Polymerization of (*o*-Alkylphenyl)acetylenes and Polymer Properties

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ABSTRACT: (*o*-Alkylphenyl)acetylenes (alkyl: Et, *n*-Bu, *n*-C₆H₁₃, *n*-C₈H₁₇, and *iso*-Pr) polymerized in high yields with W and Mo catalysts. MoCl₅-based catalysts, which are not very active to phenylacetylene (PA), exhibited high activity like the WCl₆ counterparts. The weight-average molecular weights ($\bar{M}_w$) of the polymers having *o*-*n*-alkyl groups were in the range 2×10^4 – 55×10^4 , being similar to or slightly higher than those of poly(PA), while the highest $\bar{M}_w$ value of poly(*o*-*iso*-Pr-phenylacetylene) [poly(*iso*-PrPA)] reached 1×10^6 . The formed polymers were dark red, and had the structure $[\text{CH}=\text{C}(\text{C}_6\text{H}_4\text{-alkyl})]_n$. They were thermally more stable than poly(PA) according to the thermogravimetric analysis. The polymers with long *o*-*n*-alkyl groups were soluble in aliphatic solvents (*e.g.*, hexane) unlike poly(PA), and their softening points were lower. Poly(*o*-*iso*-PrPA) was film-forming, and fairly gas-permeable (P_{O_2} 27 barrers, $P_{\text{O}_2}/P_{\text{N}_2}$ 2.2).

KEY WORDS Substituted Acetylene / (*o*-Alkylphenyl)acetylene / Transition-Metal Catalyst / Metathesis Polymerization / Substituted Polyacetylene / Gas Permeability /

In the polymerization of monosubstituted acetylenes by W and Mo catalysts, a general tendency has been observed that monomers with bulky substituents provide high molecular weight polymers. For instance, 1-hexyne, which is sterically not crowded, forms only oligomers whose weight-average molecular weights ($\bar{M}_w$) are a few thousand.^{1,2} In contrast, *tert*-butylacetylene, which is very crowded, produces a polymer whose $\bar{M}_w$ exceeds 1×10^5 .^{1–4} The steric effect of phenylacetylene is moderate, and the $\bar{M}_w$ of the polymer formed is usually 2×10^4 – 3×10^4 .^{1,5}

Thus it is interesting to examine how high the molecular weight of the polymer becomes when a substituent is introduced onto the *ortho* position of phenylacetylene to increase steric crowding. In fact, we studied the polymerization of (*o*-methylphenyl)acetylene (*o*-MePA) to find the formation of a polymer having high molecular weight ($\bar{M}_w$ up to 8×10^5 with

W(CO)₆-*hν* catalyst) and good thermal stability.⁶ It has recently been found that phenylacetylenes with even bulkier *ortho* groups (*e.g.*, CF₃⁷ and Me₃Si^{8,9}) yield polymers with very high molecular weight ($\bar{M}_w$ 1×10^6 and above).

The present study deals with the polymerization of (*o*-alkylphenyl)acetylenes, namely, phenylacetylenes having ethyl, *n*-butyl, *n*-hexyl, *n*-octyl, and *iso*-propyl groups at the *ortho* position (*o*-EtPA, *o*-*n*-BuPA, *o*-*n*-C₆H₁₃PA, *o*-*n*-C₈H₁₇PA, and *o*-*iso*-PrPA, respectively) [eq 1]. The structure and properties of the product polymers have also been investigated.

EXPERIMENTAL

Three monomers having *o*-*n*-Bu, *o*-*n*-C₆H₁₃, and *o*-*n*-C₈H₁₇ groups were prepared from

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phenylacetylene by modifying the literature method [eq 2].¹⁰ The preparation of *o*-*n*-C₆H₁₃PA is detailed below.

o-C₆H₁₃PA: After flushed with dry nitrogen, a 1-liter round-bottomed flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. A hexane solution of *n*-BuLi (250 ml, 0.40 mol) was placed in the flask, and a part of hexane (*ca.* 130 ml) was evaporated with an aspirator. Tetrahydrofuran (THF; 130 ml; dried over sodium) was added dropwise at -20°C . Then, a solution of phenylacetylene (22 ml, 0.20 mol) in THF (50 ml) was gradually added and the reaction mixture was left for 1 h at 0°C . After the mixture was cooled at -65°C , a solution of KO-*t*-Bu (22.5 g, 0.20 mol) in THF (200 ml) was added dropwise followed by stirring at -10°C for 2 h. At -65°C *n*-C₆H₁₃I (30 ml, 0.20 mol) was added dropwise, and the mixture was left at room temperature overnight. Water (20 ml) was carefully added. The reaction product was extracted with hexane, washed with 5% hydrochloric acid and water. The organic phase was dried over anhydrous sodium sulfate overnight. Hexane was evaporated, and the product was distilled twice from calcium hydride at reduced pressure; bp $95^\circ\text{C}/7\text{ mmHg}$, purity $>99\%$ (by gas chromatography (GC)).

The phenylacetylenes with *o*-*n*-Bu and *o*-*n*-C₈H₁₇ were prepared in the same way (*n*-BuPA bp $83^\circ\text{C}/10\text{ mmHg}$, *n*-C₈H₁₇PA bp $123^\circ\text{C}/4\text{ mmHg}$). However, both *o*-EtPA (bp $61^\circ\text{C}/12.5\text{ mmHg}$), which is difficult to perfectly separate from phenylacetylene by simple distillation, and *o*-*iso*-PrPA (bp $54^\circ\text{C}/10\text{ mmHg}$), for which the foregoing process is not applicable because of difficulty in the alkylation reaction, were prepared from 2-methyl-3-

butyn-2-ol and 1-alkyl-2-iodobenzenes by the same method as for (*o*-methylphenyl)acetylene.⁶

Transition-metal chlorides and organometallic cocatalysts were commercially obtained, and used without further purification. Toluene, CCl₄ etc. as polymerization solvents were washed by the standard methods, and distilled twice from calcium hydride.

Polymerizations were carried out under dry nitrogen in the same manner as described elsewhere.^{6,8,9} Unless otherwise stated, polymerizations were carried out in toluene (for MCl_x catalysts) or in CCl₄ [for M(CO)₆-*hv* catalysts] at 30°C for 24 h; [M]₀ = 1.0 M, [Cat] = 20 mM (MCl_x catalysts) or 10 mM [M(CO)₆-*hv* catalysts].

The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) of polymers were determined by gel permeation chromatography (GPC) with use of a polystyrene calibration. Thermogravimetric analyses (TGA) were carried out in air with a Shimadzu 20B thermal analyzer (heating rate $10^\circ\text{C}/\text{min}$). IR spectra were recorded in KBr pellets on a Shimadzu IR435 spectrophotometer. ¹³C NMR spectra were obtained with a JEOL FX90Q spectrometer (in CDCl₃). Electrical conductivities were measured by the DC steady-state method at 25°C in the dark.

RESULTS AND DISCUSSION

Polymerization of *o*-*n*-Alkylphenylacetylenes

Table I shows results for the polymerization of *o*-*n*-C₆H₁₃PA by various W and Mo catalysts. The three W catalysts in Table I provide methanol-insoluble polymers in high yields over 75%. The polymerization rate decreased in the order of WCl₆-Ph₄Sn > WCl₆ > W(CO)₆-*hv*. The $\bar{M}_w$ values of the polymers are about 6×10^4 – 1×10^5 , and the highest value of 1×10^5 was attained with the W(CO)₆-*hv* catalysts.

MoCl₅-based catalysts also formed poly(*o*-*n*-C₆H₁₃PA)s in good yields (Table I), whereas

the $\text{Mo}(\text{CO})_6\text{-}h\nu$ catalysts was hardly effective. The $\bar{M}_w$ values of the polymers obtained with Mo catalysts were similar to those with W catalysts. These findings are quite interesting when it is taken into account that phenylacetylene does not polymerize in high yield with

MoCl_5 and the $\bar{M}_w$ of the polymer is no more than several thousand.^{1,5}

As seen in Figure 1, the polymerization of *o*-*n*- $\text{C}_6\text{H}_{13}\text{PA}$ by $\text{WCl}_6\text{-Ph}_4\text{Sn}$ is completed in

Table I. Polymerization of *o*-*n*- $\text{C}_6\text{H}_{13}\text{PA}$ by W and Mo catalysts^a

Catalyst	Monomer convn/%	Polymer ^b		
		Yield/%	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
WCl_6	100	83	58	24
$\text{WCl}_6\text{-Ph}_4\text{Sn}$	100	89	63	24
$\text{W}(\text{CO})_6\text{-}h\nu^d$	100	77	100	42
MoCl_5	100	100	37	16
$\text{MoCl}_5\text{-Ph}_4\text{Sn}$	98	98	120	30
$\text{Mo}(\text{CO})_6\text{-}h\nu^d$	23	2	—	—

^a Polymerized in toluene at 30°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = [\text{Ph}_4\text{Sn}] = 20 \text{ mM}$.

^b Methanol-insoluble product.

^c Determined by GPC.

^d Polymerized in CCl_4 ; $[\text{Cat}] = 10 \text{ mM}$.

Figure 1. Time profile of the polymerization of *o*-*n*- $\text{C}_6\text{H}_{13}\text{PA}$ (in toluene, 30°C, 24 h, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = [\text{Ph}_4\text{Sn}] = 10 \text{ mM}$).

Figure 2. Effect of temperature on the polymerization of *o*-*n*- $\text{C}_6\text{H}_{13}\text{PA}$ ($\text{WCl}_6\text{-Ph}_4\text{Sn}$ (1 : 1), $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ (1 : 1): in toluene, 24 h, $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = 20 \text{ mM}$; $\text{W}(\text{CO})_6\text{-}h\nu$: in CCl_4 , $[\text{W}(\text{CO})_6] = 10 \text{ mM}$).

a few minutes, showing high activity of this catalyst. Although the $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ catalyst is less active, no induction period is observed and the reaction has reached 100% conversion after 24 h. Regarding polymerization temperature, high polymer yields are achieved at 0°C and above when $\text{WCl}_6\text{-Ph}_4\text{Sn}$ is employed, whereas it is the case at 30°C and above with $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ and $\text{W(CO)}_6\text{-}h\nu$ as catalysts (Figure 2). This also demonstrates the high catalytic activity of $\text{WCl}_6\text{-Ph}_4\text{Sn}$ for *o-n*- $\text{C}_6\text{H}_{13}\text{PA}$. The $\bar{M}_w$ of polymer was usually *ca.* 1×10^5 under conditions in Figure 2, showing

the largest value of *ca.* 2×10^5 with $\text{WCl}_6\text{-Ph}_4\text{Sn}$ at -30°C .

Polymerizations of four homologous monomers having *o-n*-alkyl groups of different lengths ($\text{R} = \text{Me}$, Et , *n*-Bu, and *n*- C_8H_{17}) were studied by using W and Mo catalysts (Table II). The data of phenylacetylene are also included in Table II for the sake of comparison. These (*o-n*-alkylphenyl)acetylenes produced polymers in high yields with W and Mo catalysts other than $\text{Mo(CO)}_6\text{-}h\nu$. The $\bar{M}_w$ values of the product polymers were in the range $1 \times 10^4\text{--}55 \times 10^4$, and tended to be higher with the $\text{W(CO)}_6\text{-}h\nu$ catalyst. Neither of the yields and $\bar{M}_w$ values of the polymers was greatly affected by the length of the *o-n*-alkyl group. It is, however, noted that all the (*o-n*-alkylphenyl)acetylenes polymerize in higher yields with $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ catalyst than does phenylacetylene.

Table II. Polymerization of (*o-n*-alkylphenyl)acetylenes by W and Mo catalysts^a

Catalyst	Monomer convn/%	Polymer ^b		
		Yield/%	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
alkyl: H				
WCl ₆ -Ph ₄ Sn	100	65	41	20
W(CO) ₆ - <i>hν</i> ^d	82	78	243	75
MoCl ₅ -Ph ₄ Sn	35	14	25	6.0
Mo(CO) ₆ - <i>hν</i> ^d	9	2	10	5.7
alkyl: Me				
WCl ₆ -Ph ₄ Sn	100	95	80	10
W(CO) ₆ - <i>hν</i> ^d	100	95	240	50
MoCl ₅ -Ph ₄ Sn	100	100	132	22
Mo(CO) ₆ - <i>hν</i> ^d	14	5	42	12
alkyl: Et				
WCl ₆ -Ph ₄ Sn	100	100	30	11
W(CO) ₆ - <i>hν</i> ^d	53	44	550	100
MoCl ₅ -Ph ₄ Sn	70	70	20	8.3
Mo(CO) ₆ - <i>hν</i> ^d	15	3	—	—
alkyl: <i>n</i> -Bu				
WCl ₆ -Ph ₄ Sn	100	100	24	9.5
W(CO) ₆ - <i>hν</i> ^d	100	98	130	57
MoCl ₅ -Ph ₄ Sn	100	93	36	9.0
Mo(CO) ₆ - <i>hν</i> ^d	17	10	150	49
alkyl: <i>n</i> -C ₈ H ₁₇				
WCl ₆ -Ph ₄ Sn	100	100	42	17
W(CO) ₆ - <i>hν</i> ^d	96	84	120	28
MoCl ₅ -Ph ₄ Sn	98	88	100	23
Mo(CO) ₆ - <i>hν</i> ^d	16	11	79	20

^a Polymerized in toluene at 30°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = 20 \text{ mM}$.

^b Methanol-insoluble product.

^c Determined by GPC.

^d Polymerized in CCl_4 ; $[\text{Cat}] = 10 \text{ mM}$.

Polymerization of (*o*-iso-Propylphenyl)acetylene

Results on the polymerization of *o*-iso-PrPA are shown in Table III. All the three W catalysts in the table polymerize this monomer in over 65% yields. The polymers obtained with $\text{WCl}_6\text{-Ph}_4\text{Sn}$ and $\text{W(CO)}_6\text{-}h\nu$ possess $\bar{M}_w$'s around 2×10^5 . MoCl_5 and its mixture with Ph_4Sn also form poly(*o*-iso-PrPA)s quantitatively.

Table III. Polymerization of *o*-iso-PrPA by W and Mo catalysts^a

Catalyst	Monomer convn/%	Polymer ^b		
		Yield/%	$\bar{M}_w/10^3$ ^c	$\bar{M}_n/10^3$ ^c
WCl_6	100	100	63	32
$\text{WCl}_6\text{-Ph}_4\text{Sn}$	100	95	270	88
$\text{W(CO)}_6\text{-}h\nu^d$	66	65	220	81
MoCl_5	100	100	59	27
$\text{MoCl}_5\text{-Ph}_4\text{Sn}$	100	100	1100	370
$\text{Mo(CO)}_6\text{-}h\nu^d$	12	5	200	55

^a Polymerized in toluene at 30°C for 24 h; $[\text{M}]_0 = 0.50 \text{ M}$, $[\text{Cat}] = [\text{Ph}_4\text{Sn}] = 20 \text{ mM}$.

^b Methanol-insoluble product.

^c Determined by GPC.

^d Polymerized in CCl_4 ; $[\text{Cat}] = 10 \text{ mM}$.

ively, whereas the $\text{Mo}(\text{CO})_6\text{-}h\nu$ catalyst is hardly effective. Quite interestingly, the $\bar{M}_w$ of the polymer with $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ exceeds 1×10^6 .

Whereas the polymerization of phenylacetylene by $\text{MoCl}_5\text{-Ph}_4\text{Sn}$ levels off and does not reach 100% conversion, those of *ortho*-substituted phenylacetylenes generally reach higher conversions. This suggests that the steric effect of *ortho*-substituted monomers makes the termination reaction (e.g., coupling of metal carbenes) difficult.

In order to gain knowledge on the relative reactivity of *ortho*-substituted monomers, their copolymerizations with phenylacetylene were carried out in toluene at 30°C; $[\text{M}_1]_0 = [\text{M}_2]_0 = 0.25 \text{ M}$, $[\text{WCl}_6] = [\text{Ph}_4\text{Sn}] = 20 \text{ mM}$. The relative reaction rates were *o*- $\text{C}_6\text{H}_{13}\text{PA}$: *o*-*iso*-PrPA : PA = 0.7 : 0.8 : 1. This indicates the *ortho* substituents decrease the reactivity in propagation.

Polymer Properties

The structure and properties of poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$) and poly(*o*-*iso*-PrPA) were studied by using the sample obtained with the $\text{WCl}_6\text{-Ph}_4\text{Sn}$ catalyst (cf., Tables I and III).

The values of elemental analysis agreed well with the ones calculated for the polymerization products; *Anal.* Poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$): Calcd for $(\text{C}_{14}\text{H}_{18})_n$: C, 86.13%; H, 9.41%. Found: C, 86.02%; H, 9.26%. Poly(*o*-*iso*-PrPA): Calcd for $(\text{C}_{11}\text{H}_{12})_n$: C, 91.70%; H, 8.30%. Found: C, 91.40%; H, 8.60%.

The IR data are: Poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$): IR (KBr) 3061 (m), 3020 (m), 2957 (s), 2856 (s), 1464 (m), 1377 (m), and 750 (s) cm^{-1} . Poly(*o*-*iso*-PrPA): IR (KBr) 3060 (m), 3021 (m), 2959 (s), 2867 (s), 1483 (s), 1458 (m), 1443 (s), 1383 (s), 1361 (s), and 752 (s) cm^{-1} . Strong absorptions at 750–752 cm^{-1} are characteristic of *ortho*-substituted benzenes. Weak bands at 1601–1607 cm^{-1} are assignable to $\text{C}=\text{C}$ stretching. The band at 3300–3310 cm^{-1} due to the $\equiv\text{C-H}$ stretching seen in the monomers has completely disappeared in the polymers.

The ^{13}C NMR spectra of poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$) and poly(*o*-*iso*-PrPA) show multiple peaks based on olefinic and phenyl carbons in the region δ 145–120 (Figure 3). Two peaks due to the acetylenic carbons in the monomer (δ 83.6 and 80.2 ppm for *o*- $\text{C}_6\text{H}_{13}\text{PA}$) and (δ 82.3 and 80.7 ppm for *o*-*iso*-PrPA) have disappeared in the polymers formed. These analytical and spectral data are compatible with the polymer structure composed of alternating double bonds in the main chain as shown in Figure 3.

Unlike poly(phenylacetylene) [poly(PA)], poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$), and poly(*o*-*iso*-PrPA) clearly shows absorption maxima in the visible region (Figure 4). Their wavelengths are somewhat longer than that of poly(*o*-MePA). It seems a general tendency that introduction of *ortho* substituents onto poly(PA) generates an absorption maximum in the visible

Figure 3. ^{13}C NMR spectrum of poly(*o*- $\text{C}_6\text{H}_{13}\text{PA}$) (a) and poly(*o*-*iso*-PrPA) (b) (CDCl_3 solution).

Table IV. Properties of poly[(*o*-alkylphenyl)acetylenes]^a

	Alkyl				
	H	<i>n</i> -Bu	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₈ H ₁₇	<i>iso</i> -Pr
Form	Solid	Solid	Solid	Rubbery	Solid
$\lambda_{\max}^b/\text{nm}$	225	487	483	457	465
($\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1}$)	(6000)	(5100)	(4700)	(4400)	(4300)
Softening pt/ $^{\circ}\text{C}$	220	180	100	70	350
$T_{\text{d}}^c/^{\circ}\text{C}$	200	240	270	250	240
σ^d/Scm^{-1}	4×10^{-15}	5×10^{-13}	1×10^{-13}	—	3×10^{-15}
Spin density/ g^{-1}	8×10^{16}	6×10^{16}	3×10^{16}	6×10^{16}	—

^a Polymer samples prepared with WCl₆-Ph₄Sn.^b Measured in CCl₄.^c Onset temperature of weight loss in TGA in air.^d Electrical conductivity. **Figure 4.** UV-Visible spectra of poly(phenylacetylenes) (CCl₄ solution).

region.⁶⁻⁹ This is probably due to that the main chain takes more conjugated conformations owing to the steric effect of *ortho* substituents, but the definite reason has not been reached at the moment.

While poly(PA) is a light brown solid, the polymers in the present study are dark red to dark brown substances. Their softening point progressively decreased as the *n*-alkyl group became longer (Table IV). The present polymers, including poly(*o*-*iso*-PrPA), began to lose weight at about 250°C in the thermogravimetric analysis (TGA) in air; these onset temperatures are higher than that of poly(PA) (200°C), indicating higher thermal stability.

Table V summarizes solubility properties of the present polymers as well as of poly(PA). The present polymers completely dissolved in

Table V. Solubility of poly[(*o*-alkylphenyl)acetylenes] in various solvents^a

Solvent	Alkyl					
	H	Et	<i>n</i> -Bu	<i>n</i> -C ₆ H ₁₃	<i>n</i> -C ₈ H ₁₇	<i>iso</i> -Pr
Hexane	}	i	ps	s	s	ps
Et ₂ O						
Toluene	}	s	s	s	s	s
(CH ₂ Cl) ₂						
THF	}	s	s	ps	i	i
Acetophenone						
Nitrobenzene	}	i	i	i	i	i
Acetone						
Acetic acid	}					

^a s, soluble; ps, partly soluble; i, insoluble.

aromatic hydrocarbons, halogenated hydrocarbons, and tetrahydrofuran (THF) irrespective of the kind of alkyl groups. The alkyl length affected the solubility property to some extent. Thus the polymers having long *n*-alkyl groups were soluble in aliphatic hydrocarbons, while insoluble in polar aromatic hydrocarbons. The films obtained by casting the *o*-*n*-alkyl-substituted polymers from toluene solution were too brittle to maintain their form, probably because their molecular weights were not high enough. In contrast, a free-standing film could be fabricated by casting poly(*o*-*iso*-PrPA) solution.

The present polymers were electrical insulators like poly(PA). Their unpaired-electron

densities (25°C) were in the order of 10^{16} spin g^{-1} .

The oxygen permeability coefficient (P_{O_2}) of poly(*o*-*iso*-PrPA) at 25°C was 27 barrers [1 barrer = $1 \times 10^{-10} \text{ cm}^3 \text{ (STP)} \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cm Hg}^{-1}$], and the separation factor against nitrogen ($P_{\text{O}_2}/P_{\text{N}_2}$) was 2.2. The P_{O_2} value of this polymer is comparable to that of natural rubber (23 barrers).¹¹ When compared with other *ortho*-substituted poly(phenylacetylenes) [poly(*o*-MePA) 8.1 barrers, poly(*o*-CF₃PA) 25 barrers, poly(*o*-Me₃SiPA) 78 barrers¹²], it turns out that bulky *ortho* groups tend to enhance the P_{O_2} value.

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