» Orders came from downtown:
no more «[1]

Epilogue

An epilogue is here and now. It marks the turnover between the past and the future. In the preceding chapters, the work that has been performed over the past few years is described. The question remains, however, what the prospect is for RAFT in the future and in what way the work in this thesis can contribute to that.

One of the most prominent challenges that exist in the field of polymer chemistry nowadays is to gain control over the intramolecular polymer structure. If one thing has become apparent over the years, it is that *average* chain lengths, *average* compositions and *average* functionality numbers do not suffice to correlate macroscopic properties to molecular characteristics. Polymers with roughly the same *average* characteristics can exhibit totaly different material properties. One of the more familiar examples that can be mentioned in this respect is that of a block-copolymer and a statistical copolymer, constructed from the same monomers.

In the area of polymer characterisation tremendous progress has been made in the recent past so that complete molar mass distributions, chemical composition distributions and functionality type distributions have been made available. The increased knowledge that has been gained by these analyses on polymer structure–property relationships is now waiting to be applied. On the synthetic side, however, construction of polymers with predetermined and well defined intramolecular structures has been restricted to a small number of systems that are compatible with ionic polymerization techniques. Clearly the need exists for robust, versatile and generally applicable methods to prepare these materials.

Living radical polymerization can fill this gap that exists in our collection of synthetic tools. RAFT polymerization in particular appeared to be robust and versatile and therefore of general use, but when the investigations described in this thesis started, RAFT was documented exclusively in the patent literature.[2] From experience in the synthesis of non-reversible addition fragmentation chain transfer agents, it was decided to prepare several RAFT agents with the aim to study their application in homogeneous and heterogeneous media. The results were encouraging. In fact, the level of control that was obtained was comparable to what colleagues in our department had achieved using atom transfer radical polymerization (ATRP). More amazing was the relative ease with which the molar mass distribution could be controlled. The quest for improved combinations of alkyl halides, ligands and metals to be used in ATRP seemed without end, whereas the RAFT agent was simply added to an existing recipe from an undergraduate practical course to yield similar results from the very first experiment. This immediately points out one of the major advantages of RAFT over other living radical polymerization techniques: the reaction conditions are identical to those of a conventional uncontrolled radical polymerization. The same temperature, solvent, monomer and initiator are used and the concentration of propagating radicals is hardly affected. As was shown in Chapter 2, the trade-off between polymerization rate and the level of 'livingness' is achieved by simply varying the concentrations of initiator and raft agent, rather than by a change of design of the ingredients as is the case in ATRP.

Another distinct advantage over ATRP is the absence of metal complexes in the product which have, up to the present day, prevented the industrial application of this technique. In this respect, however, polymer prepared via RAFT polymerization, has a comparable disadvantage. Well-controlled polymers are prepared by highly reactive RAFT agents that easily exchange the controlling moiety amongst the polymer chains during the process of preparation. These end-groups remain in the product as equally labile species, giving rise to an increased rate of degradation. In Chapter 4 it was shown that UV irradiation could cleave the dithiobenzoate moiety from its chain, thereby generating radicals. Thermogravimetric analysis revealed that poly(methyl methacrylate) samples started to degrade at around 120 °C. The weight loss corresponded to that of the dithiobenzoate moiety, but once this had been removed, a further temperature increase revealed that the themal stability of the polymer was poorer than might be expected from poly(methyl methacrylate) samples. These issues may prevent the direct application of the product after its preparation, requiring a post-polymerization end-group modification. In a more positive sense, this feature could possibly be used to its benefit in *e.g.* a UV-curable coating. These types of coating usually require the deliberate addition or incorporation of photosensitive moieties that produce cations or radicals when irradiated, which would no longer be nessecary when using a RAFT polymer.

The problem is expected to disappear when low-reactivity RAFT agents are used. Such compounds cannot be used for preparing clean and pure polymer architectures in batch reactions, as the polymer end-group is less reactive during the reaction, but the end-group is quite likely also less labile in the product. For this reason, low reactivity reagents can be desirable for a number of reasons. They eliminate the need for post-polymerization modifications, they are usually more easily synthesized and can be readily applied in emulsion polymerization. For the application of high-reactivity RAFT agents in heterogeneous media like emulsion is characterized by a low efficiency and colloidal instability. This is postulated to be due to the drastic change in the distribution of both radical and polymer chain lengths which interferes with the nucleation process and results in unacceptable retardation througout the polymerization. Although these problems may partly be eliminated by using a semi−continuous procedure, one cannot expect to obtain a robust, reliable and reproducable sytem in this way. RAFT agents of lower reactivity will not have such a significant effect on the chain length distribution and can therefore be used with similar ease as conventional transfer agents.[3] Although it will not be possible to prepare latices consisting of pure block copolymers for instance, a certain fraction of these architectures could be incorporated in the latex particles in order to influence the particle morphology and the material properties in the resulting application.

This thesis has contributed to an understanding of the application of living radical polymerization in emulsion. Although RAFT is not without its problems, it is by far more easy to use than techniques based on reversible termination (like ATRP and nitroxide mediated polymerization). From a synthetic point of view, colorless, easily prepared, high reactivity RAFT agents would be desired, but more demanding at this point is research in the relatively unexplored area of polymer properties which was mentioned at the start of this epilogue. Most studies in living radical polymerization that have been published focus, like this thesis, on the polymer synthesis, but obviously the time has come to *apply* and to see what this tremendous progress that has been achieved over the past decade can bring in terms of smart materials, intellegent additives and products that we didn’t even know we wanted to have before they existed...

References

1. Lt. Martin Castillio's typical way to end a Miami Vice episode, leaving the viewer with mixed feelings. For one knew that Crockett and Tubbs had given all that was in them, but that they had not been allowed to finish the job even though considerable progress was just around the corner. In fact, this is quite similar to the situation I experienced in september 2000, when I knew I had to stop the experimental work and start concentrating on this thesis, just a couple of weeks after we finally managed to produce pure block copolymers in miniemulsion. More advanced polymer architectures were/are in sight and the future is shining bright.
2. Le, T. P.; Moad, G.; Rizzardo, E.; Thang, S. H. Patent WO 98/01478 (**1998**) [*Chem. Abstr.* **1998**, 128:115390]
3. Monteiro, M. J.; Sjöberg, M.; Van der Vlist, J.; Göttgens, C. M. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4206