



## Computational Quantum Chemistry, Polymer Chemistry Dr Michelle Coote – ARC Fellow, Rita Cornforth Fellow Elect

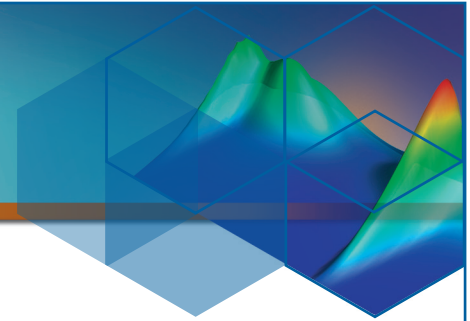
We use computer calculations to determine the structure of molecules and to help understand how molecules react with one another. Using the laws of quantum mechanics, we can calculate from first principles the structures of molecules, their vibrational frequencies and their energies. This provides detailed information on the mechanisms of reactions, as well as calculations of their kinetics and thermodynamics. Much of this information is very difficult to obtain experimentally, particularly for very reactive or hazardous compounds. Quantum chemistry provides a viable alternative approach for studying these compounds, and is thus an important complement to experimental procedures.

Our main interest is using quantum chemistry to solve practical problems in the polymer field. Polymers are long chain molecules and they can be used in a wide variety of applications, ranging from paints and adhesives, to artificial hips and contact lenses. The suitability of a polymer for a particular application depends not only upon its overall chemical composition, but also on its end-group composition, its chain length and its molecular architecture (*i.e.* whether it is linear, branched, star-shaped, etc.). These properties depend, in turn, upon the kinetics and mechanism of the polymerisation process – that is, what reactions occur and how they compete with one another. We use quantum chemistry to obtain this information and then use it to design better methods for controlling polymerisation processes and producing designer polymers. We work with leading experimental groups, both in Australia and internationally, who put our theoretical designs into practice.

During 2004, our main focus has been the RAFT polymerisation process – an important CSIRO-invented technique for controlling free radical polymerisation. Our work on this process has helped to clarify the reaction mechanism and to develop guidelines for optimising the process. Our first computer-designed RAFT agents are now being tested experimentally, in collaboration with the Centre for Advanced Macromolecular Design, University of New South Wales. We have also enjoyed a stimulating theoretical-experimental collaboration with the group of Professor Arend Schouten, University of Groningen, with whom we are working to design degradation resistant PVC. We look forward to working with Professor Bruce Wild in 2005 on a new ARC-funded project to design stereoregular polyphosphines.

### *Accurate Computational Methods*

Applying quantum-chemical methods to polymeric systems poses a major challenge. Not only do accurate methods require significant computer power, the computational cost of a method scales exponentially with the size of the molecule. In order to adapt quantum chemistry to the study of polymerisation processes we have been evaluating the accuracy of computational methods and identifying reliable low-cost procedures. We have also been designing small model reactions that effectively mimic the behaviour of real polymer systems. We have recently published guidelines on the application of quantum chemistry to free-radical polymerisation in the new edition of the *Encyclopedia of Polymer Science and Technology* (Wiley, 2004). We are designing an *ab initio* polymerisation reactor in which quantum-chemical calculations are combined with kinetic modelling, so as to predict the macroscopic outcome of a polymerisation process. (*With L Radom, R Gomez-Balderas, D J Henry*)



## Fundamental Aspects of Radical Reactions

In order to understand the mechanism of complicated radical-based processes (like polymerisation) it is important to study the prototypical systems first. During the last year we have examined reactivity and selectivity preferences in radical addition to double bonds, and have explained unusual substituent effects in alkyl-oxygen bond dissociation energies. We have used this information as a foundation for interpreting substituent effects in the RAFT polymerisation process. We have also identified the factors influencing barrier heights in hydrogen abstraction reactions involving thiols, and highlighted the important role of polar interactions in these systems. This work will assist in the design of improved chain-transfer agents in free radical polymerisation, and will also be significant for the study of these reactions in biological systems. (With K A Beare, L Radom, R Gomez-Balderas, D J Henry, and A Pross [Ben Gurion U, Israel])

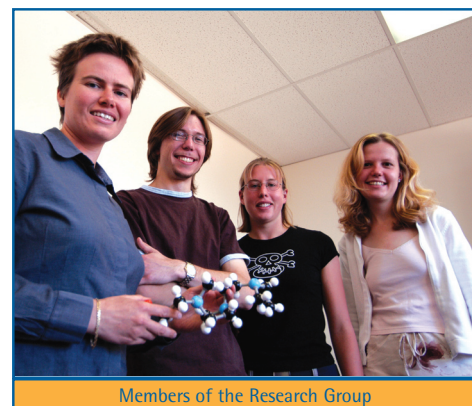
## Controlled Radical Polymerisation

The Australian-invented RAFT process was developed to control the molecular weight and architecture of polymers resulting from free radical polymerisation. We have been using quantum chemistry to build a detailed mechanistic picture of this important process with a view to designing improved RAFT agents for 'difficult' monomers, such as acrylonitrile. During the last year, we have provided explanations for why certain RAFT polymerisations are inhibited or retarded, and provided evidence for long-lived intermediate radicals in certain systems. We have also completed a major study of the effects of substituents on both the kinetics and the thermodynamics of the RAFT process. Building on these studies, we have now moved to the practical problem of RAFT agent design and our first computer-designed RAFT agent is currently being tested experimentally at the University of New South Wales. We have also been exploring the possibility of controlling free radical polymerisation using phosphorus-based RAFT agents, or *via* a new "Controlled Radical Addition Polymerisation" process that we are developing in collaboration with the University of New South Wales (With K Green, J Hodgson, D J Henry, C Barner-Kowollik, T P Davis, M H Stenzel, A Feldermann, H Chaffey-Millar [UNSW])

## Degradation-resistant PVC

The thermal and photochemical stability of poly(vinyl chloride) (PVC) is much lower than it should be on the basis of its chemical structure due to the presence of structural defects. These are formed by side reactions (such as chain transfer) during the free radical polymerisation process. If these side reactions could be minimised, the *inherent* stability of PVC would be improved and it would be possible to minimise the use of heavy metal stabilisers in the resulting polymer. To this end, we have been working with the group of Professor Arend Shouten (Groningen) to determine the origin of the structural defects in PVC, and their dependence on polymerisation process conditions. In this combined experimental-theoretical study, our *ab initio* calculations have been used to help interpret the experimental data and map out the mechanism and kinetics of structural defect formation. The information will ultimately be used to suggest (and test) improvements to the PVC polymerisation process. (With A J Schouten, J Purmova, K F D Pauwels, W van Zoelen, J E Vorenkamp [U Groningen, The Netherlands])

<http://rsc.anu.edu.au/research/coote.php>



Members of the Research Group