y.; Watanabe, T.; Wakimoto, T.; Miyaguchi, S.; Tsugida, M. *Synthetic Metals* **2000**, 111–112, 1
11. 'Polymer Electronics', Philips Research, www.research.philips.com, **1998**
12. e.g. Heller J.; Pangburn S. H.; and Penhale D. W. H.; in *Controlled-Release Technology, Pharmaceutical Applications*, Lee P. I.; and Good W. R. (Eds.), Washington DC, ACS Symposium Series, pp 172–187, **1987**
13. Handley, S, *Nylon; The Manmade Fashion Revolution*, **1999**, Bloomsbury publishing, London, p.175–176
14. *Early Plastics, Perspectives 1850–1950*, Mossman, S. (Ed.), **1997**, Leicester University Press, London
15. Meikle, J. L., *American Plastic, a cultural history* **1995**, Rutgers University Press, New Brunswick, New Jersey
16. Otsu, T. *J. Polym. Sci., Part A Polym. Chem.* **2000**, 38, 2121
17. Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*, 1st ed.; Elsevier Science Ltd.: Oxford, **1995**
18. Gilbert, R. G. *Emulsion Polymerization: A Mechanistic Approach*; Academic: London, **1995**
19. Stevens, M. P. *Polymer Chemistry, an introduction* **1990**, 2nd ed., Oxford University Press, New York, p.189

