

# Metathesis copolymerization of phenylacetylene with cycloolefins catalysed by $WCl_6-n-Bu_4Sn$

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Copolymerizations of phenylacetylene with various polycyclic olefins (norbornene, dimethanooctahydronaphthalene, deltacyclene, norbornadiene, benzonorbornadiene, ethylidenebicycloheptene and trimethylsilylnorbornadiene) by  $WCl_6-n-Bu_4Sn$  catalyst were investigated. Phenylacetylene and these cycloolefins were simultaneously consumed. Formation of random copolymers was confirmed by the g.p.c. curves, u.v.–visible spectra and H–H COSY n.m.r. spectra of the copolymerization products. The copolymer composition curves were obtained and the monomer reactivity ratios were determined. The reactivities of these cycloolefins were close to or lower than that of phenylacetylene. Most of the  $r_1 \times r_2$  values were about unity or lower. In the case of norbornene-type monomers, the larger the ring strains of cycloolefins, the larger the reactivities to the phenylacetylene propagating end. Monocyclic olefins were scarcely or not consumed in the copolymerization with phenylacetylene. © 1997 Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

Ring-opening metathesis polymerization (ROMP) of various cycloolefins proceeds in the presence of group 5 and 6 transition metal catalysts<sup>1,2</sup>. The propagating species in this polymerization are metal carbenes, which is demonstrated by living polymerizations using metal carbene initiators<sup>3,4</sup>.

Substituted acetylenes also polymerize with group 5 and 6 transition metal catalysts to form polymers having alternating double bonds in the main chain<sup>5,6</sup>. The metathesis mechanism has recently been accepted on the basis of both living polymerizations by metal carbene initiators<sup>7,8</sup> and chain transfer reactions to acyclic olefins<sup>9,10</sup>.

Because both propagating species in the above-mentioned two polymerizations are metal carbenes, there is a possibility that cycloolefins copolymerize with substituted acetylenes. In fact, we have reported the formation of copolymers in the copolymerizations of norbornene with substituted acetylenes<sup>11</sup>. This fact supports the idea that polymerization of substituted acetylenes by group 5 and 6 transition metal catalysts proceeds via the metathesis mechanism. The reactivities of ring-substituted phenylacetylenes depend on the electronic and steric effects of the ring substituents, and the coordinating abilities of the monomers to active species govern the reactivities of the monomers in these copolymerizations<sup>12</sup>. Copolymerizations of norbornene with chlorine-containing acetylenes by Mo catalysts<sup>13</sup> and with *tert*-butylacetylene by a W carbene complex<sup>14</sup> have also been reported.

In general, the reactivity of cycloolefins in ROMP is greatly affected by the ring strain, and the scission of metallacyclobutane rings plays an important role in the propagation reaction. It is hence interesting to determine the reactivity of the cycloolefins in the copolymerization with substituted acetylenes.

This study deals with the copolymerizations of phenylacetylene with various cycloolefins catalysed by  $WCl_6-n-Bu_4Sn$ . Norbornene (NBE), dimethanooctahydronaphthalene (DMON), deltacyclene (DC), norbornadiene (NBDE), benzonorbornadiene (BN), ethylidenebicycloheptene (EBH) and trimethylsilylnorbornadiene (TMSN) were used as cycloolefins (*Figure 1*). The formation of random copolymers in these copolymerizations was confirmed. Their copolymer composition curves were depicted and the monomer reactivity ratios were determined. The relationship between the structure and reactivity of cycloolefins is discussed.

## EXPERIMENTAL

### Materials

Phenylacetylene (Aldrich) was distilled twice from calcium hydride at reduced pressure before use. NBE and NBDE (Aldrich) were commercially obtained, and DMON and EBH were donated by Mitsubishi Chemical Co. and San Petrochemical, Ltd., respectively. DC<sup>15</sup>, BN<sup>16</sup> and TMSN<sup>17</sup> were prepared according to the literature methods. All these cycloolefins were distilled twice from calcium hydride under a nitrogen atmosphere or at reduced pressure. Toluene and *o*-xylene as polymerization solvents were purified by standard methods.  $WCl_6$  (Strem) was used as purchased. *n*- $Bu_4Sn$  was distilled before use.

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Copolymerization

Copolymerizations were carried out under dry nitrogen in a prebaked flask equipped with a three-way stopcock. The polymerization conditions were: in toluene (in *o*-xylene for EBH and TMSN; to measure g.c.), 30°C (0°C for NBDE and TMSN; to decelerate polymerization),  $[M]_{0,\text{total}} = 0.50 \text{ M}$ ,  $[\text{WCl}_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ . The catalyst solution was aged at 30°C for 15 min before use. The conversions of both monomers were determined by measuring the initial and final monomer concentrations by g.c. The copolymerization products for characterization were isolated by precipitation of reaction mixtures into a large amount of methanol, filtered off and dried to constant weight under vacuum at room temperature and employed for various analyses.

Product characterization

The g.p.c. analyses were performed with a Jasco Trirotar liquid chromatograph equipped with Shodex A803, A804 and A805 polystyrene gel columns (Showa Denko Co., Japan) and a refractive index/u.v. (r.i./u.v.) dual detector. The eluent was  $\text{CHCl}_3$ , and a polystyrene calibration was used. U.v.-visible spectra were measured in  $\text{CCl}_4$  with a Shimadzu UV2200 spectrophotometer. H-H COSY n.m.r. spectra were observed on a JEOL GSX-270 spectrometer in  $\text{CDCl}_3$  at room temperature.

Calculation of monomer reactivity ratios

Monomer reactivity ratios were calculated by the method of Yezrielev *et al.* from nearly ten pairs of  $f_1$  (an average mole fraction of monomer 1 ( $M_1$ ) in the copolymerization system) and  $F_1$  (a mole fraction of  $M_1$  unit in the copolymer) obtained from copolymerizations carried out at several monomer feeds. A detailed procedure has been described in a previous paper<sup>12</sup>.

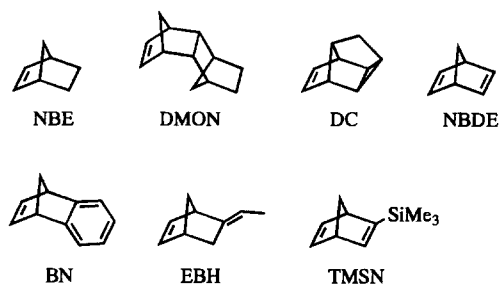


Figure 1

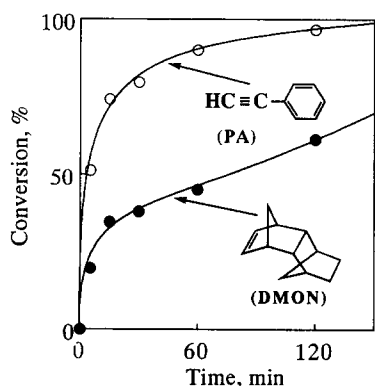


Figure 2 Copolymerization of phenylacetylene with DMON by  $\text{WCl}_6$ - $n\text{-Bu}_4\text{Sn}$  (in toluene, 30°C,  $[\text{WCl}_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ ,  $[M_1]_0 = [M_2]_0 = 0.25 \text{ M}$ )

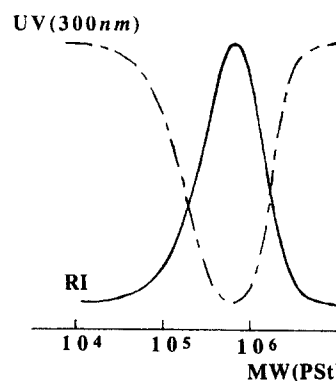


Figure 3 Molecular weight distribution curves of the product in the copolymerization of phenylacetylene with DMON (sample: the products at 120 min in Figure 1)

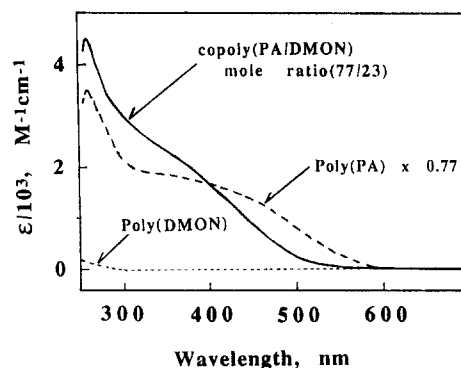


Figure 4 U.v.-visible spectra of the products in the co- and homo-polymerization of phenylacetylene with DMON (sample: the products at 120 min in Figure 1)

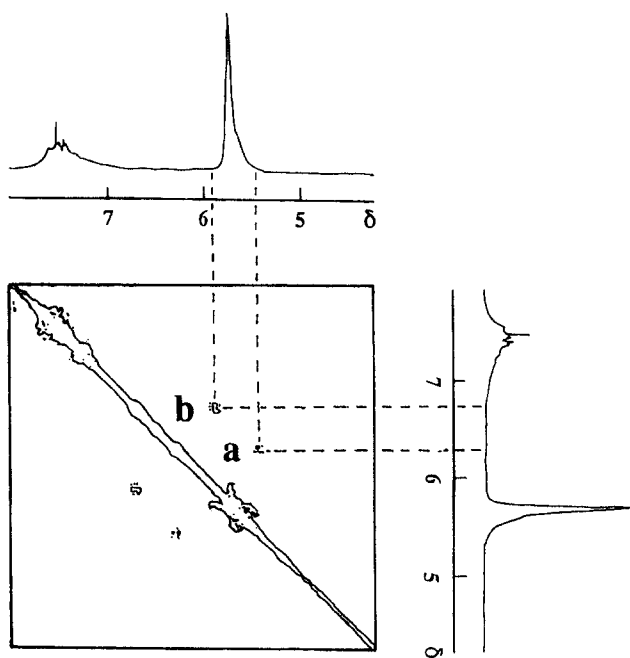


Figure 5 H-H COSY n.m.r. spectrum of the product in the copolymerization of phenylacetylene with DMON (sample: the products at 120 min in Figure 1; 270 MHz, in  $\text{CDCl}_3$ )

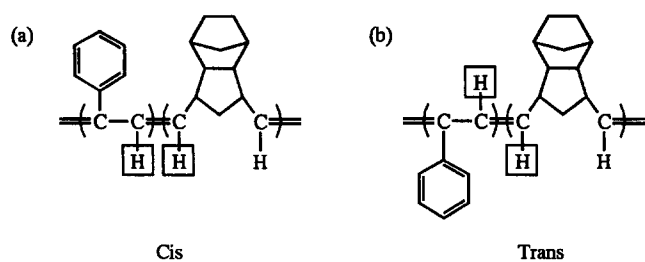


Figure 6

## RESULTS AND DISCUSSION

## Copolymerization of phenylacetylene with DMON: confirmation of copolymer formation

Figure 2 demonstrates the time-conversion curves for the  $WCl_6$ - $n$ -Bu<sub>4</sub>Sn-catalysed copolymerization of phenylacetylene with DMON at a 1:1 monomer feed ratio. Both monomers were simultaneously consumed without an induction phase. Phenylacetylene was more reactive than DMON. The product of copolymerization for 120 min was used for analyses stated below.

The g.p.c. curve of the product is shown in Figure 3. The weight-average molecular weight ( $M_w$ ) was about 52 000. The molecular weight distribution was unimodal and hardly

depended on whether the detector was the r.i. or u.v. detector. Both phenylacetylene and DMON sequences are observable with the r.i. detector, while only the phenylacetylene sequence is visible with the u.v. detector. Hence this finding suggests the formation of a copolymer in which the two monomer units are randomly distributed.

Figure 4 shows u.v.-visible spectra of the present copolymer and poly(phenylacetylene). Since the mole ratio of phenylacetylene:DMON in this copolymer was 77:23, the spectrum of poly(phenylacetylene) was multiplied by the mole fraction (0.77) of the copolymer for the sake of comparison. Poly(DMON) has no absorption above 300 nm, and hence this spectrum of poly(phenylacetylene) can be regarded as the spectrum of a mixture of homopolymers that has the same composition as the copolymer does. Obviously, the absorption of the copolymer is stronger below 400 nm and weaker above 400 nm than that of the poly(phenylacetylene). This suggests that the conjugation of the phenylacetylene sequence is shortened by insertion of DMON.

The H-H COSY n.m.r. spectrum of the copolymer is shown in Figure 5. Correlation peaks **a** ( $\delta$  6.3 and 5.5) and **b** ( $\delta$  6.8 and 5.9) show the existence of cis and trans phenylacetylene-DMON dyads, respectively (Figure 6).

These results clearly show the formation of a random

Table 1 Homo- and copolymerization of phenylacetylene ( $M_1$ ) and cycloolefins ( $M_2$ ) by  $WCl_6$ - $n$ -Bu<sub>4</sub>Sn<sup>a</sup>

$M_2$	Time, min	Monomer conversion, %		Polymer <sup>b</sup>		$M_1$ , mol%	
		$M_1$	$M_2$	Yield, wt%	$M_w^c$	From monomer convn <sup>d</sup>	From <sup>1</sup> H n.m.r. <sup>e</sup>
none <sup>f</sup>	120	83	—	73	14000	100	100
	120	54	100	78	48000	65	64
	60	27	91	84	52000	77	77
	120	24	67	60	28000	74	68
	90	90	96	88	— <sup>h</sup>	52	— <sup>h</sup>
	20	46	99	95	99000	68	66
	50	79	99	77	57000	56	53
	40	71	95	85	69000	57	57

<sup>a</sup> Polymerized in toluene at 30 °C,  $[WCl_6] = [n\text{-Bu}_4\text{Sn}] = 10$  mM,  $[M_1]_0 = [M_2]_0 = 0.25$  M

<sup>b</sup> MeOH-insoluble part

<sup>c</sup> Determined by g.p.c.

<sup>d</sup> Determined by measuring monomer conversions with g.c.

<sup>e</sup> Determined by the <sup>1</sup>H n.m.r. spectrum of polymer

<sup>f</sup>  $[M_1]_0 = 0.50$  M

<sup>g</sup> Polymerized at 0 °C

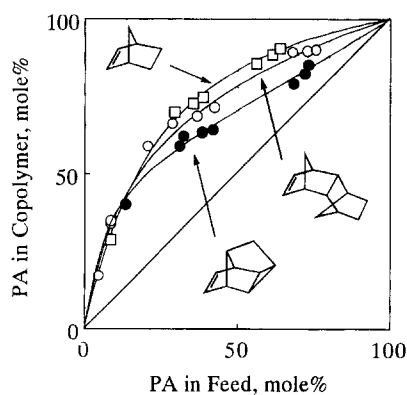
<sup>h</sup> Insoluble in  $CHCl_3$  ( $CDCl_3$ )

<sup>i</sup> Polymerized in *o*-xylene

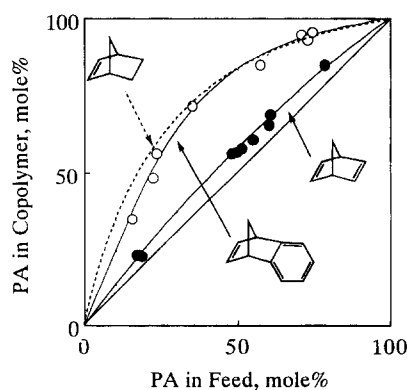
copolymer in the copolymerization of phenylacetylene with DMON.

#### Copolymerizations of phenylacetylene with polycyclic olefins: reactivity of cycloolefins

Copolymerizations of phenylacetylene with various polycyclic olefins (NBE, DC, NBDE, BN, EBH and TMSN) by  $WCl_6$ - $n$ -Bu<sub>4</sub>Sn catalyst were investigated. The results for a 1:1 monomer feed ratio are summarized in Table 1, along with the results of homopolymerizations of phenylacetylene and its copolymerization with DMON. The formation of random copolymers in all these copolymerizations was confirmed by time-conversion curves, g.p.c. curves, u.v.-visible spectra and H-H COSY n.m.r. spectra as in the above-stated copolymerization of phenylacetylene with DMON. The copolymerization of phenylacetylene with NBDE yielded a polymer insoluble in CHCl<sub>3</sub> and CCl<sub>4</sub> at high monomer conversions. The molecular weights of these copolymers were higher than that of the phenylacetylene homopolymer. The reactivities of the present cycloolefins are obviously different from one another. As the apparent copolymer compositions determined from the monomer consumption by means of g.c. analysis coincided with the counterparts from the <sup>1</sup>H n.m.r. spectra of the copolymers, the side reactions that involve only either comonomer can be denied. Hence, copolymer composition curves were determined from monomer conversions by means of g.c. analyses.



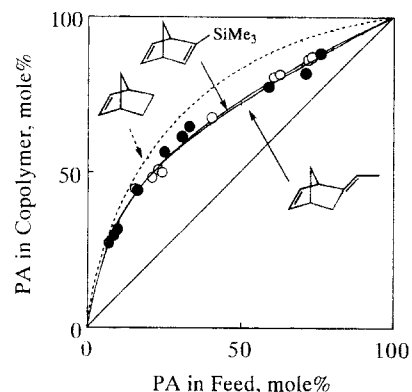
**Figure 7** Composition curves for the copolymerization of phenylacetylene with NBE, DMON and DC (in toluene, 30°C,  $[WCl_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ ,  $[M]_{0,\text{total}} = 0.50 \text{ M}$ )



**Figure 8** Composition curves for the copolymerization of phenylacetylene with NBE, NBDE and BN (in toluene, 30°C (NBE, BN) or 0°C (NBDE),  $[WCl_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ ,  $[M]_{0,\text{total}} = 0.50 \text{ M}$ )








The composition curves for the copolymerization of phenylacetylene with the cycloolefins are shown in Figure 7 for NBE, DMON and DC, in Figure 8 for NBDE and BN and in Figure 9 for EBH and TMSN. For comparison, the composition curve for the copolymerization of phenylacetylene with NBE is shown as a dotted curve in Figures 8 and 9. All of the copolymer composition curves stay over the diagonal line, indicating that phenylacetylene is more reactive than the cycloolefins. Among these cycloolefins, NBDE is the most reactive, while NBE is the least polymerizable.

Table 2 lists the monomer reactivity ratios  $r_1$ ,  $r_2$  and their product  $r_1 \times r_2$ . NBE shows a reactivity of about one-fifth that of phenylacetylene towards both of the phenylacetylene



**Figure 9** Composition curves for the copolymerization of phenylacetylene with NBE, EBH and TMSN (in toluene (NBE) or *o*-xylene (EBH, TMSN), 30°C (NBE, EBH) or 0°C (TMSN),  $[WCl_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ ,  $[M]_{0,\text{total}} = 0.50 \text{ M}$ )

**Table 2** Monomer reactivity ratios for the copolymerizations of phenylacetylene ( $M_1$ ) with cycloolefins ( $M_2$ )<sup>a</sup>






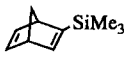

Cycloolefin ( $M_2$ )	$r_1$	$r_2$	$r_1 r_2$
	5.15	0.23	1.18
	3.14	0.15	0.48
	1.62	0.11	0.18
 <sup>b</sup>	1.47	0.78	1.08
	6.24	0.51	3.34
 <sup>c</sup>	1.92	0.15	0.28
 SiMe <sub>3</sub> <sup>b, c</sup>	2.10	0.16	0.33

<sup>a</sup> Polymerized in toluene at 30 °C,  $[WCl_6] = [n\text{-Bu}_4\text{Sn}] = 10 \text{ mM}$ ,  $[M]_{0,\text{total}} = 0.50 \text{ M}$

<sup>b</sup> Polymerized at 0 °C

<sup>c</sup> Polymerized in *o*-xylene

**Table 3** Reciprocal  $r_1$  for the copolymerizations of phenylacetylene ( $M_1$ ) with cycloolefins ( $M_2$ )<sup>a</sup> and <sup>13</sup>C n.m.r. data of cycloolefins

Cycloolefin ( $M_2$ )	$1/r_1 (= k_{12}/k_{11})$	$\delta(C_{sp^2}),$ ppm	$J_{=C-H},$ Hz
	0.19	135.2	164.8
	0.32	135.1	166.7
	0.52	135.9 134.4	163.9 169.9
	0.62	135.0	167.8
-----			
	0.16	142.5	173.0
	0.48	142.3 143.1	171.9 173.0
	0.68	142.9	173.0

<sup>a</sup> See Table 2 for polymerization conditions

and NBE propagating ends. In the case of DMON, both  $r_1$  and  $r_2$  are smaller than those of NBE, and  $r_1 \times r_2$  is about 0.5, showing a slight alternating tendency. This is more evident with DC, and  $r_1 \times r_2$  is about 0.2. NBDE showed the highest reactivity among the present cycloolefins, which is close to that of phenylacetylene. In contrast, the reactivity of BN is similar to that of NBE. The  $r_1$  of EBH was smaller than that of NBE. The self-propagation of TMSN seems more difficult than that of NBDE from the small  $r_2$  value. Many of the  $r_1 \times r_2$  values are approximately unity or smaller. The result that the  $r_1 \times r_2$  values are smaller than unity suggests that the self-propagation of the cycloolefins is difficult owing to steric effects.

Table 3 summarizes the reciprocal  $r_1$  values and <sup>13</sup>C n.m.r. data of cycloolefins, in which the cycloolefin monomers have been divided into NBE-type (NBE, DMON, EBH and DC) and NBDE-type (BN, TMSN and NBDE) groups and arranged according to the magnitude of  $1/r_1$ . The  $1/r_1$  values stand for the relative reactivity of a cycloolefin to phenylacetylene towards the phenylacetylene propagating end. The reactivity of the cycloolefin monomer is thought to be governed by the electron density of its double bond, the ring strain, steric hindrance, etc. The  $\delta(C_{sp^2})$  values can be correlated to the electron density of the double bond of the cycloolefins, and are about 135 and 142–143 ppm for NBE- and NBDE-type monomers, respectively. Whereas the  $\delta(C_{sp^2})$  values show no significant difference in each group, the reciprocal  $r_1$  values differ greatly from one another. Thus the correlation between  $\delta(C_{sp^2})$  and  $r_1$  is negligible. The coupling constant  $J_{=C-H}$

can be correlated to the ring strain of cycloolefins. For the NBE-type monomers, the order of  $J_{=C-H}$  corresponds to that of  $1/r_1$ , suggesting that the relative reactivity is explicable in terms of ring strain. Hence, in this case, the scission of metallacyclobutane should be rate-determining in the propagation. On the other hand, for the NBDE-type monomers, the  $J_{=C-H}$  is almost constant, whereas the reciprocal  $r_1$  varies in the range 0.16–0.68. Therefore, the relative reactivity of these monomers seem to be governed by factors other than the scission of the ring.

#### Copolymerization of phenylacetylene with monocyclic olefins

Copolymerizations of phenylacetylene with monocyclic olefins such as cyclopentene, cyclohexene, cyclooctene, cyclododecene, etc. were examined under the same conditions as for the above-stated polycyclic olefins. Phenylacetylene was completely consumed after 24 h, while these cycloolefins were scarcely consumed. This result shows the low reactivity of these cycloolefins.

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