Chain Transfer Reaction by Trimethylvinylsilane in the Polymerisation of Substituted Acetylenes

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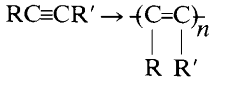
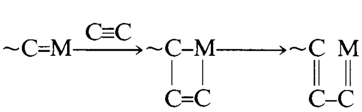
Trimethylvinylsilane works as an effective chain transfer agent in the polymerisation of various substituted acetylenes by Mo and W catalysts, which enables the control of polymer molecular weight and verifies the metal–carbene mediated polymerisation mechanism.

Chain transfer agents are useful for the control of polymer molecular weight. Further, the effectiveness of compounds as transfer agents is closely related to polymerisation mechanism itself. In the ring-opening metathesis polymerisation of cycloalkenes, which proceeds by the metal carbene mechanism, linear alkenes are known to serve as transfer agents.[1,2]



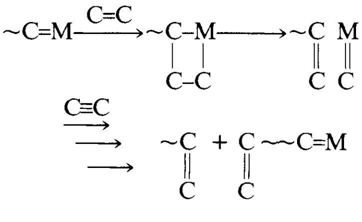
$$RC{\equiv}CR' \rightarrow \left(\underset{R}{C}{=}\underset{R'}{C} \right)_n \qquad (1)$$

A number of substituted polyacetylenes have recently been synthesised by using group 5 and 6 transition metal catalysts [eqn. (1)].[3,4] The metal carbene mechanism has also been proposed for this polymerisation [eqn. (2)].[5,6] If it is valid, suitable alkenes are expected to effect the chain transfer reaction [eqn. (3)]. Here we report on trimethylvinylsilane as the first example of an effective transfer agent in the polymerisation of substituted acetylenes by Mo and W catalysts.



$$\sim C{=}M \xrightarrow{C\equiv C} \sim\begin{array}{c}C{-}M\\ |\quad |\\ C{=}C\end{array} \longrightarrow \sim\begin{array}{c}C\quad M\\ \|\quad \|\\ C{-}C\end{array} \qquad (2)$$

(M: metal)



$$\sim C{=}M \xrightarrow{C=C} \sim\begin{array}{c}C{-}M\\ |\quad |\\ C{-}C\end{array} \longrightarrow \sim\begin{array}{c}C\quad M\\ \|\quad \|\\ C\quad C\end{array} \xrightarrow{C\equiv C} \sim\begin{array}{c}C\\ \|\\ C\end{array} + \begin{array}{c}C\\ \|\\ C\end{array}\!\sim\!\sim C{=}M \qquad (3)$$

As shown in Table 1, 1-chlorooct-1-yne ($ClC{\equiv}C\text{-}C_6H_{13}{}^n$) polymerises with a 1 : 1 mixture of $MoCl_5$ and $Bu^n{}_4Sn$ to provide a high molecular weight polymer. In contrast, the molecular weight of polymer more or less decreased in the presence of Si-containing and aliphatic alkenes. In particular, trimethylvinylsilane (1 : 5 equivalents to monomer) reduced the polymer molecular weight to less than 1/10 that in the absence of the alkene. The effectiveness of trimethylvinylsilane is attributable to the suitably electron-donating nature of the trimethylsilyl group (*cf.* alkenes with stronger electron-donating groups like vinyl ethers undergo cationic oligomerisation in this system, and hence they are not useful as transfer agents).

Table 1 Effects of various alkenes on the polymerisation of $ClC{\equiv}C\text{-}C_6H_{13}{}^n$ by $MoCl_5\text{-}Bu_4{}^nSn$[a]

Alkene	Monomer convn. (%)	Polymer[b] $\bar{M}_n/10^3$	$\bar{M}_w/10^3$
None	100	419	1190
$H_2C{=}CHSiMe_3$	100	34	116
$H_2C{=}CHSiMe_2Ph$	95	59	289
$H_2C{=}CHSi(OMe)_3$	94	149	364
$H_2C{=}CH(CH_2)_5Me$	100	206	388
$MeCH{=}CH(CH_2)_4Me$	100	241	414

[a] Polymerised in toluene at 30 °C for 24 h; $[C{\equiv}C] = 0.50$ mol dm^{-3}, $[MoCl_5] = [Bu_4{}^nSn] = 10$ mmol dm^{-3}, $[C{=}C] = 0.10$ mol dm^{-3}. [b] $\bar{M}_n$ and $\bar{M}_w$ determined by gel permeation chromatography using polystyrene samples for calibration.

Table 2 Effect of $H_2C{=}CHSiMe_3$ **1** on the polymerisation of substituted acetylenes[a]

Monomer	Catalyst[b]	[**1**]/mol dm^{-3}	Monomer convn. (%)	Polymer[c]	
				$\bar{M}_n/10^3$	$\bar{M}_w/10^3$
$ClC{\equiv}C\text{-}C_6H_{13}{}^n$	Mo	0	100	419	1190
		0.10	100	34	116
$ClC{\equiv}CPh$	Mo	0	100	189	458
		0.10	100	13	75
$MeC{\equiv}C\text{-}C_5H_{11}{}^n$	Mo	0	100	168	488
		0.10	71	91	299
$HC{\equiv}CC_6F_4\text{-}p\text{-}Bu^n$	W	0	100	125	293
		0.10	80	6	14
$HC{\equiv}CC_6H_4\text{-}o\text{-}CF_3$	W	0	100	182	301
		0.10	100	29	61
$HC{\equiv}CC_6H_4\text{-}o\text{-}C_6H_{13}{}^n$	W	0	100	24	63
		0.10	100	9	18
$HC{\equiv}CC_6H_4\text{-}o\text{-}SiMe_3$	W	0	100	180	367
		0.10	100	56	150

[a] Polymerised in toluene at 30 °C for 24 h; [C=C] = 0.50 mol dm^{-3}, [Cat] = [Cocat] = 10 mol dm^{-3}. [b] Mo: $MoCl_5$–$Bu_4{}^nSn$; W: WCl_6–Ph_4Sn. [c] See footnote *b* of Table 1.

Table 2 shows the effect of trimethylvinylsilane on the polymerisation of various substituted acetylenes (active catalysts were selected for the disubstituted acetylenes and ring-substituted phenylacetylenes). Among the disubstituted acetylenes, those with the electron-withdrawing chlorine atom suffered chain transfer to a considerable extent. In the case of ring-substituted phenylacetylenes, electron-withdrawing substituents also brought about large decreases in molecular weight. These results can be explained in terms of the notion that the acetylenes with electron-withdrawing groups have only a weak ability to coordinate to the metal carbene and in turn a low reactivity for polymerisation [see eqn. (2)]. This idea is supported by the relative reactivity of substituted acetylenes observed in copolymerisation.[3]

The features of the polymerisation of 1-chlorooct-1-yne in the presence of trimethylvinylsilane include the following. (i) The reaction is slower than in the absence of the alkene, but proceeds to completion. (ii) The molecular weight of polymer remains low irrespective of monomer conversion. (iii) The molecular weight distribution of the polymer is hardly affected by trimethylvinylsilane ($\bar{M}_w/\bar{M}_n$ 2–3). (iv) The $\bar{M}_n$ of the polymer decreases to a few thousands in the presence of a large amount (*e.g.*, 3 mol dm^{-3}) of trimethylvinylsilane, and the trimethylsilyl group (several percent relative to monomer units) is found in the polymer product according to the IR and NMR spectra.

In conclusion, an effective chain transfer agent for the polymerisation of substituted acetylenes has been found for the first time. This chain transfer by trimethylvinylsilane was remarkable for the monomers with electron-withdrawing groups.

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