Review article

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Reversible-Deactivation Radical Polymerisation: chain polymerisation made simple

Abstract: Reversible-Deactivation Radical Polymerisation (RDRP) is one of the most exciting developments in chemistry over the past few decades, but it is rarely mentioned when polymerisation mechanisms are introduced in the final years of secondary education or first years of tertiary education. We propose that this is unfortunate, as RDRP is simpler than conventional Radical Polymerisation both conceptually and in terms of setting quantitative problems, and that it illustrates several other important features of chemistry as a human endeavour: How essential mechanistic unities are hidden by the details of how we write a chemical reaction, how a 'bug' in one stage of development of a process can become a 'feature' in a later stage, and how exciting changes can occur quite suddenly in fields thought to be mature and uninteresting.

Keywords: chain reaction; history of science; mechanism; polymerisation; Reversible-Deactivation Radical Polymerisation.

Bliss was it in that dawn to be alive… (William Wordsworth)

Introduction

Reversible-Deactivation Radical Polymerisation (RDRP) – formerly known as Controlled Radical Polymerisation, even more formerly known as Living Radical Polymerisation – is a family of reactions discovered in the 1990s that have become increasingly important over the last few decades.

Radical Polymerisation is an example of a 'chain' reaction (Morton, 1973). The main chain reactions we see in textbooks tend to be one version or another of the ones implicated in ozone depletion (Rowland, 1991). While this is a 'feel good' story (we did stop the chlorofluorocarbons and start reversing the depletion of the ozone layer), it grows wearying with repetition, and there are other chain reactions that are equally upbeat and interesting. One of these reactions is Radical Polymerisation, the process by which many common materials are made, such as polystyrene, poly(methyl methacrylate) (Perspex), and poly(acrylamide) (the hyperabsorbent sand-like stuff you find if you tear open a disposable nappy/diaper). While Radical Polymerisation is arguably conceptually simpler than the complex net of ozone-depleting reactions, this article will argue for teaching a chain reaction that is conceptually even simpler – RDRP.

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Although RDRP systems have not yet made a big impact on our everyday lives, RDRP has made a huge impact on the narrow world of polymer chemistry, where it has made a lot of people wildly enthusiastic. Since we are some of those people, we would include RDRP in any general chemistry course anyway, but in this article we will argue that RDRP is a valuable topic to include in teaching chemistry for a number of other reasons.

– RDRP is a good example of sudden exciting change happening in a field that was thought to be 'mature' (i.e. uninteresting).
– RDRP is a good example of a set of chemical reactions that look very different written down on the page but have the same core mechanism in essence.
– RDRP is a good example of a process that we can visualise and/or model in many different ways.
– RDRP is a good example of how a bug in one stage of development (sulfur- or halogen-containing end-groups left behind) can become a feature in a later stage (handy functionalities for doing useful chemistry).
– RDRP is a good example of a chain reaction that is not the same-old one commonly used in textbooks.
– Finally, RDRP is simpler than conventional Radical Polymerisation both conceptually (in terms of side processes that can be neglected) and practically (in terms of being much easier to set and do quantitative problems about), so there is no reason not to introduce it in a general chemistry course at the same time as chain polymerisation.

Why is radical polymerisation important?

Radical Polymerisation is a process that produces many of the synthetic polymers we are familiar with in our everyday lives (Table 1). Since practically any molecule with a carbon-carbon double bond can be polymerised by radical polymerisation, polymers with a very wide range of different properties can be obtained in this way. The reaction is less sensitive to impurities than other polymerisation chain reactions and can be applied to a wider range of monomers (For more information about radical polymerisation, see the article in this issue by Shipp, Rossi, and Russell).
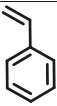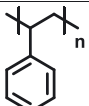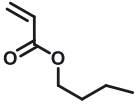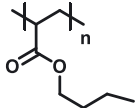
What is a chain reaction?
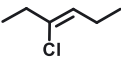
The International Union of Pure and Applied Chemistry (IUPAC) defines a chain reaction as follows: A reaction in which one or more reactive reaction intermediates are continuously regenerated, usually through a repetitive cycle of elementary steps (Laidler, 1996; Muller, 1994; Svehla, 1993).

In radical polymerisation, the continuously regenerated reaction intermediate is the polymer radical. While each successive polymer radical is not exactly the same (unlike small molecule chain reactions) the chemical differences in each successive radical are typically so distant from the reactive centre that they are the same species for all practical purposes.

A chain reaction can be typically broken into three stages: initiation, propagation, and termination (Figure 1). Initiation is formation of the initial reactive centre; termination is the final reaction that eliminates the reactive centre; and for each initiation and termination reaction, there will be typically very many propagation reactions.

Due to the speed of the individual propagation reactions, polymer chains are generated rapidly on the scale of the overall reaction. Stopping the reaction at 1% monomer conversion, you will find polymer molecules of about the same size as you will at 99% conversion – there will just be fewer of them. As radical-radical reactions are very rapid (there is essentially no activation energy to be overcome), the termination step will be physically rather than chemically controlled. Smaller species will combine more rapidly than large species, but beyond a certain length, all chains can be considered to be equal – any one is equally likely to combine with any other.

Table 1: Chemical structures of common monomers and their corresponding polymers produced by radical polymerisation, and some of their common applications.

Monomer	Polymer	Common applications
Styrene	Polystyrene	Eskies, plastic cups
Butyl Acrylate	Poly(butyl acrylate)	Latex paints
Methyl methacrylate	Poly(methyl methacrylate)	Greenhouses, LEDS, Motorcycle windshields
Vinyl chloride	Poly(vinyl chloride)	Water pipes, vinyl car seats
Tetrafluoroethene	Polytetrafluoroethtlene	Non-stick frypans, Gore-Tex™
Acrylic acid	Poly(acrylic acid)	Dispersants
Acrylamide	Polyacrylamide	Flocculants, superabsorbents
2-chloro-1,3-butadiene	Polychloroprene (Neoprene)	Wetsuits

Limitations of radical polymerisation

What are some of the limitations that arise from the radical polymerisation mechanism?

The most obvious is – in complete contrast to typical reactions in synthetic organic chemistry – that there is very little control over the molar mass of the product. While the average molar mass can be readily calculated, the reaction will generate a broad distribution of molecules of different lengths.

The broadness of a distribution can be characterised by a dispersity, $Đ_M$, which is defined by IUPAC as follows (Stepto, 2009): $Đ_M = M_w/M_n$

1) Initiation: Radical generated from peroxide initiator; addition to monomer to form first polymer radical
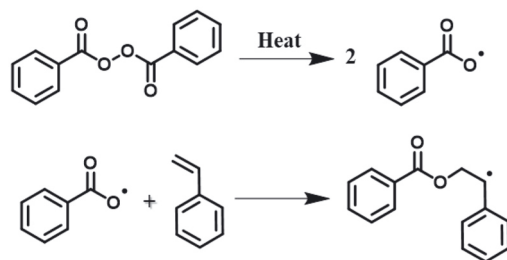
2) Propagation: Monomer units are added to the active polymer radical; n goes from 1 to 10, 100, 1000, 10,000 …
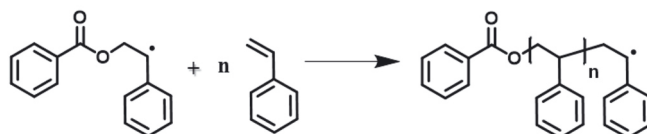
3) Termination: Combination or disproportionation
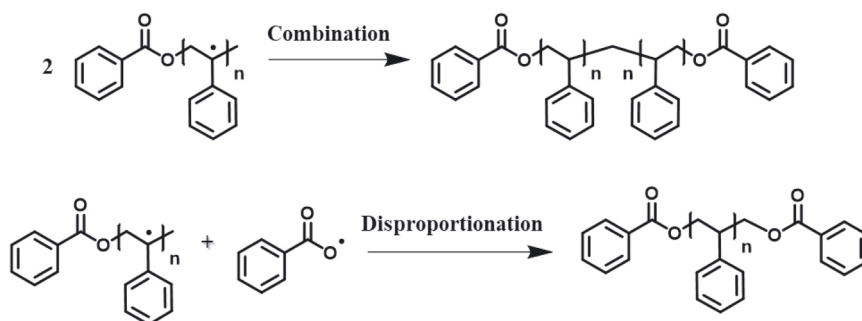
Figure 1: A typical Radical Polymerisation reaction: Polymerisation of styrene with benzoyl peroxide initiator.

where M_w is the mass-average molar mass (or molecular weight) and

M_n is the number-average molar mass (or molecular weight).

(where M_w is defined as $\Sigma M_i w_i$, where w_i is the mass fraction of molecules of molar mass M_i, and M_n is defined as $1/\Sigma(w_i/M_i)$.)

A perfectly well-behaved radical polymerisation with no side reactions will give a dispersity between 1.5 and 2.0, depending on the termination mechanism.

Question 1: Try calculating the M_w and M_n of a population of polymer chains consisting of only three polymer sizes-say, for example, (25% $M = 1000$, 25% $M = 3000$, and 50% $M = 5000$). You are almost certain to find that the dispersity is smaller than you expected.

An important consequence of the large number of propagation reactions needed to make a single polymer chain is that minor side reactions that would be of no importance in a conventional organic synthesis can have dramatic effects on a radical polymerisation. Radicals are reactive not only in addition and combination reactions, but in abstraction reactions.[1] If for every thousand propagation reactions, there is even one abstraction reaction – to solvent, monomer, polymer, or some other species present in the system – the

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1 Abstraction reaction are reactions where a single atom and unpaired electron are transferred from a molecule to a radical centre, transferring the radical centre from one species to another. See Figure 2.

distribution of molar masses will be dramatically different (unless the reaction was designed to generate a fairly short molecule). An abstraction reaction where the reactive centre is regenerated on a molecule other than the original propagating polymer chain is referred to as 'chain transfer'. This means that the chain reaction – the kinetic chain – is transferred to another centre (while the physical polymer chain is terminated). Chain transfer to small molecules that can re-initiate polymerisation will give a population of chains smaller than predicted by the ideal theory. Chain transfer to polymer molecules will also give a population of chains larger than predicted by the ideal theory, and beyond a certain level of chain transfer reactions – which is not hard to reach – give a cross-linked network of 'infinite' molar mass. Chain transfer can also give rise to defect structures on chain ends, which may make the polymer susceptible to degradation reactions – for example, a bond at the end of the molecule that is weaker than a carbon-carbon bond can be more easily broken thermally or photochemically, giving the potential for depropagation reactions that 'unzip' the polymer.

Many common polymers are copolymers, composed of more than one monomer species. In principle, this allows the exploration of a vast volume of 'property space', as properties anywhere between the properties of the homopolymers can be obtained – for example, a copolymer of styrene (the homopolymer of which has a glass transition temperature, T_g, of about 95 °C) and vinyl acetate (homopolymer T_g about 30 °C) could have a glass transition temperature anywhere between 30 and 95 °C.[2] However, as monomers have different reactivities, for all but the most carefully selected and highly artificial circumstances the composition of the copolymer formed will change over the course of the reaction. Consider the extreme case of two monomers A and B, of which the monomer A prefers to react with the polymer radical A and the monomer B also prefers to react with the polymer radical A. A 50:50 mixture of A and B will give rise to a population of chains that start out almost entirely A and end up almost entirely B after monomer A is depleted – and if you were hoping to get the properties of a copolymer that was 50% A and 50% B, you will be out of luck.

The termination mechanism of classical radical polymerisation unavoidably generates defect structures: either head-to-head additions (where an incoming asymmetrical monomer adds the 'wrong way around') in termination by combination, which are typically more sterically hindered than head-to-tail bonds and hence weaker; or unsaturated groups, which are reactive groups susceptible to photooxidation and other decomposition reactions.

Reversible-Deactivation Radical Polymerisation

The name of the mechanism tells us the key difference between RDRP and conventional radical polymerisation. In RDRP, a new reaction is introduced – reversible deactivation of the chain ends. In order for RDRP to be effective, this reaction has to occur often on the timescale of propagation – ideally, a chain will be deactivated and reactivated several times for each propagation reaction (see the left side of Figure 2).

What are the consequences of this reversible deactivation on the limitations of radical polymerisation we have discussed in the previous section?

Some of the most important are that the lifetime of a growing chain is hours rather than seconds; such that chain length increases continually with monomer conversion (in contrast to radical polymerisation which produces high molar mass molecules throughout the reaction), and that different monomers can be added sequentially to produce block copolymers.

In contrast to conventional polymer chains which are formed irreversibly, RDRP techniques can offer a way to form polymer chains with predetermined molar masses and narrow molar mass distribution. Molar mass will typically be controlled by the amount of the RDRP agent, the species that makes reversible deactivation possible – while this will give a lower molar mass than would be obtained without the RDRP agent, it will also have a narrower dispersity. As the end-groups will also largely be derived from the RDRP agent, the defect structures from combination and disproportionation will be much less evident. Critically, the chemistry

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2 The glass transition temperature is the temperature at which a hard, glass-like solid polymer will change into a soft, rubbery one.
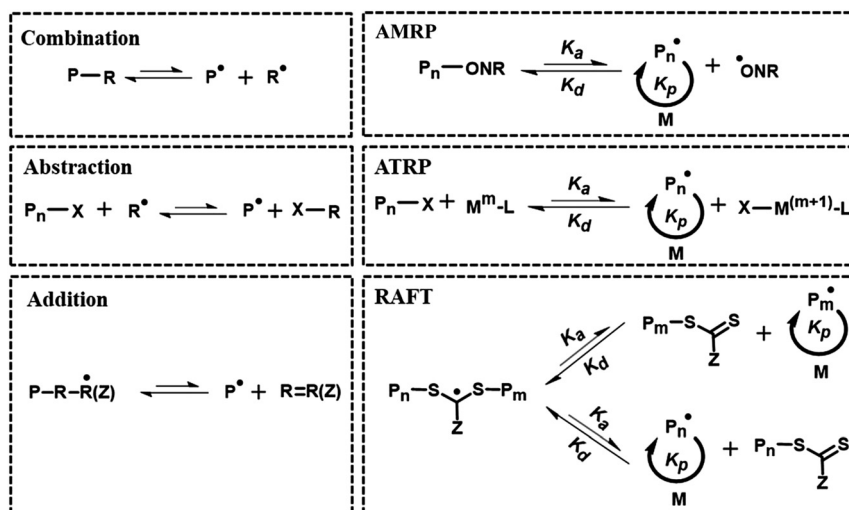
Figure 2: The three fundamental mechanisms of RDRP, and their approximations by the three most common RDRP methods. P: polymer chain, X: halide (e.g. Br, Cl), M: transition metal, L: complexing ligand, Z: reactivity-modifying group.

of the RDRP-derived end-groups can be exploited to further extend the chains with a different monomer to make block copolymers, or to attach small molecule species with valuable functionality.

And for copolymers, RDRP ensures that composition drift occurs within a copolymer chain, rather than across the population of copolymers. As the reactive centre is rapidly passed from one polymer chain to another and each chain spends most of its time dormant, almost all chains will be initiated in the earliest stages of the polymerisation and still be able to participate in propagation reactions at the end. This means that the badly behaved A + B mixture discussed above will not give an ill-characterised mixture of almost homo(A) and almost homo(B), but a well-defined gradient block copolymer where each chain smoothly transitions from an A-rich block at one end to a B-rich block at the other.

It should be noted that RDRP does not prevent termination. It may well reduce it (either by reducing the concentration of reactive centres, or by reducing the proportion of short-chain polymer radicals), but it does not control radical polymerisation by getting rid of termination.

Types of RDRP

There are in principle three ways to reversibly deactivate a reactive centre. By a reversible combination reaction, a reversible abstraction reaction, or a reversible addition reaction (Figure 2). The three most common forms of RDRP – Aminoxyl-Mediated Radical Polymerisation, Atom-Transfer Radical Polymerisation, and Reversible-Addition-Fragmentation chain Transfer Polymerisation – correspond more or less to these three possibilities.

In **Aminoxyl-Mediated Radical Polymerisation** (AMRP, more commonly called Nitroxide-Mediated Polymerisation, NMP), the polymer radicals are reversibly deactivated by aminoxyls (Figure 2). These are radicals that are stable (thermodynamically unreactive: fundamentally less reactive due to delocalisation of the unpaired charge) and persistent (kinetically unreactive: reacting more slowly than other radicals). The most common aminoxyl radicals used are things like the tetramethylpiperidinoxyl radical (TEMPO), where the delocalised aminoxyl centre is sterically prevented from approaching other molecules close enough to react by the four bulky methyl groups around it – this combination of delocalisation and steric hindrance also stops these radicals from terminating by reacting with each other. In AMRP the deactivating agent and the initiator are usually provided in one compound: an alkoxyamine, where the aminoxyl radical is capped with a group that provides the initiating radical – the phenylethyl group is very commonly used (see structures in Question 2).

On heating, the relatively weak O−C bond will break, and the initiating radical will be liberated – it will add a monomer, and then be capped again, giving a species with very similar behaviour to the initial alkoxyamine.

As each initiating radical is paired with a stable radical 'hat', every polymer chain should be controlled, and the theoretical degree of polymerisation of the resulting polymer at 100% conversion can be easily calculated – it should be simply the initial concentration of monomer divided by the initial concentration of alkoxyamine.

Question 2: Which of these two alkoxyamines will have a more easily broken C−O bond?
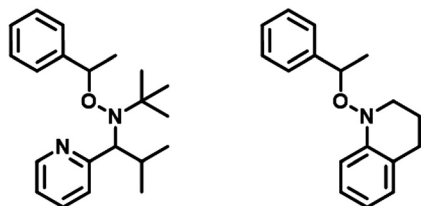
Question 3: What would the molar mass be at 100% conversion from a reaction mixture of 2 M styrene and 0.02 M alkoxyamine?

In **Atom Transfer Radical Polymerisation** (ATRP), the polymer radicals are reversibly deactivated by transfer of a halogen atom, usually bromine. Usually a bromoalkane is supplied as an initiator, together with a transition metal complex of a metal with two oxidation states relatively close together in energy (e.g. Cu(I) and Cu(II)). In the transfer process, the bromine radical is abstracted by this complex from the alkane, with the metal centre in the transition metal complex changing from its lower to its higher oxidation state. Removal of the halide generates an initiating radical, which will go on to add monomer. Because the two oxidation states are close together in energy, this process of bromine radical removal can readily go back the other way, sticking a bromine radical back on to a growing polymer chain. In exactly the same way as AMRP, the ideal polymer degree of polymerisation at 100% conversion will be given by the initial monomer concentration divided by the concentration of the initiator.

Question 4: 400 mg of ethyl-2-bromo-2-methylpropionate is used as an ATRP initiator to polymerise 25 g of butyl acrylate. What will the average molar mass of the polymer produced be at 100% conversion?

In **Reversible Addition Fragmentation chain Transfer** (RAFT)[3] the polymer radical adds to a double bond (typically a S=C bond) to form a low-reactivity radical. RDRP could in theory be based on this alone, if the new C−S single bond was labile enough for the addition to be reversible, but in RAFT the stable intermediate radical formed can fragment in two different ways: either to regenerate the initial polymer radical, or another radical which can act as an initiator of polymerisation.

Clearly, if this second reaction occurs to any significant extent, pretty soon all the stable radicals present will have a polymer radical on both sides, and the effect of the ongoing process will be to continually pass the RAFT end-group 'cap' from one polymer radical to another.

Unlike ATRP and AMRP, RAFT requires an initial source of radicals to kick the reaction off. Once this happens the transfer of the reactive centre means that most chains will be initiated by the initiating group derived from the RAFT agent and again the degree of polymerisation at 100% conversion can be easily predicted from the ratio of the amount of monomer to the amount of RDRP agent. For more details about RAFT, see the article by Moad and Moad in this issue.

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3 Yes, that is the acronym.

Question 5: The picture shows a possible RAFT agent. If a polymerisation is initiated with an azo initiator and this RAFT agent in a 1:9 M ratio, what end-group would you expect to find at the beginning of at least 90% of the macromolecules in your final polymer? What group would you expect to find at the end?
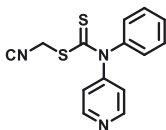
What's in a name?

Reversible Deactivation Radical Polymerisation is a beautiful name from the viewpoint of pedantic accuracy, but it does not exactly roll off the tongue. When these reactions were first discovered in the 1980s and 90s, they were given the more evocative name of 'Living Radical Polymerisation'. This is because something already existed that was called 'Living Polymerisation' – where the reactive centre did not terminate, but remained active so that the reaction could be continued just by adding more monomer at any stage. These had been known for a long time in anionic polymerisation, and had been discovered relatively recently for cationic and ring-opening metathesis polymerisation. In fact, ATRP was discovered by groups who consciously set out to find a method of radical polymerisation that would be 'living'; Mitsuo Sawamoto, who we will say more about below, had been a major player in discovering living cationic polymerisation and possibly wanted to 'complete the set'.

However, pedants soon jumped on the fact that in these reactions the reactive centre isn't really living – sure, it can 'rise from the dead', or be passed indefinitely from one chain to another, but the polymer science community was not ready to accept more accurate and vivid terms such as 'Zombie Radical Polymerisation' or 'Viral Radical Polymerisation'. As the 1990s ended, the very dull term 'Controlled Radical Polymerisation' was recommended and became general. However, as pedants again pointed out, this is an uninformative and non-specific name, as there are any number of ways in which you could 'control' radical polymerisation. For instance, a phenomenon very dear to us is that copolymerisations with a tendency towards alternation can often be induced to become very much more alternating by addition of certain Lewis Acids (Yabumoto, Ishii, & Arita, 1970). Thus, in 2010 IUPAC recommended the use of the term Reversible-Deactivation Radical Polymerisation in preference to either 'Controlled' or 'Living' radical polymerisation (Jenkins, Jones, & Moad, 2010).

Question 6: We are stuck with 'RDRP' in English, but IUPAC is a strange example of an international organisation whose only official language is English, so it has no authority in other languages. Can you think of a name for RDRP in your native language that captures the essential features of the process but is not long and boring? If you can, you should press for your local chemical society to adopt it.

History and people of RDRP

Mitsuo Sawamoto: diverse approaches to ATRP

On September 6th, 1994, Mitsuo Sawamoto and three co-authors from Kyoto University submitted to the journal 'Macromolecules' a paper with the catchy title "Polymerisation of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris- (triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-tert-butylphenoxide) Initiating System: Possibility of Living Radical Polymerisation" (Kato, Kamigaito, Sawamoto, & Higashimura, 1995). (Actually, it is probably only the bit after the ":" that is catchy). This has gone on to be cited almost 4000 times and is the first published record of ATRP.

Ruthenium of course has a reputation for being expensive and exotic, but shortly afterwards Krzysztof Matyjaszewski and Jin-Shan Wang of Carnegie-Mellon University, who had been investigating numerous strategies for achieving 'living radical polymerisation', published work on a similar system using copper rather than ruthenium (Matyjaszewski & Wang, 1995). And while in the decades since then Matyjaszewski has become one of the world's most cited scientists by applying the copper-catalysed system with haloalkanes to a breathtaking array of different monomers and polymer architectures, Sawamoto has demonstrated the breadth of ATRP possibilities (while continuing to publish prolifically in cationic polymerisation and many other areas). By 2000 Sawamoto had used nickel(0) and nickel(II), iron(II), rhenium and rhodium, as well as analogues of ATRP using pseudo-halogen initiators (e.g. dithiocarbamates; since they involve the transfer of more than one atom, we can't really call them Atom Transfer Radical Polymerisation). In 2017 Matyjaszewski and Sawamoto were jointly awarded the Benjamin Franklin Medal in chemistry, which we understand to be a pretty prestigious award, and are regularly mentioned as possible winners in the lead up to each Nobel Prize in Chemistry.

CSIRO: 2/3 of the world's insect biomass is ants, and 2/3 of RDRP was discovered in Melbourne

Aminoxyl-mediated radical polymerisation was first described in a patent in 1984 filed by the Commonwealth Science and Industry Research Organisation (CSIRO) in Australia (Solomon, Rizzardo, & Cacioli, 1986), though the method passed largely unnoticed by the wider research community until 1993. The group that discovered AMRP was established and led by David Solomon, who is most well-known for pioneering polymer banknotes (first used in Australia and now common in many countries around the world) but also has the distinction of having been booked for speeding on his bicycle. He has experience in almost every area of applied polymer chemistry and can be counted on, if you present your latest idea in this field, to direct you to a paper where he had the same idea in 1965 (Solomon & Rolfe, 1966)!

The same polymer group in CSIRO went on to discover RAFT, under the leadership of Ezio Rizzardo (Rizzardo & Solomon, 2012). This began with fundamental research – an effort to understand the minor defect structures found in radical polymerisation, such as head-to-head additions (where an incoming asymmetrical monomer adds the 'wrong way around') and the double-bonds found at the ends of chains that terminate by disproportionation. In polymerisation of methyl methacrylate, these double-bond terminated polymers are common, and Rizzardo's team wanted to know what further reactions they could undergo during polymerisation. They found that these 'macromonomers' could add to growing chains, but instead of adding more monomer, these very hindered species would more commonly fragment (a reverse addition reaction), leaving one chain with a terminal double bond and another chain with a radical capable of propagation. This chain transfer process controlled molar mass, but it was impractical having an entire polymer chain to encourage fragmentation over propagation – could it be replaced with something shorter? After a great deal of work directed at this goal, the CSIRO team found that compounds containing a thioester (−CS−S−) group were most effective. (Just like ATRP, though, RAFT was effectively discovered in two places simultaneously – scientists at the French company Rhodia discovered and patented a process using xanthates (compounds of the structure −O−CS−S−) at practically the same time as CSIRO was patenting the rest of RAFT (Chiefari, Mayadunne, Moad, Rizzardo, & Thang, 1997; Destarac, Charmot, Zard, & Gauthier, 1999).

Chris Bowman and Cyrille Boyer: bugs into features

When RAFT was first discovered, the sulfur-containing end-groups were considered to be the big negative mark against the method in comparison to the other RDRP possibilities. These make the polymers coloured,

which is not such a big deal – there are few applications where an orange or pink colour will make a polymer unfit for purpose. More importantly, these end-groups fall off relatively easy to give volatile molecules that smell unpleasant even in tiny amounts – which makes RAFT-derived polymers unfit for many other purposes. However, this bug has been transformed into a feature. If the main part of the RAFT-derived end-group is removed, what you end up with is a thiol at one end of the molecule. This can be used to assemble polymers on gold surfaces, since gold and sulfur have a strong affinity. And the thiol functional group is very reactive in adding to carbon-carbon double bonds, in what are known as 'thiol-ene' or 'thiol-Michael' reactions (Figure 3) (Moad, Rizzardo, & Thang, 2011). This means that it is very easy to functionalise RAFT derived polymers. While there are many reasons you might want to add things to the ends of polymers, the most exciting possibility this opens up is the production of well-defined polymer networks. You can produce the bits of the net to whatever well-defined size, or distribution of size, that you like, using RAFT. Then you can knit them together into a crosslinked network using these reactions between thiols and alkenes. Some of these reactions are photo-induced 'click' reactions, allowing you to form your network precursor into exactly the shape you want it to be before photocuring it. Some of these reactions are reversible photo-induced 'click' reactions, allowing you to cure your polymer network into one shape, then shine a different wavelength of light on it to make it deformable again. These thiol-ene reactions have been a tremendously productive area of research for Chris Bowman of the University of Colorado, who is also a Professor of Dentistry – these dynamic light-driven reactions are very useful if you want to do polymer chemistry in people's mouths (Huang et al., 2018).

Early RDRP systems typically relied on thermal initiators to generate radicals; however, as these systems evolved, a variety of stimuli, such as enzymes, ultrasound and light have been exploited to reduce their dependence on elevated temperature. Indeed, light has been the preferred stimulus for radical generation in RDRP systems as it offers high degrees of spatial and temporal control on polymerisation at low temperature (Dadashi-Silab, Doran, & Yagci, 2016).

Since the colour associated with RAFT agents indicates that they are interacting with light (chromophores), the growing research area of 'photoRAFT' is another example of a bug becoming a feature. Exposure of tri-thiocarbonate RAFT species to visible light results in the cleavage of the C–S bond and thereby generation of carbon-centered radicals to initiate polymerisation and induce chain transfer in a photoRAFT process (Otsu, 2000). More recently, Boyer and colleagues at the University of New South Wales showed that redox-active catalytic species can also initiate and control the activation-deactivation equilibrium of RAFT polymerisation under visible or near-infrared light (Xu, Jung, Atme, Shanmugam, & Boyer, 2014). This process, which is termed photoinduced electron or energy transfer RAFT (PET-RAFT), is based on electron/energy transfer from an excited catalyst to a RAFT agent resulting in the cleavage of the weak C–S bonds and thus generation of active radical
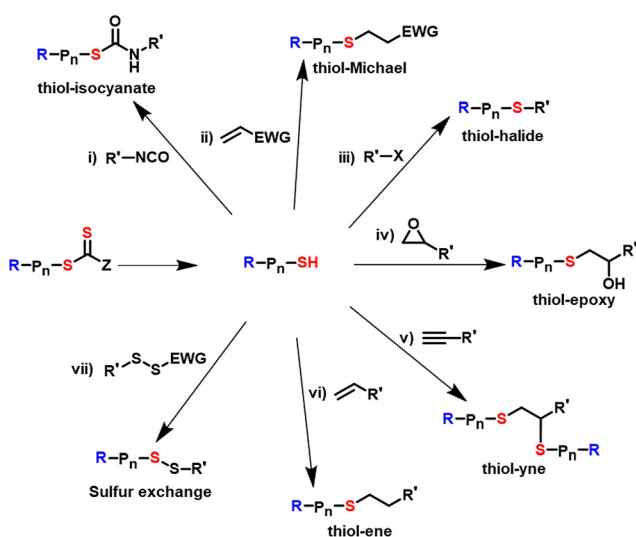
Figure 3: Chemical reactions of RAFT-derived thiol end-groups. Reactions "i" to "iv" are nucleophilic reactions, reaction "v" and "vi" are radical reactions and reaction "vii" is a sulfur exchange reaction. EWG: electron-withdrawing group.

species and a stabilised RAFT agent fragment. Light harvesting ideas in some of these polymerisation systems have been inspired by the photosynthesis process responsible for sustaining life. Similar to chlorophylls found in plants, some bacterial pigments can be also used as pigments for light harvesting and electron transfer reactions required to drive photoRAFT polymerisations (Shanmugam, Xu, & Boyer, 2016).

Likewise, systems in which photo-sensitive molecules could be used for controlling an ATRP-type polymerisation under visible light irradiation (known as photoATRP) have been developed (Fors & Hawker, 2012). These light controlled systems not only facilitated control over the activation-deactivation equilibrium of RDRP systems, but also enabled externally regulated "on and off" systems which was not achievable in conventional radical polymerisation processes.

New stuff

Polymer science is a field in which new developments have often been driven by industry, rather than academia, and it was industry that first took notice of the potential of RDRP. The first time most of the world realised RDRP existed was when an AMRP process was patented as a means of making photocopier toner particles with more controllable fixing temperatures (Georges, Veregin, Kazmaier, & Hamer, 1995) – since phase transitions of polymers are controlled by molar mass, a more controlled molar mass gives better control of these transitions. Industry is also interested in well-defined block copolymers, much more easily made by RDRP than any other process, which are ideal for stabilizing solid/solid dispersions – e.g. of a pigment in a solidified paint (Mühlebach, Auschra, & Eckstein, 1999). Other applications of block copolymers derived from RDRP have been in optoelectronics, as coatings for biomedical devices, and in drug delivery applications, while star polymers made by RAFT are used as viscosity control agents in vehicle lubricants (Moad et al., 2013).

As well as generating copolymers of controlled size, structure, and composition, RDRP is an excellent way to create low dispersity 'telechelic' polymers – that means, polymers with particular functional groups at one end. The light responsive trithiocarbonate groups can be used for light-induced RAFT-driven 3D printing of materials containing dormant RAFT functionalities (Bagheri et al., 2020). In another example, relatively low molar mass poly(acrylic acid) prepared with ATRP with hydrophobic end-groups derived from the ATRP initiator has been found to give improved performance in preventing the deposition of scale-forming minerals such as calcium carbonate (Al-Hamzah & Fellows, 2015).

Visualisations of RDRP

Drawn out in chemical formulae, the reactions of individual RDRP processes often look nothing like one another. The chemical formulae of the reagents look nothing alike and the nets of reactions involved in the overall reversible-deactivation process can fill pages with arrows and structures. Visualisations are particularly important for demonstrating what is going on in RDRP. Not only can they show the commonalities in different-looking reactions, they can make the simple concept at the heart of the process clear.

There are two different points of view that we can take in an animated visualisation. One is the point of view of an individual growing polymer molecule. We see a chain initiated – by a conventional radical initiator, by a radical derived by cleavage of a haloalkane C–X bond, or by a radical derived from an alkoxyamine – but instead of taking off and propagating like a normal radical polymerisation, we see it almost immediately shut down again. At intervals the 'cap' is removed – usually it is put back on again with nothing happening, but sometimes a monomer is added. This goes on until we run out of monomer.

Alternatively, we can follow the point of view of the capping agent. In RAFT, we will see it swapped in a giddying fashion from one growing polymer molecule to another, never coming to rest until the last radical centre is consumed. In ATRP, we will follow a metal complex – probably spending a lot of time in close association with one polymer chain, pulling its halogen on and off, then diffusing away to another polymer chain in a more leisurely fashion to do the same thing. In AMRP, we will have a similar situation, but with an

aminoxyl radical – coming off and on, and every so often diffusing away for a long wander before recombining with a different radical somewhere else. For examples of these different ways of considering an RDRP reaction, see the paper by Moad and Moad in this issue.

One thing one of us attempted to implement many years ago was an online 'virtual reactor', where anyone could log in, enter values for the type(s) of monomer, amount of initiator, temperature, etc., and sit back and watch the progress of their reaction and the characteristics of the product they are making (and probably, try to make it explode). This never ended up happening because of the many simplifications to the reaction kinetics necessary to make it practicable to code. In RDRP, nature has made the simplifications for us, so implementing a virtual reactor becomes a much simpler process. We can predict the molar mass from the amount of monomer consumed according to a very straightforward reaction. Because all the chains are approximately the same length, radical termination processes become simpler – and, usually, we can assume that the radical concentration is constant throughout the reaction, since there are limited opportunities for radical recombination. We will have composition drift within individual chains if we do a copolymerisation, but our product will have just one well-defined composition, rather than being a mixture of copolymer molecules of differing compositions. For these same reasons, RDRP is more suitable than conventional radical polymerisation for undergraduate laboratory experiments in polymer chemistry. Laboratory exercises in AMRP (Tillman, Contrella, & Leasure, 2009), ATRP (Koshut, Arnold, Smith, Wright, & Sydlik, 2019; Matyjaszewski, Beers, Metzner, & Woodworth, 2001; Tsarevsky, Woodruff, & Wisian-Neilson, 2016), and RAFT (Nguyen, Bennet, Stenzel, & Barner-Kowollik, 2008) have been published and are used in many undergraduate chemistry courses, including that at the University of New England.

It's difficult to make predictions, especially about the future

There is an apocryphal quote, commonly attributed to Lord Kelvin, saying in 1900 that all the interesting things in physics had already been discovered and that it was just a matter of measuring constants to more and more decimal points. Although according to the good folks at Wikipedia he never actually said anything like this, something eerily similar was said about radical polymerisation about 50 years ago.

In 1972, the renowned polymer chemist Frank Mayo wrote a brief editorial in the Journal of Chemical Technology, reviewing the advances made in radical polymerisation during the preceding quarter century (Mayo, 1972). Among other things, he exhorted graduates to avoid the field of radical polymerisation if they wanted to work on the cutting edge of polymer science. He wrote:

> "I foresee no developments or problems whose solutions will have a substantial impact on general theory or industrial practice."

We are fortunate that Mitsuo Sawamoto and many others did not take this well-intentioned advice! RDRP has had an exhilarating (and substantial) impact on the general theory of radical polymerisation and is beginning to have an impact on industrial practice. We suggest that RDRP has also been a development with important implications for the teaching of chemistry, as a conceptually simpler introduction to Radical Polymerisation, and as a fascinating example of rapid change in a field where experts could once confidently assert that we already knew everything important.

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[1: You should get M_w = 4285, M_n = 3500, $Đ_M$ = 1.22.]

[2: The one on the left. The one on the right has less steric hindrance and has a phenyl group (electron-donating) directly attached to the N–O bond]

[3: Approximately 100 times the molar mass of styrene, so 10 400 g, plus whatever the mass of the alkoxyamine is. Taking the significant figures given in the question, we should say 1×10^4 g]

[4: The molar mass of the initiator is about 195 g mol^{-1} and that of butyl acrylate about 126 g mol^{-1}, so the molar ratio of butyl acrylate to initiator is 97 – which should also be the degree of polymerisation at full conversion, giving a total molar mass of 1.2×10^4 g mol^{-1}]

[5: At least 90% of the chains should be initiated with the CN–CH$_2$ group on the left of the RAFT agent pictured, and a similar fraction should have the rest of the RAFT group (–S–CS–N(Py)$_2$) attached to the other end.]