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Polymerization of *o*-chloro- and *o*-bromo-substituted phenylacetylenes and polymer properties

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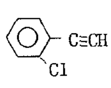
SUMMARY

(*o*-Chlorophenyl)acetylene (*o*-ClPA), (*o*-bromophenyl)acetylene (*o*-BrPA), and (*o*,*o*,*p*-trichlorophenyl)acetylene (Cl_3PA) polymerized in high yields in the presence of W and Mo catalysts. Nb and Ta catalysts were also effective in producing poly(Cl_3PA). Poly(*o*-ClPA) formed was soluble in such solvents as toluene and $CHCl_3$, and its maximum weight-average molecular weight was 3×10^5. Though poly(*o*-BrPA) obtained with WCl_6-Ph_4Sn was soluble, those obtained with other catalysts were insolble in any solvent. Further, poly(Cl_3PA) was insoluble irrespective of the kind of catalyst. These polymers were dark brown solids and did not lose weight below 230°C, being more stable than poly(phenylacetylene).

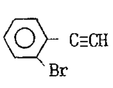
INTRODUCTION

Various ortho-substituted derivatives of phenylacetylene (PA) have been polymerized with W and Mo catalysts by Masuda and Higashimura; e.g., $HC{\equiv}CC_6H_5$-*o*-CH_3 (1), $HC{\equiv}CC_6H_5$-*o*-CF_3 (2), $HC{\equiv}CC_6H_5$-*o*-$SiMe_3$ (3). The product polymers have higher molecular weights than poly(PA). Thus the ortho substituents seem to favor the increase of polymer molecular weight. Recently, (*p*-butyl-*o*,*o*,*m*,*m*-tetrafuluorophenyl)acetylene, which can be regarded as *o*,*o*-difluoro-substituted PA derivative, has been polymerized to produce a polymer whose maximum weight-average molecular weght ($\bar{M}_w$) reached up to 2×10^6 (4).

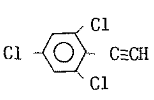
(*o*-Chlorophenyl)acetylene (*o*-ClPA), (*o*-bromophenyl)acetylene (*o*-BrPA), and (*o*,*o*,*p*-trichlorophenyl)acetylene (Cl_3PA) are other monomer candidates among *o*-halogeno-substituted PAs, and chlorine and bromine are expected to exhibit different steric and electronic effects compared with fluorine. Therefore, it is intresting to study their polymerization behavior.



o-ClPA



o-BrPA

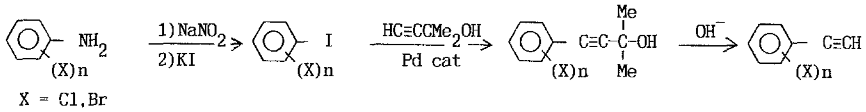


Cl_3PA

This paper reports the polymerization of *o*-ClPA, *o*-BrPA and Cl_3PA. The structure and properties of the product polymers are also clarified. The results are compared with those for PA and other *o*-substituted PAs.

EXPERIMENTAL

The monomers were synthesized from the corresponding anilines according to the following scheme with reference to the literature method (1,5). Cl_3PA is a new compound.



o-ClPA: overall yield 48%, purity 99% [gas chromatography (GC)], bp 63°C/10mmHg, d_4^{20} 1.146 [lit. (6), bp 71°C/18mmHg, d_4^{20} 1.125]. o-BrPA: overall yield 52%, purity 99% (GC), bp 83°C/10mmHg , d_4^{20} 1.427 [lit.(6), bp 92°C/20mmHg, d_4^{20} 1.443]. Cl_3PA: overall yield 30%, purity 99%(GC), mp 66°C.

Transition-metal catalysts and organometallic cocatalysts were commercially obtained and used without further purification. Solvents for polymerization were purified by usual methods. All the procedures for catalyst preparation and polymerization were carried out under a dry nitrogen atomosphere. Monomer conversions were determined by GC, and yields of methanol-insoluble polymers were determined by gravimetry.

The number-average molecular weights ($\overline{M}_n$) and $\overline{M}_w$ of the polymer were determined by gel permeation chromatography (GPC) (Waters 510, eluent $CHCl_3$, polystyrene calibration). IR spectra and UV-visible spectra were recorded with Jasco IR-700 and Shimadzu UV-160A spectrophotometers, respectively. ^{13}C NMR spectra were taken with a JEOL EX270 spectrometer. Thermogravimetric analysis (TGA) was carried out with a Seiko TG/DTA 200 thermal analyzer (heating rate 10°C/min, in air).

RESULTS AND DISCUSSION

Polymerization of o-ClPA, o-BrPA, and Cl_3PA

Table I gives results for the polymerization of o-ClPA by groups 5 and 6 transition-metal catalysts. W catalysts yielded methanol-insoluble polymers virtually quantitatively. Polymerization by WCl_6-Ph_4Sn in toluene completed within 2 min, being fairly rapid, and the $\overline{M}_w$ of polymer was 9×10^4. Polymerization by $W(CO)_6$-$h\nu$ was slower, and achieved a higher $\overline{M}_w$ around 2×10^5. Although $MoCl_5$-Ph_4Sn also produced a polymer in high yield, $Mo(CO)_6$-$h\nu$ hardly formed the polymer. Nb and Ta catalysts mainly afforded methanol-soluble oligomers; the main products were cyclotrimers according to GPC and IR.

Figure 1 illustrates the effect of temperature on the polymerizations of o-ClPA by WCl_6-Ph_4Sn and $W(CO)_6$-$h\nu$. The polymer yields with WCl_6-Ph_4Sn and $W(CO)_6$-$h\nu$ were virtually quantitative at 30°C and above. The $\overline{M}_w$ with WCl_6-Ph_4Sn showed a maximum at 30°C. The $\overline{M}_w$ with $W(CO)_6$-$h\nu$, on the other hand, increased with decreasing temperature, reaching 3×10^5 at 0°C. This $\overline{M}_w$ value is more or less higher than that of poly(PA) (2×10^5), but lower than those of other poly(o-substituted PAs) (8×10^5-20×10^5).

Polymerization of o-BrPA was examined to clarify the effect of bromine as an o-substituent. As shown in Table II, all the W and Mo catalysts, including $Mo(CO)_6$-$h\nu$, were effective in producing poly(o-BrPA) in high yields. The product polymers, however, were partly or completely insoluble in any solvent except that obtained with WCl_6-Ph_4Sn. The $\overline{M}_w$ of poly(o-BrPA) with WCl_6-Ph_4Sn was not higher than that of poly(o-ClPA) obtained under the same condition.

Table I

Polymerization of o-ClPA by Various Catalysts[a]

Catalyst	Monomer	Polymer[b]		
	convn,%	yield,%	$\overline{M}_w/10^3$[c]	$\overline{M}_n/10^3$[c]
WCl_6-Ph_4Sn	100	100	97	39
$W(CO)_6$-hν[d]	98	96	193	73
$MoCl_5$-Ph_4Sn	100	94	34	15
$Mo(CO)_6$-hν[d]	37	5		
$NbCl_5$-Ph_4Sn[e]	97	14		
$TaCl_5$-Ph_4Sn[e]	13	0		

[a] Polymerized in toluene at 30°C for 24 h; $[M]_0$ = 1.0 M, [Cat] = [Ph_4Sn] = 10 mM.

[b] Methanol-insoluble product.

[c] Determined by GPC.

[d] Polymerized in CCl_4.

[e] Polymerized at 80°C.

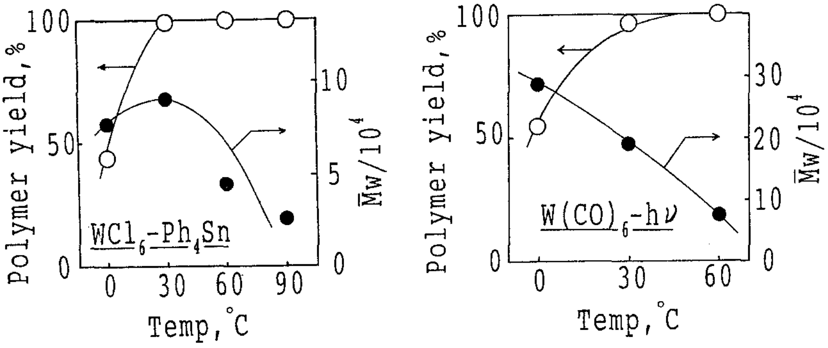


Figure 1. Effect of temperature on the polymerization of o-ClPA by WCl_6-Ph_4Sn(1:1) and $W(CO)_6$-hν (in toluene, 24 h, $[M]_0$ = 1.0 M, [Cat] = 10 mM; in CCl_4 in case of the $W(CO)_6$-hν catalyst)

Table II

Polymerization of *o*-BrPA by Various Catalysts[a]

Catalyst	Monomer convn,%	Polymer[b] yield,%
WCl_6-Ph_4Sn	100	95[c]
$W(CO)_6$-hν[d]	100	92
$MoCl_5$-Ph_4Sn	87	73
$Mo(CO)_6$-hν[d]	86	80
$NbCl_5$-Ph_4Sn[e]	100	33
$TaCl_5$-Ph_4Sn[e]	100	3

[a] Polymerized in toluene at 30°C for 24 h; $[M]_0$ = 1.0 M, [Cat] = 10 mM.

[b] Methanol-insoluble product.

[c] $\bar{M}_w$:63x10^3, $\bar{M}_n$:28x10^3 (GPC).

[d] Polymerized in CCl_4

[e] Polymerized at 80°C.

Table III

Polymerization of Cl_3PA by Various Catalysts[a]

Catalyst	Monomer convn,%	Polymer[b] yield,%
WCl_6-Ph_4Sn	100	96
$W(CO)_6$-hν[c]	71	60
$MoCl_5$-Ph_4Sn	86	81
$Mo(CO)_6$-hν[c]	59	42
$NbCl_5$-Ph_4Sn[d]	100	97
$TaCl_5$-Ph_4Sn[d]	100	97

[a] Polymerized in toluene at 30°C for 24 h; $[M]_0$ = 0.50 M, [Cat] = 10 mM.

[b] Methanol-insoluble product.

[c] Polymerized in CCl_4.

[d] Polymerized at 80°C.

Cl_3PA contains chlorines at both ortho positions, and would behave differently in polymerization owing to the steric hindrance. Table III lists results for the polymerization by various catalysts. Interestingly, not only W and Mo but also Nb and Ta catalysts afforded poly(Cl_3PA) in high yields, which is in contrast to the case of *o*-ClPA and *o*-BrPA. It has been known that Nb and Ta catalysts selectively give cyclotrimers from most monosubstituted acetylenes except those with bulky substituents (7). Hence, it can be said that chlorines at both ortho positions play an important role in polymerization by Nb and Ta catalysts. All poly(Cl_3PA)s, however, were insoluble in any solvent, irrspective of the kind of catalysts employed.

In order to gain knowledge on the relative reactivity of *o*-ClPA, *o*-BrPA, and Cl_3PA, 1:1 copolymerizations of *o*-ClPA with PA, *o*-BrPA, and Cl_3PA were carried out with WCl_6-Ph_4Sn catalyst. In the copolymerization with PA, *o*-ClPA was slightly less reactive than PA. *o*-ClPA was consumed at a rate similar to that of *o*-BrPA in their copolymerization. Further, in the copolymerization with Cl_3PA, *o*-ClPA reacted much faster than the comonomer. Thus the relative reactivity of these monomers can be expressed as follows: PA > *o*-ClPA $\simeq$ *o*-BrPA > Cl_3PA. This order is in correspondence with the general tendency that a monomer having bulkier and/or more strongly electron-withdrawing substituent exhibits a lower relative reactivity in the copolymerization. The similar reactivities of *o*-ClPA and *o*-BrPA are probably due to compensation of steric and electronic effects.

Structure and Properties of Polymers

The structure of the present polymers did not essentially differ with the polymerization conditions. The data stated below have been obtained with the polymer samples prepared with WCl_6-Ph_4Sn.

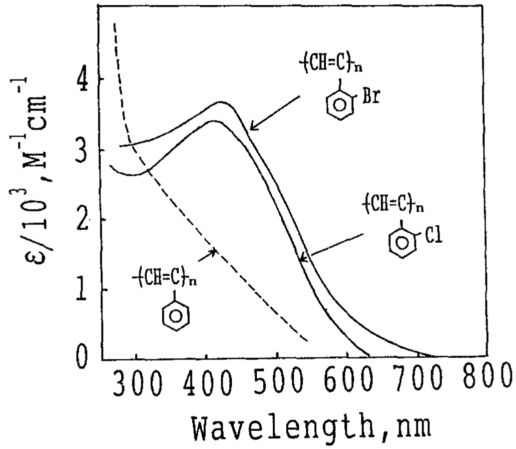


Figure 2. UV-visible spectra of poly(phenylacetylenes) (in THF)

The elemental analysis data of polymers agreed well with their theoretical values: Poly(*o*-ClPA): Calcd for $(C_8H_5Cl)_n$: C 70.35%, H 3.69%, Cl 25.96% Found: C, 70.96%, H 4.01%, Cl 24.87%. Poly(*o*-BrPA): Calcd for $(C_8H_5Br)_n$: C 53.08%, H 2.78%, Br 44.14% Found: C, 52.66%, H 3.02%, Br 43.77%. Poly(Cl_3PA): Calcd for $(C_8H_3Cl_3)_n$: C 46.77%, H 1.47%, Cl 51.76% Found: C, 46.34%, H 1.30%, Cl 52.13%.

The IR spectra of the polymers exhibited no absorptions characteristic of the H-C≡ (3290 cm^{-1}) and C≡C (2110 cm^{-1}) bonds which were seen in the monomers. The ^{13}C NMR spectra of poly(*o*-ClPA) showed a multiplet only in the region δ 145-115. The two peaks due to acetylenic carbons of *o*-ClPA monomer [68.1 (HC≡) and 89.9 (≡CAr)] disappeared in the polymer. The IR and ^{13}C NMR spectra thus support the idea that the polymers possess alternating double bonds in the main chain. No information about the geometric structure of the main chain, however, could be obtained from these spectra.

In the UV-visible spectra of poly(*o*-ClPA) and poly(*o*-BrPA), absorption maxima are seen at 420 nm and 430 nm, respectively, while that of poly(PA) is below 300 nm (Figure 2). The absorption bands of poly(*o*-ClPA) and poly(*o*-BrPA) are in a region of longer wavelength than that of poly(PA). In general, the absorption maximum and absorption band of *o*-substituted poly(PA) shift to longer wavelengths with increasing bulkiness of the substituent (2). The results for poly(*o*-ClPA) and poly(*o*-BrPA) are consonant with it.

Poly(*o*-ClPA), poly(*o*-BrPA) and poly(Cl_3PA) have the form of dark brown solid irrespective of polymerization conditions. Poly(*o*-ClPA) disssolved in many organic solvents; it was soluble in benzene, toluene, xylene, CCl_4, $CHCl_3$, PhCl, PhBr, anisole, 1,4-dioxane, tetrahydrofuran, N,N-dimethylacetamide. Its nonsolvents include hexane, cyclohexane, ethyl acetate, acetone, triethylamine, dimethyl sulfoxide, and methanol. These solubility properties resemble those of poly(PA) and other *o*-substituted poly(PAs). In contrast to this, solubility of poly(*o*-BrPA) and poly(Cl_3PA) was fairly poor. They were partly or completely

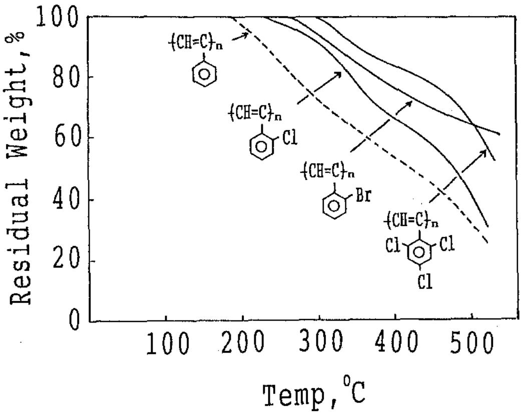


Figure 3. TGA curves of poly(phenylacetylenes) in air

insoluble in any solvent stated above except poly(o-BrPA) obtained with WCl_6-Ph_4Sn, which dissolved in toluene, $CHCl_3$, PhCl, PhBr, and tetrahydrofuran. Inferior solubility of poly(o-BrPA) and poly(Cl_3PA) is probably due to that the presence of the bulky rigid o-bromophenyl group and o,o,p-trichlorophenyl group makes the polymers very stiff as in the case of poly(1-adamantyl-acetylene) (8).

Poly(o-ClPA), poly(o-BrPA), and poly(Cl_3PA) began to lose weight at about 230°C, 250°C, and 300°C, respectively, in air (Figure 3). These temperatures are higher than that of poly(PA) (200°C), and comparable with those of other o-substituted poly(PAs) (250-300°C). These results can be interpreted in terms that the o-substituents sterically protect main-chain double bonds from attack by oxygen.

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