

# Metathesis Catalysed by the Platinum Group Metals

A NEW STRATEGY FOR THE SYNTHESIS OF ORGANIC COMPOUNDS AND POLYMERS  
PART III: ACYCLIC DIENE METATHESIS REACTIONS AND RING-OPENING METATHESIS POLYMERISATIONS

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*The first two parts of this paper appeared in the April and July issues of this Journal. Part I looked at types of platinum group metals catalysts and metathesis activity and selectivity. Part II examined specific syntheses catalysed by these catalysts, in particular, reactions catalysed by ruthenium carbenes. This resulted in the syntheses of various carbocycles, heterocycles, metallacycles, crown ethers, polycyclic polymers, natural compounds and sub-units of biologically active compounds. The concluding part of this review deals first with acyclic diene metathesis and then with ring-opening metathesis polymerisations, and ranges of products formed by these reactions are given.*

Following on from Part II of this review in which platinum group metals catalysts taking part in ring-closed metathesis reactions were considered, Part III looks at this group of catalysts as they are used for acyclic diene metathesis reactions and for ring-opening metathesis polymerisations.

## Acyclic Diene Metathesis Reactions

The acyclic diene metathesis (ADMET) reaction of divinylsilanes and divinylsiloxanes was performed in the presence of homogeneous ruthenium- and rhodium-containing systems in combination with cocatalysts of the HSi-type, see Equation (xxxix), (62).

The application of ruthenium hydride complexes, in particular  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ , as catalysts in

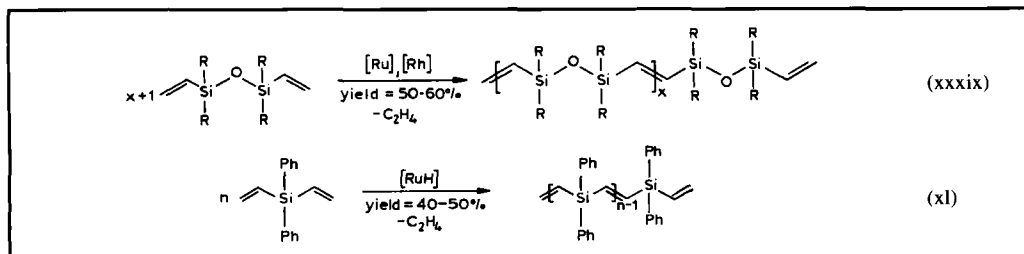
the ADMET reaction of vinylsilanes turned out to be particularly effective, see Equation (xl) below, (63).

## Ring-Opening Metathesis Polymerisation

Ring-opening metathesis polymerisations (ROMPs) have great industrial significance. The use of metathesis platinum group metals catalysts in polymer synthesis by ROMP has become a ubiquitous catalytic process in polymer chemistry.

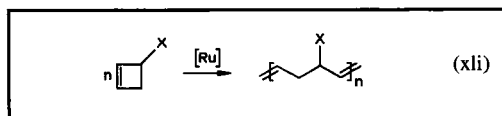
### ROMP of Functionalised Cycloolefins

Since their early application in ROMP of norbornene and its derivatives (10), salts and complexes of ruthenium, iridium and osmium,



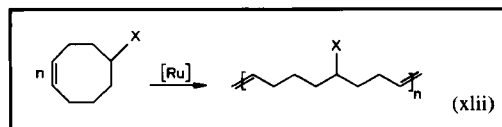
because of their tolerance toward functional groups, have been widely employed in metathesis polymerisation of a variety of functionalised cycloolefins. Solvents used have been various mixtures of water, ethanol and halogenated organic solvents (1(a), 1(b)).

A first example of ROMP is the living ring-opening polymerisation of 3-substituted cyclobutenes bearing a wide range of various functional groups, under the influence of catalysts such as  $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ , **1a**, or  $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PCy}_3)_2$ , ( $\text{Cy} = \text{cyclohexyl}$ ), leading to functionalised polybutenamers, see Equation (xli), (64),



where  $\text{X} = \text{OCH}_2\text{Ph}$ ,  $\text{OCPh}_3$ ,  $\text{OC}(\text{O})\text{Ph}$ ,  $\text{OH}$ ,  $\text{N}(\textit{i}\text{-Pr})_2$ ,  $\text{OCH}_2\text{COOMe}$ ,  $(\text{CH}_2)_3\text{COOH}$ ,  $(\text{CH}_2)_4\text{OH}$ ,  $(\text{CH}_2)_3\text{CONHBU}$  or  $(\text{CH}_2)_3\text{COOMe}$ . Depending on the nature of the substituent, the polymer yields varied between 87 and 97 per cent. Thus, a new class of functionalised polybutadienes that are difficult to prepare by conventional methods have been synthesised by this route.

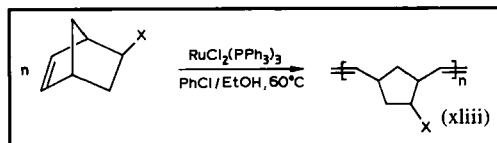
Among the ruthenium carbene complexes, of general formula  $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PR}_3)_2$ , the one bearing tris(cyclohexyl)phosphine ligands ( $\text{R} = \text{Cy}$ ), has proved to be the most active and able to polymerise less strained olefins such as cyclooctene and derivatives, see Equation (xlii),



(65), where  $\text{X} = \text{OH}$ ,  $\text{Ac}$ ,  $\text{Br}$  or  $\text{OCOCH}_3$ . A family of ternary copolymers of butadiene, ethylene and vinyl derivatives was manufactured by this method.

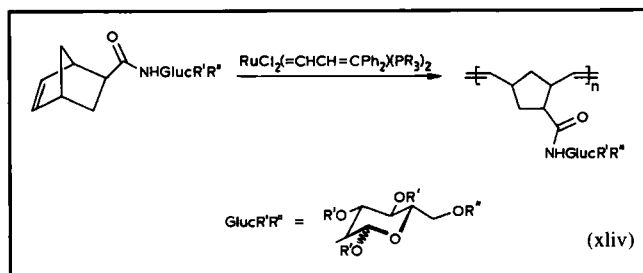
Of great interest is the synthesis of polynorbornene substituted with silicon-containing groups, using ruthenium complexes as the cata-

lysts. For instance, 5-(trimethylsiloxy)norborn-2-ene, 5-(triethylsiloxy)norborn-2-ene and 5-(trimethylsiloxy)methylnorborn-2-ene readily give silicon-containing polymers in the presence of  $\text{RuCl}_2(\text{PPh}_3)_3$  catalyst with chlorobenzene/ethanol as solvent, see Equation (xliii), where  $\text{X} = \text{Si}(\text{OR})_3$



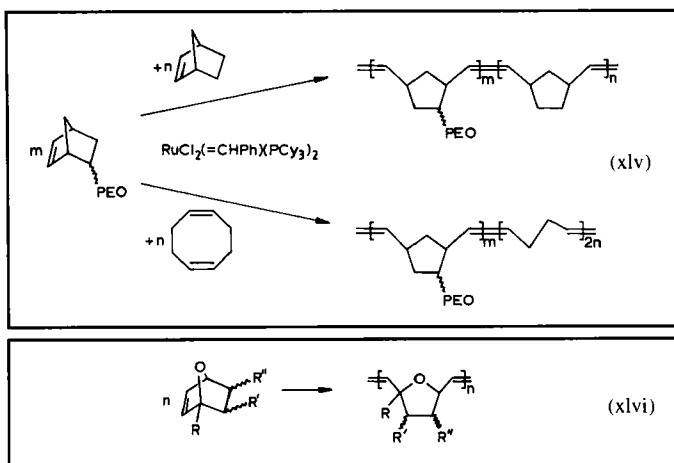
or  $\text{CH}_2\text{OSiMe}_3$ . Functionalised oligomers and polymers prepared according to this procedure are useful as components of gas separation membranes, materials with valuable electrophysical properties, adhesives, precursors of ceramics and thermosetting products.

A new class of glycopolymers was prepared, in a controlled manner, by the living ring-opening polymerisation of sugar-substituted norbornenes using  $\text{RuCl}_2(=\text{CHCH}=\text{CPh}_2)(\text{PR}_3)_2$  ( $\text{R} = \text{phenyl}$  or  $\text{Cy}$ ) as the catalyst, see Equation (xliv), where  $\text{R}'$ ,



$\text{R}'' = \text{H}$ ,  $\text{COCH}_3$ ,  $\text{CH}_2\text{Ph}$ ,  $\text{SiEt}_3$  or  $\text{R}' = \text{H}$  and  $\text{R}'' = \text{CPh}_3$ , (66). This type of glycopolymer finds interesting applications in the modulation of cell adhesion, immobilisation of particular cell types and the study of multivalency in extracellular interactions.

With the recent development of a new generation of carbene metal complexes that are more tolerant to protic solvents and water, living ROMP of cyclic olefins can now be carried out in these media under rigorously-controlled conditions (67). Latex particles based on polynorbornene and polybutadiene were thus obtained by ROMP of norbornene and 1,5-cyclooctadiene in a mixture of



dichloromethane/ethanol, using  $\alpha$ -norbornenyl-PEO ((poly(ethylene oxide), a water-soluble resin) macromonomer as a stabiliser and the ruthenium benzylidene complex,  $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ , **1a**, as initiator, see Equation (xlv).

This was the first time that such a polymerisable surfactant was used to obtain latex particles by dispersion ROMP of cycloolefins. These PEO-based macromonomers function both as co-monomers of cycloolefins in the ROMP process and as stabilisers of the formed polyalkenamers. The presence of the norbornenyl group at one end of the chain helps these novel surfiners (surfactant monomers) to anchor chemically onto solid supporting particles, while their hydrophilic part serves as a steric barrier.

### ROMP of Heterocyclic Olefins

Because of their tolerance toward heteroatoms, it became possible for numerous catalysts containing platinum group metals to be employed in the ring-opening polymerisation of heterocyclic monomers. The first successful ROMP of a series of monomers based on 7-oxanorbornene was

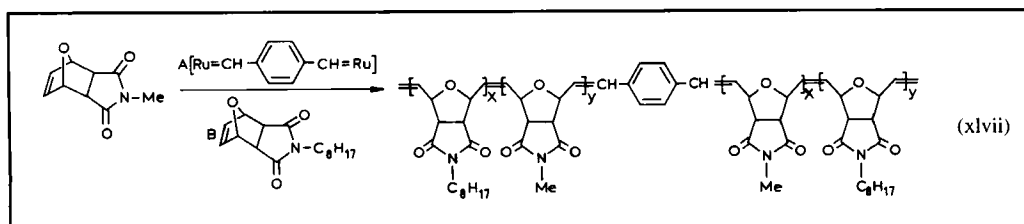
reported by Novak and Grubbs (9) using  $\text{RuCl}_3$ ,  $[\text{RuCl}_3(1,5\text{-COD})]$  and  $\text{OsCl}_3$  (1,5-COD = 1,5-cyclooctadiene), see Equation (xlvi), where  $\text{R} = \text{H}$ ;  $\text{R}' = \text{H}, \text{CH}_2\text{OH}, \text{CH}_2\text{OCH}_3$  or  $\text{CH}_2\text{OTMS}$ ;  $\text{R}'' = \text{CH}_3, \text{CH}_2\text{OH}, \text{CH}_2\text{OCH}_3$  or  $\text{CH}_2\text{OTMS}$ . The poly(7-oxanorbornenes) resulting from the selective metathesis polymerisation of the 7-oxanorbornene monomers are of keen interest for their potential ionophoric properties.

In addition to binding ions in solution, these polymers act as ion permeable membranes.

This reaction has been successfully applied to a large number of heterocyclic monomers using various ruthenium complexes (21, 68–70). As a result of these developments, the direct synthesis of ABA triblock copolymers of different 7-oxanorbornene derivatives has been efficiently performed by living ROMP using the well-defined, bimetallic ruthenium catalyst, of general formula,  $\text{RuCl}_2(\text{PR}_3)_2(=\text{CHC}_6\text{H}_4\text{CH}=\text{RuCl}_2(\text{PR}_3)_2)$ , **5**. Starting for instance from *N*-methyl-7-oxanorbornene-2,3-dicarboxylic imide and the bimetallic ruthenium catalyst, **5**, a homopolymer is first obtained. Then by adding *N*-octyl-7-oxanorbornene-2,3-dicarboxylic imide the ABA triblock copolymer is readily formed, see Equation (xlvi) below, (26). Such copolymers have low polydispersities and a controlled molecular weight.

### ROMP in Water

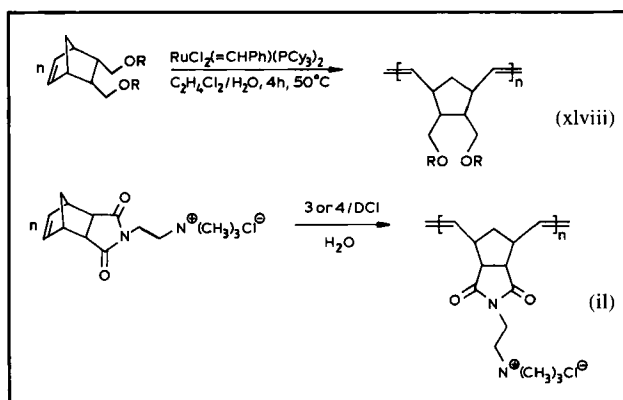
Nowadays, there is extensive documentation for the ROMP of strained, cyclic olefins in aqueous media, initiated by platinum group metals salts



and coordination complexes, particularly by those of ruthenium (23(a), 71–73). We mention here the living ROMP of hydrophobic monomers derived from 5,6-disubstituted norbornenes under the action of  $\text{RuCl}_2(=\text{CHPh})(\text{PCy}_3)_2$ , 1a, in the presence of water, see Equation (xlviii), (74), where  $\text{R} = \text{OMe}$  or  $\text{OSi}(\text{t-Bu})(\text{Me})_2$ . The reaction in the presence of an emulsifier yielded latexes of nearly monodisperse products which are ideal for the preparation of tacky polymers. Although these complexes served as robust metathesis polymerisation catalysts in water, polymerisations were not always living and inefficient initiation steps produced erratic results (typically less than 1 per cent of the metal centres were converted to catalytically active species).

However, true living ring-opening polymerisation of functionalised cycloolefins in water has been achieved with ruthenium complexes 3 and 4 (see Part I) (75) in the presence of a Brønsted acid. Thus, an *N*-substituted norbornene-2,3-dicarboxylic imide has been quickly and quantitatively polymerised with catalysts 3 or 4 and DCl (1 equivalent relative to alkylidene) in the absence of surfactant or organic solvents, see Equation (ii), (25).

Water soluble polymers and block copolymers with low polydispersities and controlled molecular weight have been prepared by this technique (25). For instance, block copolymers of *N*-substituted ammonium salts of 7-oxanorbornene-2,3-dicarboxylic imide and *N*-substituted ammonium salts



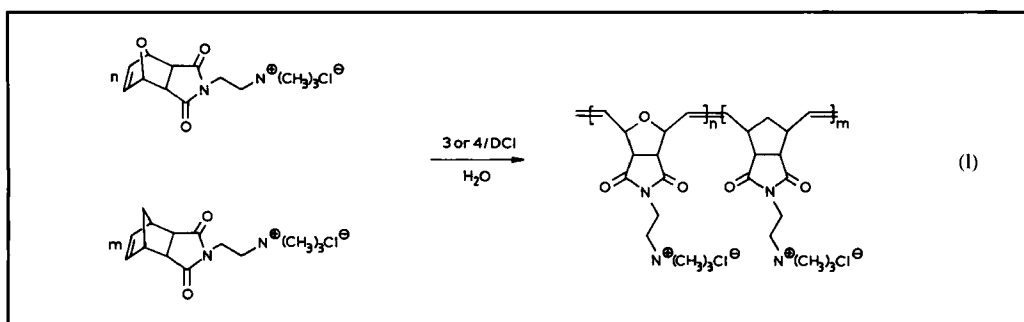
of norbornene-2,3-dicarboxylic imide have been prepared quantitatively with soluble ruthenium alkylidenes 3 and 4, see Equation (i).

It is noteworthy that polymerisations are not “living” in the absence of acid. The role of the acid in these systems appeared to be two-fold: first to eliminate the traces of hydroxide ions which could cause catalyst decomposition and second to enhance the catalyst activity and stability by protonation of one of the phosphine ligands.

In fact, the most efficient ROMP catalyst described so far (combining activity comparable to the molybdenum-based catalysts and stability like other ruthenium-based catalysts) appears to be 1a, but with one of the phosphine ligands being replaced by an electron-donating imidazoline carbene ligand having two *N*-mesityl groups (76).

## Concluding Remarks

Metathesis catalysts based on platinum group metals exhibit numerous advantages over their classical heterogeneous and homogeneous counterparts. Essentially these catalysts:



- (a) extend the metathesis reaction in polar and protic solvents including alcohols and even water or much more acidic environments (for example, phenols or strong acids such as trichloroacetic acid)
- (b) tolerate well many heteroatom-containing (for example, O, N, P, Cl, Br) functional groups, hence a wide profile of substrates
- (c) allow working under normal temperature and pressure, in common solvents, without special purification and
- (d) can be conveniently stored in air without substantial decomposition – even for weeks.

Recently a new generation of catalysts, derived mainly from Grubbs' ruthenium carbenes, has been designed and applied successfully in the metathesis of functionalised olefins and cycloolefins, in ring-closing and ring-opening metathesis and in living metathesis polymerisation of functionalised cycloolefins and heterocycloolefins. Particular attention is presently being devoted to creating attractive methods for the synthesis of new heterocycles, natural compounds with biological activity and sub-units of biologically-interesting organic compounds having complex architecture.

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### Silphenylenesiloxane Polymers

Polysiloxanes are polymers with an alternating chain of silicon and oxygen atoms. Polysiloxanes have a range of very valuable properties which are utilised commercially: inertness, resistances to water and oxidation, and high thermal stabilities. However, little work has been done to develop dehydrocoupling polymerisation to give polysiloxanes. A team of scientists at the University of Cincinnati have now developed a general method of dehydrocoupling polymerisation to give alternating copolymers of silphenylenesiloxanes from bis-silanes and disilanol, under mild conditions, using Wilkinson's catalyst,  $\text{RhCl}(\text{Ph}_3\text{P})_3$ , (R. Zhang, J. E. Mark and A. R. Pinhas, *Macromolecules*, 2000, 33, (10), 3508–3510).

Silphenylenesilane polymers with controllable microstructures and average molecular weight of  $10,100 \text{ g mol}^{-1}$  were produced. The best polymerisation occurred between *p*-bis(dimethylsilyl)benzene and *p*-bis(dimethylhydroxysilyl)benzene. Among other alternating copolymers produced were poly-(tetramethyl-*p*-silphenylenesiloxane) (poly-TMPS) and a combination of tetramethyl-*m*-silphenylenesiloxane and TMPS. The rhodium catalyst was very efficient and robust under the reaction conditions.