Living Polymerization of Substituted Acetylenes by $MoCl_5$- and $MoOCl_4$-based Catalysts

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New catalyst systems composed of $MoCl_5$ (or $MoOCl_4$), $Bu^n{}_4Sn$, and ethanol (molar ratio 1 : 1 : 0.5) effect living polymerisations of 1-chloro-oct-1-yne and *o*-(trimethylsilyl)phenylethyne, which are the first examples of living polymerisation of acetylenes.

Living polymerisation, *i.e.* polymerisation without termination and chain transfer reactions, provides a useful technique for the preparation of tailor-made polymers such as monodisperse polymers and block copolymers. Whereas living anionic polymerisation has been extensively investigated,[1] only a few living polymerisations initiated by transition metal catalysts have so far been reported.[2] In these examples monomers such as norbornene, propene, and butadiene have been used. It is known that group 5 and 6 transition metal catalysts (Nb, Ta, Mo, and W) polymerise various substituted acetylenes very effectively.[3] Here we report the living polymerisations of two kinds of substituted acetylenes: 1-chloro-oct-1-yne and *o*-(trimethylsilyl)phenylethyne by $MoCl_5$- and $MoOCl_4$-based catalysts.

$MoCl_5$ alone, and as a 1:1 mixture with $Bu^n{}_4Sn$, polymerised 1-chloro-oct-1-yne to give a high molecular weight polymer ($\bar{M}_w$ 1×10^5—2×10^6), but the molecular weight distribution (MWD) of the polymer was rather broad ($\bar{M}_w/\bar{M}_n$ *ca.* 2).[4] Aiming at the stabilisation of the propagating species, we examined the effects of ethanol on the $MoCl_5$–$Bu^n{}_4Sn$ catalyst in the formation of living polymers.

As seen in Table 1, a three-component catalyst, $MoCl_5$–$Bu^n{}_4Sn$–EtOH (1:1:0.5) produced poly(1-chloro-oct-1-yne) having a very narrow MWD ($\bar{M}_w/\bar{M}_n$ 1.1—1.2), and the $\bar{M}_n$ of the polymer was found to increase in proportion to monomer conversion. Furthermore, when a new monomer feed was supplied at 100% conversion, the $\bar{M}_n$ increased progressively. All these results suggest that this polymerisation is 'living'. The ratio of polymer chains to Mo catalyst ([P]/[Mo]) was however *ca.* 2%, a relatively small value.

Owing to the importance of the oxo group in active species involved in olefin metathesis,[5] which is also mediated by metal carbenes,[6] $MoOCl_4$ was employed instead of $MoCl_5$. The polymerisation of 1-chloro-oct-1-yne by $MoOCl_4$–$Bu^n{}_4Sn$–EtOH (1:1:0.5) proceeded almost instantaneously, and formed a polymer having a similarly narrow MWD (Table 1). When new monomer feeds were provided successively, the $\bar{M}_n$ of the polymer increased proportionally to the amount of the monomer added. Thus $MoOCl_4$–$Bu^n{}_4Sn$–EtOH also proves effective in the living polymerisation of 1-chloro-oct-1-yne. In contrast, $MoOCl_4$ alone, and the $MoOCl_4$–$Bu^n{}_4Sn$ mixture gave polymers with broader MWD's.

The living polymerisation by $MoOCl_4$–$Bu^n{}_4Sn$–EtOH was also possible using other 1-chloroalk-1-ynes having different

Table 1. Living polymerisation of substituted acetylenes by $MoCl_5$-($MoOCl_4$)-$Bu^n{}_4Sn$-EtOH (1 : 1 : 0.5).[a]

Mo catalyst	Time/ min	Monomer % conversion	$10^{-3}\bar{M}_n$[b]	MWD[c]	[P]/[Mo][d]
Monomer: $ClC{\equiv}CC_6H_{13}$-n					
$MoCl_5$	0.5	28	53	1.11	0.019
$MoCl_5$	1	56	95	1.23	0.021
$MoCl_5$	60	100	160	1.23	0.023
$MoOCl_4$[e]	5	100	36	1.17	0.020
$MoOCl_4$[e]	10	200	50	1.20	0.029
$MoOCl_4$[e]	15	300	94	1.14	0.023
Monomer: $HC{\equiv}CC_6H_4SiMe_3$-*o*					
$MoCl_5$	3	32	16	1.15	0.087
$MoCl_5$	6	52	28	1.08	0.081
$MoCl_5$	60	100	43	1.07	0.10
$MoOCl_4$	1.5	34	9.5	1.15	0.16
$MoOCl_4$	4	62	21	1.11	0.13
$MoOCl_4$	60	100	45	1.11	0.097

[a] Polymerised in toluene at 30 °C; [Mo cat] = 20 mM, $[\text{monomer}]_0$ = 0.50 M. [b] Determined by g.p.c. [c] MWD = $\bar{M}_w/\bar{M}_n$. [d] Ratio of polymer chain to Mo catalyst. [e] 'Monomer addition' experiments; $[\text{monomer}]_0$ = $[\text{monomer}]_{\text{added}}$ = 0.10 M.

alkyl lengths such as 1-chlorohex-1-yne and 1-chlorohexadec-1-yne ($\bar{M}_w/\bar{M}_n$ 1.1—1.2). Hence the preparation of A–B–A and B–A–B type triblock copolymers was attempted with 1-chlorohex-1-yne and 1-chlorohexadec-1-yne. On addition of the second and third feeds of monomers, the $\bar{M}_n$ values increased progressively, while the MWD's remained narrow, strongly suggesting that triblock copolymers had been formed.

Interestingly, the $MoCl_5$–$Bu^n{}_4Sn$–EtOH and $MoOCl_4$–$Bu^n{}_4Sn$–EtOH catalysts gave a living polymer also from *o*-(trimethylsilyl)phenylethyne, a different type of monomer. Both the narrow MWD's and the progressive increases in $\bar{M}_n$ with monomer conversion that are seen in Table 1 clearly demonstrate the 'living' nature of this polymerisation. The [P]/[Mo] ratios were roughly 10% with this monomer. As in the case of 1-chloro-oct-1-yne, these molybdenum chlorides alone or their mixtures with $Bu^n{}_4Sn$ produced high molecular weight poly[*o*-(trimethylsilyl)phenylethyne] ($\bar{M}_w$ 1×10^5—1×10^6), but the MWD's were not as narrow.

The present polymerisations are the first examples of living polymerisations of acetylenes. It is inferred that ethanol replaces a chlorine ligand of the propagating species (metal carbene) with an ethoxy group and this enhances the stability of the propagating species by lowering its Lewis acidity. A more detailed study on these new living polymerisations is under way.

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References

1 M. Szwarc, *Adv. Polym. Sci.*, 1983, **49**, 1.

2 L. R. Gilliom and R. H. Grubbs, *J. Am. Chem. Soc.*, 1986, **108**, 733; K. C. Wallace and R. R. Schrock, *Macromolecules*, 1987, **20**, 448; R. R. Schrock, J. Feldman, L. F. Cannizzo, and R. H. Grubbs, *ibid.*, p. 1169; Y. Doi, S. Suzuki, and K. Soga, *ibid.*, 1986, **19**, 2896; P. Hadjiandreou, M. Julemond, and P. Teyssie, *ibid.*, 1984, **17**, 2455.

3 T. Masuda and T. Higashimura, *Adv. Polym. Sci.*, 1986, **81**, 121; *Acc. Chem. Res.*, 1984, **17**, 51.

4 T. Masuda, T. Yoshimura, K. Tamura, and T. Higashimura, *Macromolecules*, 1987, **20**, 1734; T. Masuda, K. Tamura, and T. Higashimura, *J. Chem. Soc., Chem. Commun.*, 1985, 1615.

5 A. K. Rappe and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1982, **104**, 448; *Nature*, 1980, **285**, 311; M. T. Mocella, R. Rovner, and E. L. Muetterties, *J. Am. Chem. Soc.*, 1976, **98**, 4689.

6 K. J. Ivin, 'Olefin Metathesis,' Academic Press, London, 1983; V. Dragutan, A. T. Balaban, and M. Dimonie, 'Olefin Metathesis and Ring-opening Polymerization of Cyclo-olefins,' Wiley, New York, 1986.