Alternating ring-opening metathesis copolymerization of bicyclo[2.2.1]hept-2-ene and cyclopentene

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Almost alternating copolymers of bicyclo[2.2.1]hept-2-ene and cyclopentene have been formed by ring-opening metathesis polymerization using a $RuCl_3$–phenol catalyst system; this highly novel result is attributed to differential steric influences exerted by a hydrogen-bonded solvent cage which encloses the catalyst site.

Copolymerization is an aspect of polymer chemistry that continues to attract widespread interest, not only because it affords the opportunity to prepare and study polymers with a wide variety of main chain architectures but also because of the mechanistic insights which may be gained from a detailed analysis of the microstructure of such materials.[1,2]

The primary microstructural variant in copolymers of a given comonomer composition is the distribution of the different monomer units in the chain and this variable depends to a large extent on the choice of monomer pairs. For example, in the field of coordination polymerization, monomers of similar polarity generally give rise to statistical copolymers, although block copolymers may be obtained by the sequential addition of a variety of monomers to living catalyst systems. Alternating distributions may be obtained either by copolymerization of monomers of dissimilar polarity; for example, the Ziegler–Natta copolymerization of CO[3] or styrene[4] with ethylene, or they may result from regiospecific ring-opening metathesis polymerization (ROMP)[5] or acyclic diene metathesis (ADMET)[6] homopolymerizations. Alternating copolymerization of olefinic monomers which have the same olefinic double bond polarity is extremely rare.[7–9]

We now report the alternating ring-opening metathesis copolymerization of cyclopentene and norbornene, two non-polar monomers, using a simple $RuCl_3$-based catalyst system.

Although readily available and remarkably tolerant of a wide range of monomer functionality, classical Ru-based ROMP initiators are rather sluggish, so a number of studies have been directed towards increasing the activity whilst retaining the robust properties of this class of catalyst.[10–12] The working catalytic species in metathesis polymerization is a metallacarbene[13] and a strategy we have employed is to increase the polarity of the Ru=C π-bond, and hence its activity, by providing harder acidic ligands at the Ru centre. A measure of success has been achieved using isolated complexes such as Ru(trifluoroacetate),[14] or $RuCl_3$ in the presence of acidic diol solvents, such as dimethyl tartrate,[15] and in these cases an enhanced catalyst activity, judged by the increased incorporation of the relatively unreactive cyclopentene in cyclopentene (CPE)–bicyclo[2,2,1]hept-2-ene (norbornene, NBE) copolymerizations, was noted. In continuation of these studies we have been examining the role of phenolic solvents both as reaction media and as potential ligands and we have found, not only a greatly enhanced catalyst activity, but remarkably, a highly alternating distribution of CPE and NBE units which is maintained throughout a range of yields (~2% to ~20%).† It is also significant that the final concentration of CPE in these copolymerizations, even at higher yields, exceeds its equilibrium monomer concentration.[7]

The alternating nature of these copolymers is unambiguously shown by the olefinic region of their rather simple ^{13}C NMR spectra, Fig. 1(*a*). Here the predominant signals at 128.2 and 135.13 ppm arise from isolated cyclopentene $M_2\mathbf{M}_1M_2$ (CPE = M_1) and norbornene $M_1\mathbf{M}_2M_1$ (NBE = M_2) units respectively,‡ the low intensity signals arising from homopolymer sequences, $M_1M_1M_1$ and $M_2M_2M_2$.[16] Fine structure is attributed to the effects of double bond isomerism and it is noteworthy that the *cis* double bond content (~30%) is higher than for less reactive Ru-based catalysts.[16]

The formation of such a copolymer requires that propagation occurs at a novel catalyst site and although its structure is at this stage a matter of some speculation we believe it to be based on

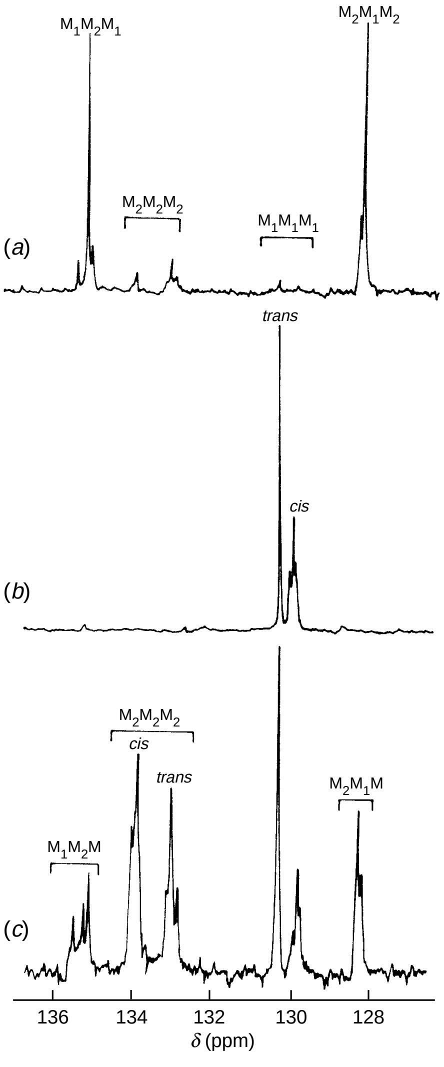

Fig. 1 The olefinic regions of the 125 MHz ^{13}C NMR spectra (in $CDCl_3$ with Me_4Si internal standard) of polymers prepared from NBE (M_2) and CPE (M_1) at a molar feed ratio of 1 : 8; (*a*) a highly alternating copolymer prepared using the $RuCl_3$–dry phenol catalyst, (*b*) a CPE homopolymer prepared using a $OsCl_3$–dry phenol catalyst and (*c*) a random copolymer prepared using the $OsCl_3$ catalyst in a 100 : 1 phenol–water solvent

$$\begin{array}{lll} \mathbf{P_C} + \mathrm{CPE} \xrightarrow{k_{\mathrm{CC}}} \mathbf{P_C} & & \mathbf{P_N} + \mathrm{CPE} \xrightarrow{k_{\mathrm{NC}}} \mathbf{P_C} \\ & k_{\mathrm{CN}} >> k_{\mathrm{CC}} & \qquad\qquad\qquad\qquad k_{\mathrm{NC}} >> k_{\mathrm{NN}} \\ \mathbf{P_C} + \mathrm{NBE} \xrightarrow{k_{\mathrm{CN}}} \mathbf{P_N} & & \mathbf{P_N} + \mathrm{NBE} \xrightarrow{k_{\mathrm{NN}}} \mathbf{P_N} \end{array}$$

Scheme 1

a Ru-carbene complex bearing η^1-coordinated phenoxide ligands, formed *in situ* by the action of excess phenol on $RuCl_3$. Phenol (solvent) molecules are then associated with this complex through the medium of hydrogen bonding, in a manner analogous to that described recently for other Ru–phenoxy complexes,[17] forming, in effect, a cage around the catalyst site such that the differential steric effects of cyclopentylene and pentylene chain ends are greatly emphasised with respect to access of incoming monomer, NBE and CPE respectively.

The process is therefore governed primarily by the steric demands of the chain end coupled with the different steric and electronic properties of the approaching monomers and it is envisaged that propagation involves different forms of the metallacarbene, $\mathbf{P_N}$ and $\mathbf{P_C}$, (**N** = cyclopentylene, **C** = pentylene). Thus, with $\mathbf{P_N}$, the bulky norbornene is denied access to the site and the much less bulky cyclopentene has then the opportunity to react, leading to $\mathbf{P_C}$. The less sterically constrained $\mathbf{P_C}$ is now relatively accessible to both monomers but reacts preferentially with norbornene due to its electronically much more reactive double bond, and thus a $\mathbf{P_N}$ site is generated. This sequence of events may be described by the above kinetic scheme, Scheme 1, where the apparent reactivity ratios, $r_1 = k_{\mathrm{CC}}/k_{\mathrm{CN}}$, and $r_2 = k_{\mathrm{NN}}/k_{\mathrm{NC}}$, estimated from the spectra of the copolymers, are numerically very small, as demanded by an alternating mechanism.

We have accumulated several pieces of experimental evidence which support the existence of the proposed catalyst site and propagation mechanism. For example, the other noble metal-based metathesis catalysts, $IrCl_3$ and $OsCl_3$, behave in an analogous manner when used in phenolic solvents with the same monomer feed. $IrCl_3$, gives a somewhat less alternating product than $RuCl_3$ but significantly $OsCl_3$, Fig. 1(*b*), yields essentially a CPE homopolymer. This seemingly inconsistent result may however still be explained by the above mechanism if it is assumed that the hydrogen-bonded cage is now very tightly arranged around the Os-centred catalyst site, primarily as a consequence of the stronger ligand field exerted by the third row metal ion,[14] and that NBE is therefore denied access (Scheme 1, $k_{\mathrm{CN}} = k_{\mathrm{NN}} = 0$).

As expected, copolymers become less alternating as the solvent system is changed progressively from pure phenol to non-hydrogen bonded solvents such as chlorobenzene, but the essentially hydrogen-bonded nature of the cage is best illustrated by the effect of the addition of small quantities of water (1.0 wt% phenol) to the catalyst. Now with each metal a random copolymer is formed, illustrated here by reference to the $OsCl_3$, Fig. 1(*b*) and (*c*); we believe that random copolymer is formed as a result of propagation at a much less crowded site at which the hydrogen-bonding water has profoundly altered the nature of the solvent cage so that both monomers have now equal access. The high level of incorporation of CPE in these random copolymers however indicates that although water may have disrupted the solvent cage, a very active Mt(phenoxide) complex is still the propagating species.

Finally, we have noted that the *cis* double bond content of the polymer is essentially the same whether or not water is present in the system, and typically, in both $OsCl_3$ cases, Fig. 1(*b*) and (*c*), M_1M_1 units are 35% *cis*. We believe that this indicates that the solvent cage, which is not directly bonded to the metal, exerts a second order effect, merely helping to control monomer access but does not control the orientation of the intermediate metallacycle and hence the stereochemistry of the [2 + 2] cycloaddition step,[13] a first order effect. We have previously emphasised that these latter effects, *e.g.* a dramatic increase in the *cis* content of the polymer, may be caused by steric crowding due to various bulky spectator ligands directly bonded to the metal.[2] Examples are the addition of esters to WCl_6 and $MoCl_5$-based systems and various dienes and acetylenes to noble metal catalysts and can be used to modify catalyst systems and produce high *cis* content polymers.[2]

Footnotes and References

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† Catalyst systems were prepared by dissolving commercial samples of $RuCl_3\cdot xH_2O$, $OsCl_3$ or $IrCl_3\cdot 3H_2O$ (8 mg) in phenol (2 ml) distilled from P_2O_5. A mixture of cyclopentene (1.7, 24 mmol) and norbornene (0.3, 3 mmol), both dried by distillation from CaH_2, was then added and the reaction mixture kept at room temperature overnight. Polymer was recovered by dissolving the gel in chloroform followed by precipitation in methanol and vacuum drying to yield typically 240 mg copolymer, M_w 1.3 × 10^6 (polystyrene standards). When other phenolic solvents such as *p*-chloro- and *p*-fluoro-phenol, as well as trifluoroethanol are used in the same manner, alternating copolymers are also produced.

‡ Taking into account variations due to *cis* and *trans* double bonds there are eight possible, closely positioned and partially overlapping, heterotriad resonances for the olefinic carbon atoms centred on M_2 units: $M_1t\mathbf{M_2}tM_1$, $M_1c\mathbf{M_2}tM_1$, $M_1t\mathbf{M_2}cM_1$, $M_1c\mathbf{M_2}cM_1$ and $M_2t\mathbf{M_2}tM_1$, $M_2c\mathbf{M_2}tM_1$, $M_2t\mathbf{M_2}cM_1$, $M_2c\mathbf{M_2}cM_1$. We have previously identified most of these[2] and are now confident that the three peaks labelled as $M_1M_2M_1$ in Fig. 1(*a*) are the first three of these with the central peak, $M_1tM_2tM_1$, the most abundant as expected from the higher *trans* content of the largely alternating copolymer. The corresponding resonances for the heterotriads centred around M_1 are less well resolved, but those labelled $M_2M_1M_2$ in Fig. 1(*a*) also agree with previous assignments as being M_2tM_1M (major peak) and M_2cM_1M (minor peak) (M is either M_1 or M_2).

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