NOTES

Polymerization of (o-Phenylphenyl)acetylene and (2,5-Di-tert-butylphenyl)acetylene and Polymer Properties

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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. Thus, it has recently been found that highly sterically crowded phenylacetylenes (PAs) having bulky groups at the ortho position produce polymers in good yields, and the product polymers have higher molecular weights than that of poly(phenylacetylene) [poly(PA)]: e.g., poly($HC \equiv CC_6H_4$-o-iso-Pr), weight-average molecular weights ($\bar{M}_w$) 1×10^6;[1] poly($HC \equiv CC_6H_4$-o-GeMe$_3$), $\bar{M}_w$ 7×10^5;[2] and poly($HC \equiv CC_6H_3$-2-SiMe$_3$-4-OSiMe$_2$-t-Bu), $\bar{M}_w$ 9×10^5;[3] cf. poly(PA), $\bar{M}_w$ $\sim 3 \times 10^4$. Consequently these ortho-substituted poly(PAs) can be fabricated into tough films unlike poly(PA). Therefore it will be interesting to examine the effect of as bulky or even bulkier ortho hydrocarbon groups on the polymerizability, polymer molecular weight and polymer properties of PAs.

The present note deals with the polymerization of PAs having a very bulky hydrocarbon group at the ortho position. The monomers used are (o-phenylphenyl)acetylene (o-PhPA) and (2,5-di-tert-butylphenyl)acetylene [2,5-(t-Bu)$_2$PA]. The structure and properties of the product polymers have also been invesitigated.

EXPERIMENTAL

The two monomers (new compounds) were synthesized according to Scheme 1; i.e., o-PhPA was prepared by the Sandmeyer reaction[4] of o-aminobiphenyl followed by Pd-catalyzed coupling with 2-methyl-3-butyn-2-ol and base-catalyzed acetone elimination.[5] o-PhPA: bp 100 °C (3 mmHg), d 1.079. 2,5-(t-Bu)$_2$PA was prepared from benzene via 1,4-di-tert-butylbenzene[6] and its iodination product[7] and then in a similar way. 2,5-(t-Bu)$_2$PA: bp 140°C (3 mmHg), d 0.899. Transition-metal compounds and organometallic cocatalysts were commercially obtained, and used without further purification.
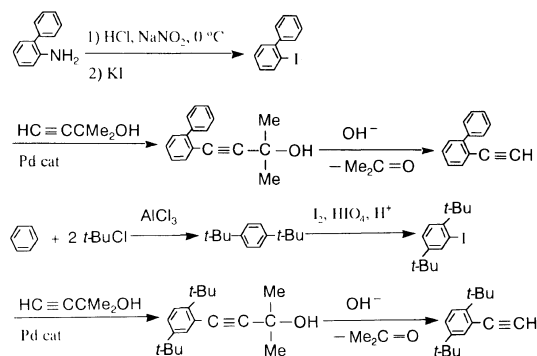
Scheme 1.

All the procedures for catalyst preparation and polymerization were carried out under dry nitrogen. The monomer conversions were determined by gas chromatography, and the yields of methanol-insoluble polymers were determined by gravimetry. Ultraviolet (UV)-visible spectra of solid polymer samples were

measured by a Shimadzu UV-2200 spectrophotometer at Shimadzu Co., Japan. Thermogravimetric analyses (TGA) were performed with a Shimadzu 20B thermal analyzer (heating rate $10°C \min^{-1}$, in air). IR spectra were recorded in KBr pellets on a Shimadzu FTIR-8100 spectrophotometer.

RESULTS AND DISCUSSION

Polymerization of (o-Phenylphenyl)acetylene (o-PhPA)

Table I summarizes results for the polymerization of o-PhPA by group 6 and 5 transition-metal catalysts. When WCl_6 alone and WCl_6–Ph_4Sn were used, methanol-insoluble polymers were obtained in good yields of ca. 80%. With the $W(CO)_6$–CCl_4–hv catalyst, however, both monomer conversion and polymer yield were lower. Mo catalysts ($MoCl_5$ alone, $MoCl_5$–Ph_4Sn and $Mo(CO)_6$–CCl_4–hv) also produced polymers in high yields. $NbCl_5$– n-Bu_4Sn and $TaCl_5$–n-Bu_4Sn, which give cyclotrimers selectively from sterically uncrowded monosubstituted acetylenes, provided polymers in moderate yields. The methanol-soluble products formed with W and Mo catalysts consisted of linear oligomers and cyclotrimers, while those with Nb and Ta catalysts were mostly cyclotrimers. In the polymerization of phenylacetylene, the polymer yield remains rather low with Mo catalysts,[8] and is null (cyclotrimers are selectively formed) with Nb and Ta catalysts.[9] Therefore it is interesting that introduction of a very bulky phenyl group onto the ortho position does not render the phenylacetylene unreactive but forms a polymer in sufficiently high yields.

Polymerization of (2,5-Di-tert-butylphenyl)acetylene [2,5-(t-Bu)$_2$PA]

Polymerization of 2,5-$(t$-$Bu)_2$PA was examined by using group 5 and 6 transition-metal catalysts (Table II). Among W catalysts, WCl_6 alone and WCl_6–Ph_4Sn afforded polymers in high yields over 50%. In contrast, $W(CO)_6$–CCl_4–hv catalyst did not show any activity for this monomer. Unlike the case of o-PhPA, none of the Mo catalysts polymerized this monomer in high yield. Among the group 5 catalysts, the $NbCl_5$–Ph_4Sn catalyst formed a polymer in ca. 50% yield. The rather low reactivity of this monomer is attributable to the remarkable steric effect of the two tert-butyl groups.

Structure and Properties of Polymers

The IR spectral data are as follows: poly(o-PhPA): IR (KBr) 3054 (m), 3019 (w), 1597 (w), 1476 (s), 1447 (m), 1431 (m), 1009 (m), 916 (m), 739 (s), and 700 (s) cm^{-1}. Poly[2,5-$(t$-$Bu)_2$PA]: IR (KBr) 2959 (s), 2869

Table I. Polymerization of o-PhPA by group 6 and 5 transition-metal catalysts[a]

Catalyst	Monomer convn %	Polymer[b] yield %
WCl_6	98	79
WCl_6–Ph_4Sn	96	85
$W(CO)_6$–CCl_4–hv[c]	46	37
$MoCl_5$	82	64
$MoCl_5$–Ph_4Sn	96	81
$Mo(CO)_6$–CCl_4–hv[c]	88	68
$NbCl_5$–n-Bu_4Sn	91	56
$TaCl_5$–n-Bu_4Sn	93	18

[a] Polymerized in toluene at 80°C for 24 h: $[M]_o =$ 0.50 M; [Cat] = [Cocat] = 20 mM.
[b] Methanol-insoluble product.
[c] Polymerized in CCl_4; [Cat] = 10 mM.

Table II. Polymerization of 2,5-$(t$-$Bu)_2$PA by group 6 and 5 transition-metal catalysts[a]

Catalyst	Monomer convn %	Polymer[b] yield %
WCl_6	88	56
WCl_6–Ph_4Sn	100	82
$W(CO)_6$–CCl_4–hv[c]	0	0
$MoCl_5$	38	2
$MoCl_5$–Ph_4Sn	26	1
$Mo(CO)_6$–CCl_4–hv[c]	34	3
$NbCl_5$–Ph_4Sn	84	54
$TaCl_5$–Ph_4Sn	21	0

[a] Polymerized in toluene at 80°C for 24 h: $[M]_o =$ 0.50 M; [Cat] = [Cocat] = 20 mM.
[b] Methanol-insoluble product.
[c] Polymerized in CCl_4; [Cat] = 10 mM.

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(m), 1603 (w), 1489 (m), 1362 (s), 1266 (m), 1202 (m), 1061 (m), and 826 (s) cm^{-1}. A strong absorption at 739 cm^{-1} in poly(*o*-PhPA) is characteristic of an *ortho*-disubstituted benzene. A band at 826 cm^{-1} in poly[2,5-(*t*-Bu)$_2$PA] is due to a 1,2,4-trisubstituted benzene. Weak bands at 1597 and 1603 cm^{-1} are assignable to C=C stretching. The bands at 3285 and 3314 cm^{-1} due to the ≡C–H stretching seen in the monomers have completely disappeared in the polymers.

Both of the present polymers have the forms of dark purple solids, whereas poly(PA) is a brown solid. The dark color suggests fairly wide conjugation systems. Unfortunately, the present polymers were insoluble in any organic solvent; this can be attributed to the bulky and rigid *ortho* substituents.

The UV-visible spectra (reflection method) of solid samples of poly(*o*-PhPA) and poly[2,5-(*t*-Bu)$_2$PA] had strong absorptions up to *ca.* 600 nm and their cutoffs were around 800 nm. This agrees with a general tendency that introduction of *ortho* substituents into poly-(PA) causes red shifts of the absorption in the UV-visible spectrum.[1–3]

Poly(*o*-PhPA) and poly[2,5-(*t*-Bu)$_2$PA] began to lose weight at 300 and 270°C, respectively, in the thermogravimetric analysis (TGA) in air (Figure 1). These temperatures are higher than that of poly(PA) (200°C). Thus these *ortho* substituents prove to be effective in enhancing the stability of poly(PA). The softening points of these polymers were above 290°C. The electrical conductivity of poly(*o*-PhPA) at 25°C was 9×10^{-13} S cm^{-1}, being in the insulator range like poly(PA). The unpaired-electron density of poly(*o*-PhPA) was 10^{18} spin/g, which is larger than the value of poly(PA) (7.9×10^{16} spin/g).[8]

CONCLUSIONS

(*o*-Phenylphenyl)acetylene and (2,5-di-*tert*-butylphenyl)acetylene polymerized with group 6 and 5 transition-metal catalysts irrespective
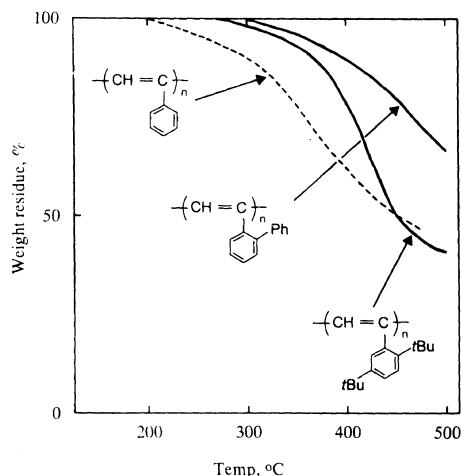

Figure 1. TGA curves of poly(phenylacetylene)s in air.

of the presence of the bulky *ortho* substituents; especially W catalysts achieved high yields of polymers. Both of the present polymers were dark purple solids and insoluble in any organic solvent owing to the rigid *ortho* substituents. The onset temperatures of weight loss of the polymers were 270°C and higher, indicating fairly high thermal stability.

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