Metathesis Copolymerisation of Cycloalkenes with Substituted Acetylenes

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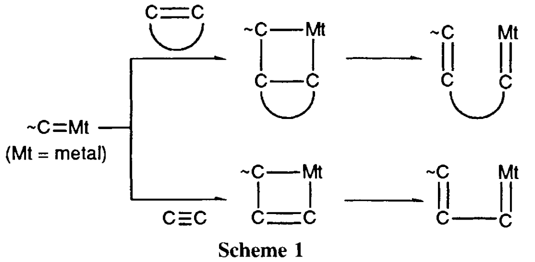
Metathesis copolymerisation of cycloalkenes with substituted acetylenes, typically norbornene with phenylacetylene, is achieved for the first time, which verifies that the polymerisation of substituted acetylenes by group 6 transition metal catalysts proceeds by the metal carbene mechanism.

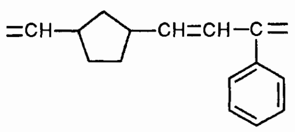
It is now generally accepted that ring-opening polymerisation of cycloalkenes proceeds *via* metal carbenes[1-3] (Scheme 1). Substituted acetylenes polymerise in the presence of group 5 and 6 transition metal catalysts,[4,5] whose active species are also believed to be metal carbenes. Therefore, there is a possibility that a cycloalkene and a substituted acetylene could copolymerise with each other. If such copolymerisation occurs successfully, it will provide a novel type of copolymer and will eventually support the metal carbene mechanism for the polymerisation of substituted acetylenes.



Scheme 1

Herein we report the copolymerisation of cycloalkenes with substituted acetylenes. Norbornene **1** and phenylacetylene **2** were mainly used as the monomers. Unless otherwise stated, copolymerisations were carried out with the WCl_6 catalyst in toluene solution at a 1 : 1 feed ratio of **1** to **2**, 30 °C, [catalyst] = 20 mmol dm^{-3} and [monomer]$_{total}$ = 1.0 mol dm^{-3}. Monomer conversions were determined by gas chromatography. Monomer reactivity ratios (MRRs) were obtained from the relative consumptions of both monomers at various feed ratios and low conversions.

In the copolymerisation of **1** with **2** at a 1 : 1 feed ratio, both monomers were consumed smoothly without any induction period. The initial copolymerisation rate of **1** was about a quarter that of **2** (**1** : **2** = 0.26 : 1). After 30 min, the conversions of **1** and **2** reached 77% and 99%, respectively; the yield of the methanol-insoluble, orange-coloured polymeric product **3** was 68 wt%. The composition of **3** was **1** : **2** = 46 : 54 (mole ratio, by ^{1}H NMR), and its $\bar{M}_n$ was 18000 [by gel permeation chromatography (GPC); polystyrene calibration, $\bar{M}_w/\bar{M}_n$ = 2.9]. The methanol-soluble product (yield 15 wt%) had a similar composition and a lower molecular weight. The MRRs were r(**1**) = 0.20 ± 0.03 and r(**2**) = 7.01 ± 0.26. Other



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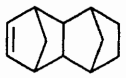
W catalysts, *i.e.* WCl_6–Ph_4Sn (1 : 1, 0°C) and $W(CO)_6$-$h\nu$ (CCl_4), also gave polymeric products with similar compositions and molecular weights.

Copolymerisation product **3** showed a unimodal GPC curve irrespective of a refractive index or UV (330 nm) detector. The H–H COSY NMR spectrum ($CDCl_3$) of **3** exhibited two correlation peaks, *i.e.* one at the intersection of δ 5.2 and 6.1 and another at the intersection of δ 5.5 and 6.6. The peaks at δ 5.2 and 5.5 are attributable to the unit of **1** (ring-opened structure), while those at δ 6.1 and 6.6 are from the unit of **2**. Hence the correlation peaks observed indicate the presence of the cross-propagation unit **4**. The two peaks are probably due to *cis* and *trans* isomers. The ^{13}C NMR spectrum ($CDCl_3$) of **3** showed a new peak at δ 131, apart from those of ring-opened poly(**1**) and poly(**2**). The UV–VIS spectrum (CCl_4) of **3** consisted of a broad absorption; it was stronger below 330 nm and weaker above 330 nm than that of a mixture of poly(**1**) and poly(**2**) having the same composition. This indicates that **3** is less conjugated than poly(**2**). All these observations have led to the conclusion that **3**, the product of the copolymerisation of **1** with **2**, is a copolymer and not a mixture of homopolymers.

Copolymerisations of **1** with other substituted acetylenes were examined. *o*-(Trifluoromethyl)phenylacetylene **5** reacted virtually at the same rate as **1** did in the copolymerisation reaction (**1** : **5** = ~1 : 1). 1-Chlorooct-1-yne **6** as another comonomer also showed a reactivity relatively close to that of **1** [**1** : **6** = 0.67 : 1 with $MoCl_5$ catalyst and 0.60 : 1 with $Mo(CO)_6$–hv (CCl_4)]. Thus, interestingly, these acetylenes are less reactive than **2** and nearer to **1** in their reactivity. This is attributable to their electron-withdrawing substituents which reduce the coordinating ability of the monomer to the metal carbene. Furthermore, *o*-(trimethylsilyl)phenylacetylene, which has an electron-donating group, was much more reactive than **1** in copolymerisation, which corresponds with the above inference.



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Copolymerisations of other cycloalkenes with **2** were also studied. Cyclopentene was not consumed until the complete conversion of **2** in the attempted copolymerisation reaction. In contrast, tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-4-ene **7**, a polycyclic strained alkene, possessed a reactivity somewhat larger than that of **1** (**7** : **2** = 0.30 : 1). Hence it is obvious that the ring strain of cycloalkenes plays an important role in enhancing their reactivity.

Consequently, combinations of **1** with acetylenes having electron-withdrawing groups (**5** and **6**) and also that of strained cycloalkenes (**1** and **7**) with **2** prove to have more or less close reactivities in copolymerisation. The products in all these copolymerisations were confirmed to be copolymers similarly to the case of **3**. Thus, metathesis copolymerisation of cycloalkenes with substituted acetylenes *via* metal carbenes was accomplished; this finding strongly supports the metal carbene mechanism for the polymerisation of substituted acetylenes by group 6 transition metal catalysts.

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