Ring-opening copolymerization of cyclohexene and cycloheptene with cyclopentene

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(Received 20 July 1979)

Attempts to polymerize cyclohexene by ring-opening have met with repeated failure[1,5], although other cycloalkenes readily undergo this type of polymerization in the presence of olefin metathesis catalysts. The reason for this failure is that the cyclohexene ring is relatively unstrained so that its free energy of polymerization ΔG is likely to be positive under all readily accessible experimental conditions.

There are, however, indications that ΔG at room temperature, though positive, may be relatively small. Thus (a) traces of telomers and oligomers have been detected in the cross-metathesis of cyclohexene with ethane[6] and pent-2-ene[7]; (b) self-metathesis of octa-1,7-diene and its cross-metathesis with cyclopentene have recently been observed to give products containing $CH_2{=}CH(CH_2)_4CH{=}CH-$ end-groups[8], and (c) the ring-opening polymerization of *cis, trans*-cyclodeca-1,5-diene gives a polymer which only slowly yields cyclohexene[9].

Many monomers which cannot homopolymerize because $\Delta G > 0$ can sometimes copolymerize with other monomers[10]. We have now shown that this is the case for cyclohexene (M_2). Its ring-opening copolymerization with cyclopentene (M_1) can be achieved at room temperature with feed ratios M_2/M_1 between 1.4 and 5.8, and using $WCl_6/EtAlCl_2(1/13)$ as catalyst system. The catalyst/cocatalyst ratio is crucial; with an Al/W ratio of 4, only homopolymer of M_1 is formed.

Proof of the occurrence of copolymerization comes from a comparison of the ^{13}C n.m.r. spectrum of the product (*Figure 1*) with the spectrum of the copolymer of cycloheptane (M_3) with cyclopentene (*Figure 2*) made with the same catalyst system, and with the spectra of the homopolymers of M_3 and M_1 respectively[11,12].

In the upfield (CH_2) region of *Figure 2* there are four groups of peaks corresponding to α(*trans*), β, γ and α(*cis*) carbons. There is some fine structure resulting from sensitivity of the chemical shift to the two nearest double bond structures; and *trans* double bonds (72%) dominate over *cis* (28%). Practically all the upfield peaks are in the same position as those observed for the homopolymers[11]. It is especially to be noted that α-carbons in M_3 units occur downfield from α-carbons in M_1 units, both for *cis* and *trans* double bonds. The resonances for β-carbons in M_1 and M_3 units are not resolved from each other, but there is a small additional peak at 29.17 ppm which cannot be definitely assigned.

In the olefinic region of *Figure 2* there are five equally spaced peaks. The second (130.32 ppm) and fourth (129.81 ppm) of these correspond to the *trans* and *cis* peaks, respectively, in *both* homopolymers. The other three (130.54, 130.06, 129.59 ppm) must therefore be assigned to the two olefinic carbons in M_1M_3 dyads. The sum of the intensities of the two outside peaks equals that of the centre peak. It is therefore reasonable to suppose that one of the M_1M_3 olefinic carbons gives peaks at 130.54 and 130.06 ppm (*trans* and *cis*, respectively) while the other gives peaks at 130.06 and 129.59 ppm (*trans* and *cis*, respectively). This corresponds to shifts of 0.24 ± 0.02 ppm downfield and upfield, respectively, from the lines for the homopolymers. The overall intensity pattern corresponds to 56% M_1 units and 44% M_3 units distributed at random.

Figure 1 may be seen to bear certain resemblances to *Figure 2*. The peaks which are additional to those for the homopolymer of M_1 are marked with an open circle and ascribed to M_1M_2 dyads since M_2M_2 dyads are unlikely to be present. In the CH_2 region there are two additional downfield resonances for both α(*trans*) carbons (32.80 and 32.54 ppm) and α(*cis*) carbons (27.45 and 27.14 ppm). The intensities are such that each pair of peaks may be ascribed to the α-carbons on either side of the double bond in an M_1M_2 dyad. The fact that the shift for the M_1 α-carbon is affected in the M_1M_2 dyad but not in the M_1M_3 dyad is somewhat surprising but presumably arises from the

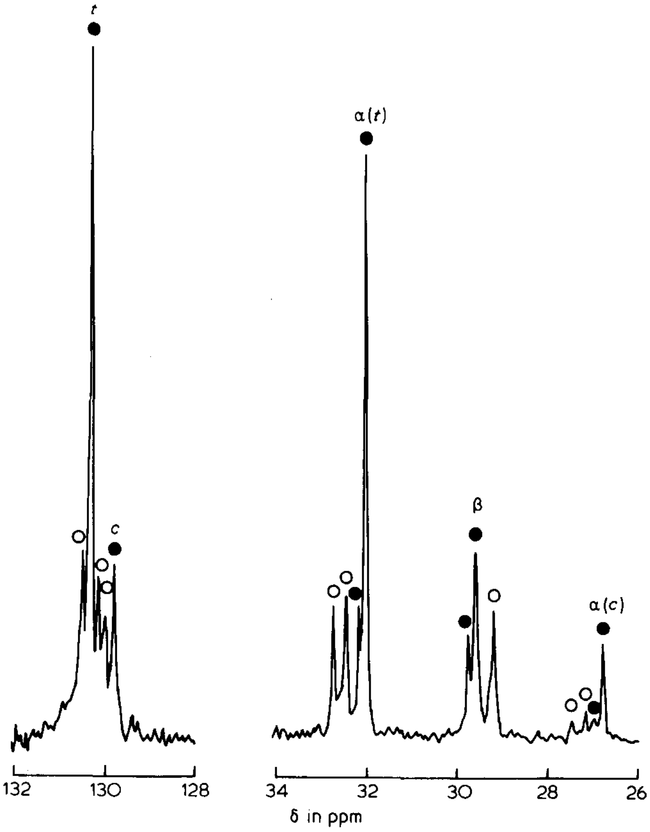

Figure 1 $^{13}C-\{^1H\}$ n.m.r. spectrum of copolymer prepared from 34 mmol cyclopentene (M_1), 99 mmol cyclohexene (M_2), 40 mg WCl_6/2.3 cm^3 chlorobenzene, 0.66 cm^3 25% $EtAlCl_2$/toluene (Al/W = 13), under N_2 at room temperature. Reaction mixture became viscous indicating formation of high polymer. Reaction terminated with ethanol. Reaction time, 1170 min; yield, 9 wt %. N.m.r. solvent, $CDCl_3$. Assignments: ●, M_1M_1; ○, M_1M_2. All peak positions are relative to TMS

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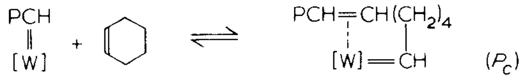
0032–3861/79/111308–02$02.00

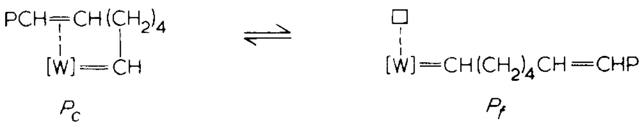
particular conformation of the M_2 unit. This may also explain the position of the β-carbon peak in M_2 units (29.21 ppm) compared with that in M_1 and M_3 units (main peak at 29.60 ppm). The intensity of the β-carbon peak in M_2 corresponds, as it should, to the sum of two of the α-carbon peaks (one *cis* and one *trans*).

The olefinic peaks in *Figure 1* presents a slightly different pattern to those in *Figure 2*. Again there are three peaks to be ascribed to M_1M_2 dyads (130.54, 130.19, 130.02 ppm), but whereas in *Figure 2* the central peak was interpreted as having two components, in *Figure 1* it appears that one of the M_1M_2 peaks is masked by one of the M_1M_1 peaks.

Figure 1 thus provides convincing evidence for the incorporation of ring-opened cyclohexene units in the polymer chain. The maximum proportion of M_2 units so far introduced is about 25%. The fact that this proportion depends markedly on the $WCl_6/EtAlCl_2$ ratio may be interpreted as follows. Addition of cyclohexene to the active metallocarbene will result initially in an internally coordinated species P_c. The reverse process by which cyclohexene is lost will be



delayed if, for a time, P_c is converted to the 'free' species P_f:



(□ denotes vacant position)

The equilibrium constant, $K = [P_f]/[P_c]$, will be governed by the strength of the coordinative bond between W and olefin which in turn is a function of the electron density in the W orbitals, especially the $d\pi$-orbitals. An increase in $EtAlCl_2/WCl_6$ may be expected to cause conversion of some of the soft ligands Cl^- on the W ions into hard ligands, such as $AlCl_4^-$, leading to a reduction in electron density at the W centre, and hence a reduced $d\pi \rightarrow p\pi^*$ back-bonding component in the W–olefin bond, and an increase in K. There is then a better chance for P_f to coordinate and add a molecule of cyclopentene, so locking in the M_2 unit already added. This explanation of the consequence of an increase in $EtAlCl_2/WCl_6$ accords with the view that the carbene carbon atom is electrophilic in character.

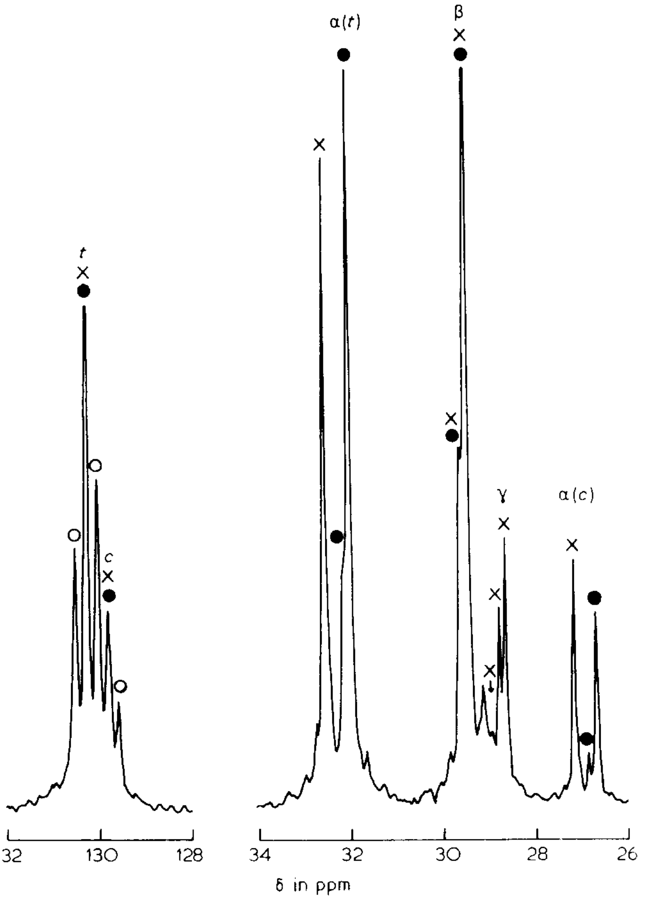


Figure 2 $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of copolymer prepared from 69 mmol cyclopentene (M_1), 152 mmol cycloheptene (M_3), approx. 100 mg WCl_6, 1.0 cm^3 25% $EtAlCl_2$/toluene, under N_2 at room temperature. Reaction time 5 min; yield 16 wt %. N.m.r. solvent, $CDCl_3$. Assignments: ●, M_1M_1; X, M_3M_3; O, M_1M_3

Acknowledgement

We acknowledge the support of the Science Research Council.

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