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Living Polymerization of 1-Chloro-1-alkynes by $MoOCl_4$–*n*-Bu_4Sn–EtOH Catalyst

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Introduction

Living Polymerization is an excellent method for the preparation of polymers with monodisperse molecular weight distribution (MWD) and controlled structure.[1] While living anionic polymerization has been investigated most extensively, many living polymerizations by other mechanisms have also been developed recently. For example, transition-metal-catalyzed living polymerizations have been achieved for norbornene,[2] propene,[3] and butadiene.[4] Especially, studies on the living polymerization of norbornene have made remarkable progress, expanding into precise preparation of block copolymers.[5] On the other hand, few polymerizations of substituted acetylenes have been claimed to be living systems: (i) 1-chloro-1-octyne/$MoCl_5$–*n*-Bu_4Sn–EtOH,[6] (ii) *tert*-butylacetylene/$MoCl_5$,[7] and (iii) 1-(trimethylsilyl)-1-propyne/$NbCl_5$.[8]

1-Chloro-1-octyne polymerizes with $MoCl_5$–*n*-Bu_4Sn (1:1) catalyst to give quantitatively a polymer whose molecular weight reaches about one million.[9] Recently we have found that a catalyst composed of $MoCl_5$, tetrabutyltin, and ethanol ($MoCl_5$–*n*-Bu_4Sn–EtOH, molar ratio 1:1:0.5) effects living polymerization of 1-chloro-1-octyne.[6] In the presence of this catalyst, the number-average molecular weight ($\bar{M}_n$) of the polymer increases in direct proportion to conversion, and the polydispersity ratio ($\bar{M}_w/\bar{M}_n$) is 1.1–1.3. The $\bar{M}_w/\bar{M}_n$ ratio, however, tends to increase owing to the partial deactivation of the propagating species when additional monomer feed is supplied to a polymerization system in which the initial feed has been consumed.

In the present note, we report on the living polymerization of 1-chloro-1-alkynes effected by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5). This catalyst is featured by high activity and superior living nature, as compared with the corresponding $MoCl_5$-based catalyst. Block copolymers comprising two kinds of substituted acetylenes have been prepared for the first time by using this catalyst.

Experimental Section

$MoOCl_4$ (Strem Chem.) was used without further purification. 1-Chloro-1-alkynes were prepared as described before[9a] and distilled twice at reduced pressure from calcium hydride. Toluene as polymerization solvent was washed by a standard method, distilled twice from calcium hydride, and kept over molecular sieves.

Polymerizations were carried out under dry nitrogen in a baked glass tube equipped with a three-way stopcock. The following procedure is exemplary (see Figure 2 for results): A glass tube was charged with 1-chloro-1-octyne (1.0 mmol, 145 mg, 0.159 mL), dodecane [0.050 mL, as internal standard for gas chromatography (GC)], and toluene (3.8 mL). In a separate glass tube were placed $MoOCl_4$ (0.50 mmol, 127 mg), toluene (11.3 mL), and a toluene solution (2.5 mL) of *n*-Bu_4Sn (200 mM), and the mixture was allowed to age at 30 °C for 15 min. To this was added a toluene solution (1.25 mL) of EtOH (200 mM), and the mixture was aged at 30 °C for another 15 min. Polymerization was initiated by adding 6.0 mL of this catalyst solution to the above monomer solution at 30 °C. The second, third, and fourth monomer feeds (1.0 mmol each) were injected as toluene solutions (toluene, 2 mL) after every 5 min. The polymerization was terminated with a mixture (1 mL) of methanol and toluene (1:4 volume ratio) after 5 min from the final monomer addition. The monomer had totally reacted according to GC (silicone DC 3m, 150 °C). Further, it was confirmed by GC in control experiments that the monomer had been completely consumed at each step. The polymerization mixture was diluted with toluene (30 mL) and poured into methanol (1 L) under stirring. The polymer precipitate was filtered off and dried to a constant weight. Triblock copolymerizations were carried out in a similar way.

The $\bar{M}_w$ (weight-average molecular weight) and $\bar{M}_n$ values of polymes were tentatively determined by gel permeation chromatography (GPC).[10] GPC curves were observed on a Jasco Trirotar chromatograph (eluent $CHCl_3$; columns, Shodex A804, A806, and A807 polystyrene gels; sample 0.10 wt % solution; polystyrene calibration).

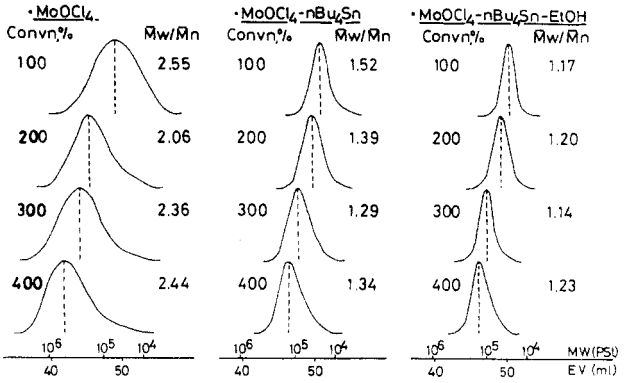

Figure 1. MWD curves of poly(1-chloro-1-octyne)s obtained with $MoOCl_4$-based catalysts (polymerized in toluene at 30 °C for 5 min for each monomer feed; $[M]_0 = [M]_{added} = 0.10$ M, $[MoOCl_4] = 20$ mM).

Results and Discussion

Living Polymerization of 1-Chloro-1-octyne. Polymerization of 1-chloro-1-octyne was studied by use of three kinds of $MoOCl_4$-based catalysts, that is, $MoOCl_4$ alone, $MoOCl_4$–*n*-Bu_4Sn (1:1), and $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5). When carried out in toluene at 30 °C, the polymerization was very quick with each catalyst, being finished within 5 min. Then monomer was repeatedly supplied every 5 min three times and was completely consumed each time.

Figure 1 shows MWD curves of the poly(1-chloro-1-octyne)s obtained in these polymerizations. Among the three $MoOCl_4$-based catalysts, the $MoOCl_4$–*n*-Bu_4Sn–EtOH catalyst produced a polymer whose $\bar{M}_w/\bar{M}_n$ ratio was 1.15–1.25, being close to unity. Furthermore, the polymer molecular weight increased progressively with each further supply of monomer, whereas the MWD remained narrow throughout this procedure. These results manifest that this polymerization is a living polymerization. In contrast, the $\bar{M}_w/\bar{M}_n$ ratio for $MoOCl_4$–*n*-Bu_4Sn was 1.3–1.5, and that for $MoOCl_4$ alone was as large as 2.1–2.6. The polymer molecular weight also increased with additional supplies of monomer in these latter polymerizations, suggesting the presence of long-lived propagating species in these systems.

As seen in Figure 2, the $\bar{M}_n$ of the polymer increased in direct proportion to the amount of monomer supply, and in turn monomer consumption, in the polymerization of

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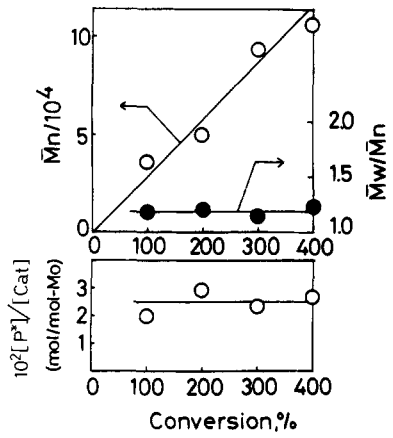

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and [P*]/[Cat] as functions of conversion in the polymerization of 1-chloro-1-octyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5) (in toluene, 30 °C, 5 min for each monomer feed; $[M]_0 = [M]_{added}$ = 0.10 M, $[MoOCl_4]$ = 20 mM).

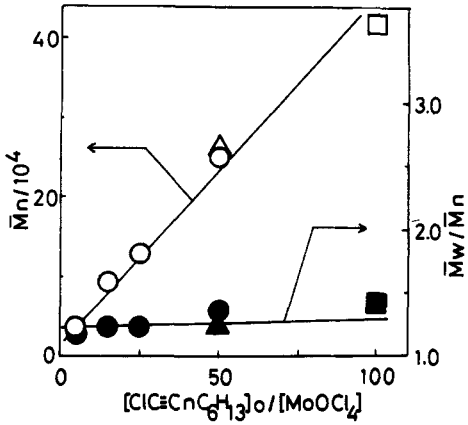

Figure 3. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ as functions of monomer-to-catalyst ratio ($[M]_0/[Cat]$) in the polymerization of 1-chloro-1-octyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5) (in toluene, 30 °C, 1 h; conversions all 100%). $[MoOCl_4]$ (mM)/$[M]_0$ (M): (○, ●) 20/0.10–0.50, (△, ▲) 10/0.50, (□, ■) 5.0/0.50.

1-chloro-1-octyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH. The $\bar{M}_w/\bar{M}_n$ stayed as low as ca. 1.2 throughout. The ratio of the propagating species to the Mo catalyst ([P*]/[Cat]), so-called "initiator efficiency", can be calculated by eq 1,

$$[P^*]/[Cat] = [M]_{consumed}/(\overline{DP}_n[Cat]) \quad (1)$$

where $\overline{DP}_n$ means the number-average degree of polymerization. The [P*]/[Cat] ratio was small, around 0.025. The ratio was unaffected by the repeated supplies of monomer.

Figure 3 depicts how the $\bar{M}_n$ of poly(1-chloro-1-octyne) can be controlled by the monomer-to-catalyst ratio ($[M]_0/[Cat]$). When the ratio was changed over the range 5–100, the $\bar{M}_n$ of the polymer was approximately proportional to this ratio, while a fairly narrow MWD was maintained irrespective of the ratio. Consequently one can control the $\bar{M}_n$ of the polymer in the range ca. 30 × 10^3–400 × 10^3 by judicious choice of $[M]_0$ and [Cat].

When compared with the corresponding polymerization by $MoCl_5$–*n*-Bu_4Sn–EtOH (1:1:0.5), the following features can be pointed out for the living polymerization of 1-chloro-1-octyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5): (i) the polymerization is much faster, (ii) the $\bar{M}_w/\bar{M}_n$ ratio is somewhat smaller (~1.15 versus ~1.25 under conditions shown in Figure 2), (iii) all the polymer molecules resume propagation when the second monomer feed is supplied after 100% conversion of the first feed, and (iv) the [P*]/[Cat] ratio is slightly larger (0.025 versus <0.020). Thus it can be said that the $MoOCl_4$-based catalysts

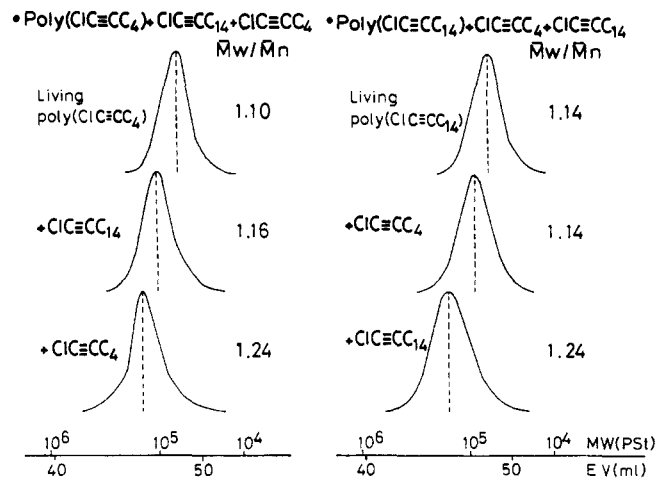

Figure 4. Triblock copolymerizations of 1-chloro-1-hexyne and 1-chloro-1-hexadecyne by $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5) (in toluene, 30 °C, 5 min for each monomer feed; $[M]_0 = [M]_{added}$ = 0.10 M, $[MoOCl_4]$ = 20 mM).

achieve more perfect living polymerization than does $MoCl_5$. In this connection, it is worth noting that the presence of the metal–oxo bond (spectator oxygen) in active species effects smooth olefin metathesis.[12]

Block Copolymerization of 1-Chloro-1-alkynes. Living polymerization of four 1-chloro-1-alkynes with different alkyl chain lengths (ClC≡CR; R = *n*-C_4H_9, *n*-C_6H_{13}, *n*-C_8H_{17}, and *n*-$C_{14}H_{29}$) was examined with $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5) catalyst. The polymerizations were carried out in toluene at 30 °C for 1 h ($[M]_0$ = 0.10 M, $[MoOCl_4]$ = 20 mM) and proceeded quantitatively. The $\bar{M}_n$ values and $\bar{M}_w/\bar{M}_n$ ratios (in parentheses) of the polymers are as follows: 67 × 10^3 (1.10) (R = *n*-C_4H_9); 36 × 10^3 (1.17) (R = *n*-C_6H_{13}); 29 × 10^3 (1.25) (R = *n*-C_8H_{17}); 66 × 10^3 (1.14) (R = *n*-$C_{14}H_{29}$). These results indicate that living polymerization of 1-chloro-1-alkynes takes place regardless of alkyl chain length. In contrast, 1-chloro-2-phenylacetylene (ClC≡CPh) produced a polymer with broader MWD ($\bar{M}_w/\bar{M}_n$ = 1.42) under the same conditions, though the $\bar{M}_n$ increased with conversion.

The above findings prompted us to try the block copolymerization of 1-chloro-1-alkynes. 1-Chloro-1-hexyne (A) and 1-chloro-1-hexadecyne (B), whose alkyl chain lengths are very different, were chosen as monomers, and A–B–A and B–A–B type copolymers were prepared under the conditions given in Figure 4. In both cases, the $\bar{M}_n$ of polymer steadily increased with each monomer addition, while the $\bar{M}_w/\bar{M}_n$ ratio remained around 1.2 until the final stage (Figure 4). This clearly supports the formation of triblock copolymers.

Poly(1-chloro-1-hexyne) is hard and brittle (T_g ~190 °C),[13] whereas poly(1-chloro-1-hexadecyne) is rubbery at room temperature and provides no free-standing film. When cast from toluene solution, a mixture of these homopolymers produced only a translucent heterogeneous film. In contrast, the above triblock copolymers afforded transparent homogeneous films.

Conclusions

The $MoOCl_4$–*n*-Bu_4Sn–EtOH (1:1:0.5) catalyst induced living polymerization of 1-chloro-1-octyne in toluene at 30 °C. The $\bar{M}_n$ of polymer increased progressively with repeated additions of monomer feed. The $\bar{M}_w/\bar{M}_n$ ratio was maintained at about 1.15. 1-Chloro-1-alkynes with different alkyl lengths underwent living polymerization as well. Triblock copolymers of A–B–A and B–A–B types could be obtained from the combination of 1-chloro-1-

hexane (A) and -1-hexadecyne (B), which are the first examples of block copolymerization of substituted acetylenes.

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Registry No. $MoOCl_4$, 13814-75-0; Bu_4Sn, 1461-25-2; EtOH, 64-17-5; $ClC{\equiv}C(CH_2)_5CH_3$ (homopolymer), 100858-77-3; $ClC{\equiv}C(CH_2)_3CH_3$ (homopolymer), 100858-76-2; $ClC{\equiv}C(CH_2)_7CH_3$ (homopolymer), 100858-79-5; $ClC{\equiv}C(CH_2)_{13}CH_3$ (homopolymer), 108711-62-2; $ClC{\equiv}CPh$ (homopolymer), 81953-16-4; $(ClC{\equiv}C(CH_2)_{13}CH_3)(ClC{\equiv}C(CH_2)_3CH_3)$ (block copolymer), 121029-94-5.

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Starlike Micelles: Their Growth in Homopolymer Solutions

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Diblock copolymers may be considered as the macromolecular counterpart of ordinary, "monomeric" surfactants. Yet, polymeric surfactants exhibit features having no direct analogue among monomeric surfactants. In the following we focus on one such trait. It concerns the behavior of micelles formed by *neutral* diblock copolymers in a selective solvent of low molecular weight. In particular, *addition of homopolymer* to certain types of micellar solutions results in an increase of the average aggregation number. This effect involves only *starlike micelles*, i.e., micelles endowed with extended coronas. Micelles having thin coronas are not affected. This phenomenon is somewhat reminiscent of the effect of added electrolyte on the size of micelles formed by charged monomeric surfactants.[1] It has, however, no analogue among micelles consisting of neutral, low molecular weight amphiphiles.

Consider micelles formed by flexible A–B diblock copolymers consisting of N_A A monomers and N_B B monomers. The micellization takes place in a highly selective low molecular weight solvent, that is, a good solvent for the A blocks but a poor one for the B blocks. The micelles thus formed are spherical, comprising two concentric regions: An inner core, consisting of immiscible B blocks in a meltlike state, and an outer corona of soluble A blocks swollen by the solvent. For a highly selective solvent the A–B junctions are localized at the sharp core–corona boundary. In effect both A and B blocks are thus grafted to the interface, i.e., attached to the surface by an end group only. This is an important point, as the deformations resulting from dense grafting play a central role in the determination of the micelle's equilibrium structure. For solutions well past the critical micelle concentration (cmc) but prior to the onset of micelle overlap, micellar properties are determined by F, the free energy per chain of a single micelle. F of a micelle consisting of f A–B coils is calculated with respect to the free energy of a free, nonaggregated chain. We approximate F as a sum of three contributions due to the core, the corona, and the interface between them:[2,3]

$$F/kT = (\gamma a^2/kT)f^{-1/3}N_B^{2/3} + f^{2/3}N_B^{-1/3} + f^{1/2}\ln(R_{core} + L)/R_{core} \quad (1)$$

The first term, $F_{interface}$, is the free energy per chain associated with the core–corona interface. For a melt of B blocks the core volume scales as fN_Ba^3 where a is a characteristic monomer size. The core surface area is accordingly proportional to $f^{2/3}N_B^{2/3}a^2$, thus leading to $F_{interface}$ as given. γ, the associated surface tension, is independent of f and N_B for highly selective solvents. As this term is a decreasing function of f, it favors micellar growth. However, the incorporation of extra chains in the micelle results in an increase of the grafting density and in stronger deformations of the grafted blocks. The accompanying free energy penalties arrest the aggregation process. Two such penalties are involved, F_{core} and F_{corona}, due, respectively, to the deformations of the core and coronal blocks. The second term in (1) is due to F_{core}. To obtain a core of radius R_{core} larger than $N_B^{1/2}a$, it is necessary to stretch some of the B blocks. This follows because the B blocks are grafted and subject to a constant density constraint, i.e., the necessity to "fill" the core's center. The associated free energy penalty per chain scales as R_{core}^2/N_Ba^2. While this form was originally justified by a uniform stretching assumption,[3] it also obtains when a full self-consistent-field calculation is carried out.[4] F_{corona} gives rise to the final contribution to F. The coronal blocks are stretched because of the balance between the osmotic pressure and the chains' elasticity. To obtain F_{corona}, we exploit the similarity between micelles and star polymers:[2] In both systems chains are grafted to spherical cores. A useful description of the corona is accordingly given by the Daoud–Cotton model for star polymers.[5] In it the corona is divided into f identical, radially aligned, and close-packed truncated cones. A coronal block is grafted to the narrow base of each of these virtual capillaries. The cone's walls set the blob size, $\xi(r)$, at a distance r from the micelles center so that $\xi(r) \approx r/f^{1/2}$. F_{corona} is then given by the kT per blob ansatz.[6] F_{corona}/kT thus obtained is proportional

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