



COMPUTATIONAL QUANTUM CHEMISTRY, POLYMER CHEMISTRY

DR MICHELLE COOTE

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 geometries 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. Our research highlights in 2005 include the design of a new radical route to polyphosphines and a new class of multipurpose RAFT agent for controlling free-radical polymerisation. These computer-designed chemical processes are now showing great promise in experimental testing by collaborators and highlight the growing potential of computational chemistry as a practical tool for the polymer field.

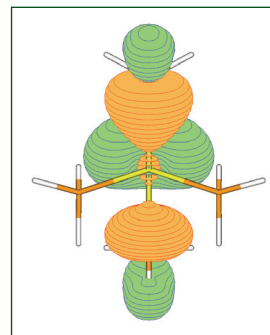
Accurate Computational Methods

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 also design small model reactions that effectively mimic the behaviour of real polymer systems. During 2005 we published the first chemically accurate computational predictions of propagation rate coefficients, and designed a computationally efficient approach to the study of addition-fragmentation rate coefficients in RAFT. We also commenced collaborative work with Dr Mansoor Namazian to tackle the important problem of modelling solvent effects on reaction rates. (*With D B R Brittain, E I Izgorodina, and M N Namazian [Yazd U, Iran]*)

Free Radical Chemistry

To understand the mechanism of complicated radical-based processes (like polymerisation) it is important to study the prototypical systems first. During 2005, we became interested in the unusual behaviour of phosphoranyl radicals. According to textbooks, these radicals should be highly stabilised; however, we found that this notion was inconsistent with the low reactivity of dithiophosphinate esters in certain radical addition reactions. Moreover their stabilities followed very different

structure-reactivity trends to their carbon-centred counterparts, which we explained using qualitative molecular orbital arguments. An important practical implication of our findings is that phosphoranyl radicals should make excellent chain carriers for organic synthesis, and we are looking forward to developing improved reagents in collaboration with fellow members of the new ARC Centre of Excellence in Free Radical Chemistry and Biotechnology. (With K L Goh, K A Green, J L Hodgson, E H Krenske)



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 ethylene. In 2005, this culminated in the development and patenting of the first multipurpose agent, capable of controlling monomers with disparate reactivities. Although designed entirely by computer, subsequent experimental testing by collaborators (led by Dr Christopher Barner-Kowollik at the UNSW) has demonstrated it to be capable of controlling free-radical polymerisation. Together, we have also designed an entirely new method for controlling free-radical polymerisation using thioketones as radical spin traps. In 2006, we look forward to applying our computational approach to the atom transfer radical polymerisation process in collaboration with Professors Kris Matyjaszewski (Carnegie-Mellon) and Rinaldo Poli (Toulouse). (With G E Cavigliasso, E I Izgorodina, E H Krenske, and V Musgrove, D J Henry [RMIT U], A Ah Toy, C Barner-Kowollik, H Chaffey-Millar, T P Davis, M H Stenzel, A Theis [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, formed by side reactions 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. 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])

Polyphosphines

Putting phosphorus into the backbones of polymers can help to impart a range of useful properties including increased polarity, metal ion binding characteristics and fire retardancy. In 2005, we designed a new synthetic method for achieving this, the free radical ring-opening polymerisation of phosphetanes. We showed computationally that these small phosphorus heterocycles would undergo facile ring opening polymerisation *via* substitution of a carbon-centred radical at phosphorus, and that free-radical copolymerisation with normal polyolefins should also be possible. The process is now being tested experimentally in the group of Professor Bruce Wild as part of our larger ARC-funded project to design stereoregular polyphosphines. (With J L Hodgson, E H Krenske, S B Wild)

