Polymer Bulletin 32, 517–524 (1994)

**Polymer Bulletin**

# Metathesis copolymerization of chlorine-containing acetylenes with NBE catalyzed by $MoCl_5$-*n*-$Bu_4Sn$

**Takuya Ohgane, Toshio Masuda, and Toshinobu Higashimura**

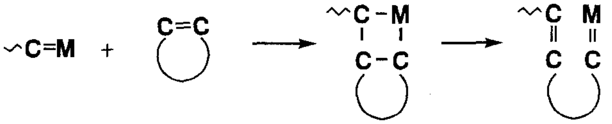
Department of Polymer Chemistry, Kyoto University, Kyoto 606-01, Japan

## Summary

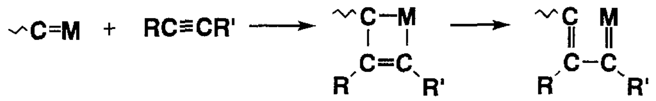
In the copolymerizations of 1-chloro-1-octyne (ClOc) and 1-chloro-2-phenylacetylene (ClPA) with norbornene (NBE) by $MoCl_5$–*n*-$Bu_4Sn$ in toluene at –20°C, both comonomers were consumed simultaneously. The GPC curves of the copolymerization products were unimodal and identical irrespective of the RI and UV (290 nm) detectors. The $^{13}C$ NMR spectra of the products exhibited the presence of cross-propagating sequences. From these results, it is concluded that the copolymerization products are copolymers and not mixtures of homopolymers. The monomer reactivity ratios were: $r_{ClOc} = 0.69$, $r_{NBE} = 6.4$; $r_{ClPA} = 1.0$, $r_{NBE} = 3.1$. The more electron-donating the ring substituent of ClPA, the more reactive the ClPA in copolymerization with NBE.

## Introduction

Group 5 and 6 transition-metal catalysts are effective in the ring-opening metathesis polymerization (ROMP) of cycloolefins, for which a large number of studies have been carried out (1–4). The active species of this polymerization are metal carbenes and the propagation reaction proceeds via metallacyclobutanes [eq. (1)].



(1)



(2)

We found that group 5 and 6 transition-metal catalysts produce high molecular weight polymer from substituted acetylenes (5), and proposed that the active species of this polymerization are also metal carbenes [eq. (2)]. Katz et al. supported our proposal on the basis of his result that isolated metal carbenes work as initiators (7).

If the metal carbene is a common active species for the polymerizations of cycloolefins and substituted acetylenes, then their mutual copolymerization will be possible. In fact, we have recently achieved the copolymerization of phenylacetylene with norbornene (NBE) catalyzed by $WCl_6$ and have revealed thereby that the polymerization of substituted acetylenes is mediated by metal carbenes (8). Further we have revealed that the more electron-donating the ring substituent of phenylacetylene, the more reactive the phenylacetylene in the copolymerization (9).

In the present study, we examined the copolymerization of substituted acetylenes with NBE catalyzed by a Mo catalyst, instead of a W catalyst. As acetylenic monomers, we used 1-chloro-1-octyne (ClOc), 1-chloro-2-phenylacetylene (ClPA) and ring-substituted ClPAs which are all polymerizable with Mo catalysts but are hardly polymerizable with W catalysts. We have proved the formation of copolymers and clarified effects of ring substituents of ClPA.

## Experimental

### *Materials*

ClOc and ClPA were prepared from 1-octyne and phenylacetylene, respectively, according to literature methods (10). Ring-substituted phenylacetylenes were prepared (11) and used for the synthesis of ring-substituted ClPAs. All the acetylenic monomers were distilled twice from $CaH_2$ at reduced pressure before use; purities >99% [gas chromatography (GC)]. NBE was commercially obtained, distilled twice from $CaH_2$ [purity >99% (GC)], and stored as toluene solution (5.0 M). $MoCl_5$ (Aldrich; purity >99.9%) was used as received.

### *Procedures*

Copolymerizations were carried out under dry nitrogen in a prebaked flask equipped with a three-way stopcock. The reaction conditions were: in toluene, at –20°C, $[M]_{0,total}$ = 0.30 M, $[MoCl_5]$ = $[n\text{-}Bu_4Sn]$ = 10 mM. Toluene solution of $n\text{-}Bu_4Sn$ (200 mM) was added to toluene solution of $MoCl_5$, and this mixture was aged at 30°C for 15 min before use. The polymerization reaction was initiated by adding a monomer solution to this catalyst solution, and quenched after a given time by adding a mixture of 1-propanol and toluene (volume ratio 1:1). Monomer conversions were determined by GC. Copolymerization products were isolated by precipitation of reaction mixtures into a large amount of methanol. Number-average molecular weights ($M_n$) and molecular weight distributions of polymers were measured by gel-permeation chromatography (GPC; eluent $CHCl_3$, polystyrene gel columus, polystyrene calibration). Monomer reactivity ratios were determined by the method of Ezrielev et al. (12) by the same procedure as in a previous paper (9).

## Results and Discussion

### *Copolymerizations of ClOc and ClPA with NBE*

Copolymerizations of ClOc and ClPA with NBE were examined by using $MoCl_5$–*n*-$Bu_4Sn$ and $WCl_6$–*n*-$Bu_4Sn$ as catalysts (Table I). In the copolymerization of ClOc with NBE by the W catalyst, the conversion did not become high even after 24 h. On the other hand, both conversion and polymer yield were appreciably high in the Mo-catalyzed copolymerization. The polymer molecular weight also became higher when the Mo catalyst rather than the W counterpart was used. The copolymerization of ClPA with NBE also showed a similar tendency. Hence the Mo catalyst was exclusively used in the following experiments. Further the compositions of copolymerization products determined by the $^1H$ NMR spectra of methanol-insoluble product agreed with the ones calculated from monomer

**Table I.** Copolymerization of ClC≡CR ($M_1$) with NBE ($M_2$) [a]

| Catalyst | Time, h | Conversion, % $M_1$ | Conversion, % $M_2$ | Polymer [b] Yield, wt% | Polymer [b] $M_n/10^4$ | $M_2$, mole% GC | $M_2$, mole% $^1H$ NMR [b] |
|---|---|---|---|---|---|---|---|
| | | | $M_1$ : ClC≡C-*n*-$C_6H_{13}$ | | | | |
| $MoCl_5$–*n*-$Bu_4Sn$ | 1 | 25 | 67 | 35 | 16 | 73 | 69 |
| $WCl_6$–*n*-$Bu_4Sn$ | 24 | 15 | 39 | 5 | 13 | – | – |
| | | | $M_1$ : ClC≡CPh | | | | |
| $MoCl_5$–*n*-$Bu_4Sn$ | 1 | 50 | 71 | 56 | 46 | 56 | 59 |
| $WCl_6$–*n*-$Bu_4Sn$ | 24 | 10 | 85 | 10 | 24 | – | – |

[a] Copolymerized in toluene at –20°C, [Cat] = [Cocat] = 10 mM, $[M_1]_0 = [M_2]_0 =$ 0.15 M. [b] MeOH-insoluble part.

consumption, and therefore the product compositions were estimated by GC in further experiments.

*Confirmation of Copolymer Formation*

Figure 1 shows time-conversion curves for the copolymerization of ClOc and NBE at a 1:1 feed ratio. Both monomers were consumed smoothly without any induction phase. The reactivity of NBE was higher than that of ClOc. The copolymerization product after 60 min was used as the sample for the analyses stated below.

The presence of both monomer units in the product was confirmed from $^1H$ and $^{13}C$ NMR spectra of the products. Figure 2 shows GPC curves of the copolymerization product. The two GPC curves, which were observed with RI and UV (290 nm) detectors, were both unimodal and coincided with each other. This indicates a uniform distribution of both monomer units in the product since poly(NBE) has no absorption at 290 nm.

Figure 3 shows the region of δ 150–120 in $^{13}C$ NMR spectra for the homopolymers and copolymerization products from NBE and ClOc. The sharp signals appearing in δ 133–132 of poly(NBE) are assignable to the olefinic carbons (Figure 3a). Poly(1-chloro-1-octyne) exhibits rather broad signals due to the $sp^2$ carbons at δ 137 and 128 (Figure 3d). In the spectra (Figures 3b, 3c) of copolymerization products, in contrast, several small peaks are seen besides the peaks of the homopolymers. These peaks are attributable to cross-propagating sequences such as the NBE–ClOc dyad,

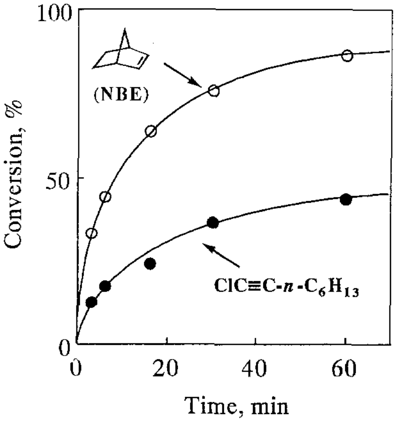


**Figure 1.** Copolymerization of ClOc with NBE by $MoCl_5$–$n$-$Bu_4Sn$ (in toluene, −20 °C, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$ mM, $[M_1]_0 = [M_2]_0 = 0.15$ M).

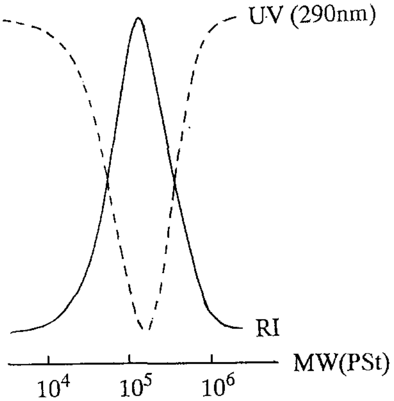


**Figure 2.** Molecular weight distribution curves of the copolymerization product from ClOc and NBE (sample: the product at 60 min in Figure 1).

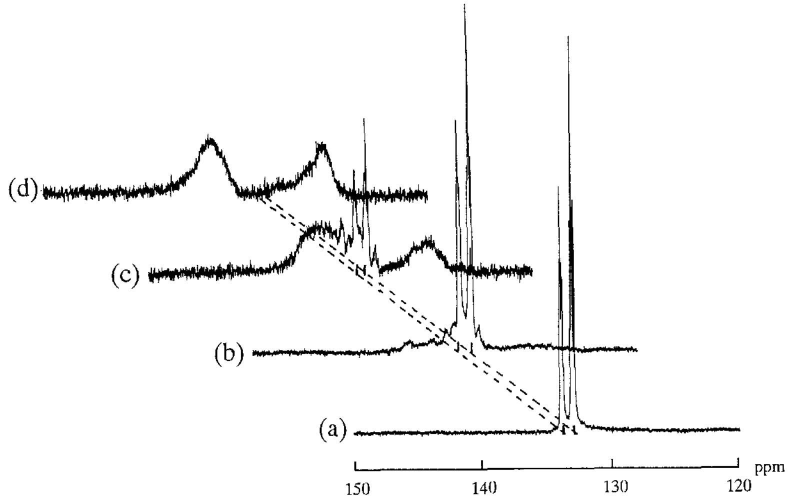


**Figure 3.** $^{13}C$ NMR spectra of the homo- and copolymerization products from ClOc and NBE (in $CDCl_3$, ClOc content of sample (mole%): (a) 0, (b) 31, (c) 74, (d) 100).

which manifests the formation of a copolymer and not a mixture of homopolymers.

Films were fabricated from the copolymerization product and from a mixture of both homopolymers with the same composition by casting them from toluene solution. The film of the homopolymer mixture was obviously inhomogeneous, i.e., showed a phase separation. In contrast, the film from the copolymerization product was uniform, indicating that the two uncompatible units are present in the same polymer molecule.

From all of the above-shown results on GPC, $^{13}C$ NMR and the film uniformity, one can conclude that the copolymerization product from ClOc and NBE is a copolymer and not a mixture of homopolymers. In the copolymerization of ClPA with NBE as well, we confirmed the formation of a copolymer from GPC and film uniformity.

The formation of copolymers, as clarified above, supports the metal-carbene mechanism for the polymerization of substituted acetylenes by Mo catalysts, since the metal-carbene mechanism is generally accepted for the polymerization of NBE by Mo catalysts (1, 2).

### *Reactivity of Acetylenic Monomers*

Figure 4 shows composition curves for the copolymerizations of ClOc and ClPA with NBE. The monomer reactivity ratios of these copolymerizations are listed in Table II. The composition curves are more or less sigmoidal, which suggests that the copolymers possess slightly blocky nature. Interestingly, NBE is more reactive than the Cl-containing acetylenes in these copolymerizations. The coordinating ability of acetylenes is, in general, higher than that of olefins. In fact, phenylacetylene is fairly more reactive than NBE in copolymerization (9). The low reactivity of the Cl-containing acetylenes is attributable to the decreased electron density on the triple bond due to the adjacent chlorine atom.

Copolymerizations of several *para*-substituted ClPAs with NBE were examined in order to elucidate the influence of ring substituents of ClPA on reactivity, whose results are shown in Figure 5 and Table II. The shapes of the copolymer composition curves do not depend on the ring substituents. The relative reactivity of the ClPA derivatives increases in the order, Cl < (H) < $CH_3$, i.e. with increasing electron-donating effect of the ring substituents. When an electron-donating ring substituent is introduced, the $^{13}C$ NMR chemical shift of the Cl-bearing acetylenic carbon ($C_\alpha$) shows an upfield shift, which indicates that the electron density on the $C_\alpha$ increases (Table II). Meanwhile the $C_\beta$ value shows a downfield shift but the degree is smaller. Therefore, it is

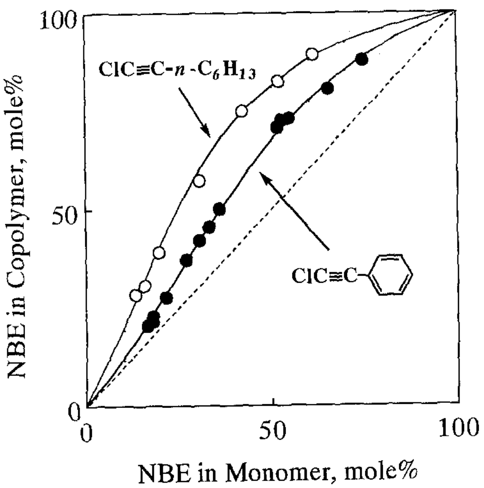


**Figure 4.** Composition curves for the copolymerizations of ClC≡CR with NBE by $MoCl_5$–*n*-$Bu_4Sn$ (in toluene, –20 °C, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$ mM, $[M]_{0,total} = 0.30$ M).

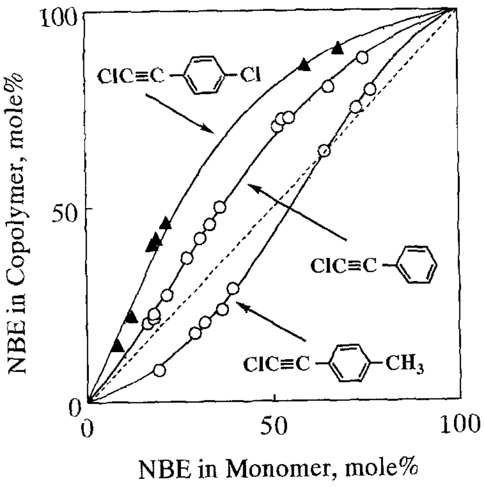
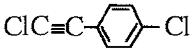
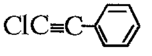
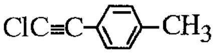


**Figure 5.** Composition curves for the copolymerizations of ClPA derivatives with NBE by $MoCl_5$–*n*-$Bu_4Sn$ (in toluene, –20 °C, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$mM, $[M]_{0,total} = 0.30$M).

**Table II.** Monomer Reactivity Ratios for the Copolymerizations of $ClC{\equiv}CR$ ($M_1$) with NBE ($M_2$) by $MoCl_5$–$n$-$Bu_4Sn$[a] and $^{13}C$ NMR Data[b]

| $M_1$ | $r_1$ | $r_2$ | $r_1 \times r_2$ | $C_\alpha$ [c], ppm | $C_\beta$ [c], ppm |
|---|---|---|---|---|---|
| $ClC{\equiv}C$–$n$-$C_6H_{13}$ | 0.69 ± 0.06 | 6.4 ± 0.43 | 4.4 | 56.9 | 69.6 |
|  | 0.58 ± 0.06 | 5.4 ± 0.54 | 3.1 | 68.3 | 69.1 |
|  | 1.0 ± 0.05 | 3.1 ± 0.14 | 3.2 | 67.9 | 69.4 |
|  | 3.5 ± 0.23 | 3.5 ± 0.19 | 8.3 | 67.1 | 69.5 |

[a] Copolymerized in toluene at –20 °C, $[MoCl_5]$ = [$n$-$Bu_4Sn$] = 10 mM, $[M]_{0,total}$ = 0.30 M. [b] Measured in $CDCl_3$. [c] $ClC_\alpha{\equiv}C_\beta$-R (R = alkyl or phenyl).

thought that an electron-donating ring substituent increases the electron density on the triple bond and, in turn, the coordinating ability of the monomer resulting in an increase in the relative reactivity of the acetylene.

The reciprocal $r_2$ stands for the relative reactivity of a ClPA derivative ($M_1$) to NBE ($M_2$) towards the NBE propagating end in these copolymerizations. A plot of $\log(1/r_2)$ vs. the substituent constant ($\sigma$), so-called Hammett plot, gave a good linear relationship, from the slope of which the reaction constant ($\rho$) was determined as –0.91 (correlation coefficient r = 0.993). This negative $\rho$ value means that the propagating end possesses an electrophilic nature. It is noted that this value is similar to those for the copolymerization of phenylacetylene with *para*-substituted phenylacetylenes by $WCl_6$ ($\rho$ = –1.2) (13) and for the copolymerization of *para*- and *meta*-substituted phenylacetylenes with NBE by $WCl_6$ ($\rho$ = –1.1) (9).

## Acknowledgement

We thank Mr. H. Makio for his technical assistance.

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**Accepted April 5, 1994 Shi**