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Polymerization and polymer properties of (2-methyl-5-*tert*-butylphenyl)acetylene: steric effects of the ring substituents

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Summary

(2-Methyl-5-*tert*-butylphenyl)acetylene (2Me5tBuPA) polymerized in the presence of $MoCl_5$–*n*-Bu_4Sn catalyst in 1,4-dioxane to give a high molecular weight polymer ($\overline{M}_w$ $8x10^5$). Not only $MoCl_5$- but also WCl_6-based catalysts were effective. The polymer obtained was a dark brown solid, soluble in organic solvents such as toluene and $CHCl_3$, and formed a free-standing film by solution casting. The onset temperature of weight loss of the polymer in air was 260 °C. Its oxygen permeability coefficient was 43 barrers, which is twice that of natural rubber. Differences from the results (usually lower molecular weight, not film-forming, and thermally less stable) of both poly(phenylacetylene) and poly[(*o*-methylphenyl)acetylene] are attributable to the synergistic steric effect of the *o*-methyl and *m*-*tert*-butyl groups.

Introduction

Phenylacetylene (PA) polymerizes with WCl_6 and $MoCl_5$, but the weight-average molecular weights ($\overline{M}_w$) of the formed polymer are usually no more than $2x10^4$–$3x10^4$ (1). Poly(phenylacetylene) [poly(PA)] does not provide a free-standing film owing to its low molecular weights. This polymer is unstable even at room temperature in air to slowly suffer oxidative degradation.

When polymerized with WCl_6- and $MoCl_5$-based catalysts, (*o*-methylphenyl)acetylene (*o*-MePA) yields a polymer whose $\overline{M}_w$ values are $2x10^5$–$4x10^5$ (2). This polymer does not give a tough film, either, probably because its molecular weight is not high enough. This polymer is thermally more stable than poly(PA) which is demonstrated by the fact that their onset temperatures (T_0) of weight loss in air are 200 °C and 250 °C, respectively.

PAs with bulkier ortho substituents such as isopropyl (3), trimethylsilyl (4), and trifluoromethyl (5) groups produce high molecular weight polymers whose $\overline{M}_w$ values reach $1x10^6$–$3x10^6$. Tough, free-standing films can be

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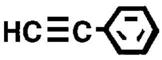
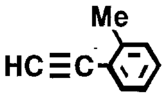
fabricated from all these polymers by casting their toluene solution. Their T_0 values are 240 °C (*i*-Pr), 280 °C (Me_3Si) and 300 °C (CF_3), indicating that the latter two polymers are thermally fairly stable.

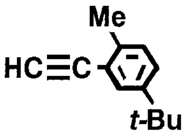
In the present study, we examined the polymerization and polymer properties of (2-methyl-5-*tert*-butylphenyl)acetylene (2Me5tBuPA) to clarify effects of the two ring substituents.



PA



***o*-MePA**



2Me5tBuPA

Experimental

Materials

2Me5tBuPA was synthesized similarly to *o*-MePA (2) by Pd-catalyzed coupling of 2-iodo-4-*tert*-butyltoluene with 2-methyl-3-butyn-2-ol followed by base-catalyzed elimination of acetone (6). 2-Iodo-4-*tert*-butyltoluene was prepared by iodination of 4-*tert*-butyltoluene (7). The crude monomer was distilled twice at reduced pressure from calcium hydride; bp 65 °C/4 mmHg, yield 57%, purity >99.9% [by gas chromatography (GC)], d_4^{20} 0.899. IR (KBr) 3293(s, $\nu_{\equiv C-H}$), 3071(m), 3025(m), 2965(s), 2869(s), 2105(s, $\nu_{C\equiv C}$), 1716(m), 1497(s), 1478(m), 1364(s), 1269(s), 1136(m), 1038(m), 895(s), and 826(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.5–7.1 (aromatic), 3.2 (s, 1, $HC\equiv$), 2.4 (s, 3, Me), and 1.3 (s, 9, 3Me) ppm. ^{13}C NMR ($CDCl_3$) δ 148.4, 137.6, 129.4, 125.9, 122.6, 121.4, 83.1($\equiv CAr$), 80.2($HC\equiv$), 34.2, 31.2, and 19.9 ppm. Transition-metal chlorides and carbonyls as well as organometallic cocatalysts were commercially obtained and used without further purification.

Procedures

Polymerizations were carried out in a Schlenk tube equipped with a three-way stopcock under a dry nitrogen atmosphere. The details have been described elsewhere (2). Monomer conversions were determined by GC. Molecular weights of polymers were determined by gel permeation chromatography (GPC; eluent, $CHCl_3$, polystyrene calibration).

IR, NMR, and UV-visible spectra, TGA, and gas permeabilities were measured in the same manner as described before (3). The analytical and spectral data of polymer (Table I, $MoCl_5$–*n*-Bu_4Sn, in 1,4-dioxane) were as follows: Calcd for $(C_{13}H_{10})_n$: C, 90.62; H, 9.38. Found: C, 89.64; H, 9.41. IR (KBr) 3065(m), 2778(m), 1889(s), 1607(s), 1495(m), 1362(s), 1266(m), 1202(s), 1032(s), 992(s), 895(s), and 816(s) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.2–

6.2 (br s, 4, C_6H_4), 5.5–5.1 (br s, 1, –CH=), 2.2–1.5 (br s, 3, Me), and 1.4–0.5 (s, 9, 3Me) ppm. ^{13}C NMR ($CDCl_3$) δ 150–120 (olefinic, aromatic), 34.2 (3Me), 31.2 (quaternary C), and 20.0 (Me) ppm.

Results and Discussion

Polymerization of 2Me5tBuPA

Polymerization of 2Me5tBuPA was examined by using various Mo and W catalysts (Table I). When $MoCl_5$-based catalysts were used as catalysts in toluene, the monomer was consumed quantitatively, and methanol-insoluble polymers were obtained in over 90% yields. When cocatalysts were added, polymerizations proceeded faster than by $MoCl_5$ alone. The polymerization proceeded virtually quantitatively not only in toluene, but also in the oxygen-containing solvents (anisole, 1,4-dioxane). The formed polymers dissolved in various organic solvents. The weight-average molecular weights ($\overline{M}_w$) of the polymers are $6x10^4$–$8x10^5$. The $\overline{M}_w$ of the polymer obtained with $MoCl_5$–*n*-Bu_4Sn in 1,4-dioxane shows the highest value of ca. $8x10^5$.

As seen in Table I, various W catalysts also gave polymers in good yields. However, the $\overline{M}_w$'s of the formed polymers were lower than those with the Mo catalysts. It is interesting to note here that W catalysts achieve higher polymer molecular weight for PA, while W and Mo catalysts yield

Table I. Polymerization of 2Me5tBuPA by Various Catalysts [a]

Catalyst	Solvent	Monomer	Polymer [b]		
		convn, %	Yield, %	$\overline{M}_w/10^3$ [c]	$\overline{M}_n/10^3$ [c]
$MoCl_5$	toluene	100	100	160	66
$MoCl_5$–*n*-Bu_4Sn	"	100	95	66	25
$MoCl_5$–Ph_4Sn	"	100	100	150	46
$MoCl_5$–*n*-Bu_4Sn	anisole	99	84	81	44
$MoCl_5$–*n*-Bu_4Sn	1,4-dioxane	100	92	830	380
$Mo(CO)_6$–hv	CCl_4	62	33	230	94
WCl_6	toluene	100	94	19	9.9
WCl_6–*n*-Bu_4Sn	"	100	100	22	7.8
WCl_6–Ph_4Sn	"	100	94	38	14
WCl_6–Ph_4Sn	1,4-dioxane	98	94	210	78
$W(CO)_6$–hv	CCl_4	100	97	66	24

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0$ = 0.50 M, [Cat] = [Cocat] = 10 mM. [b] Methanol-insoluble product. [c] Determined by GPC.

polymers of comparable molecular weights for *o*-MePA. Anyway, the present monomer produces polymers with higher molecular weights than *o*-MePA does under the same conditions. This seems due to the steric effect of the *m*-*t*-Bu group when the results of phenylacetylenes with bulky ortho substituents (3–5) are considered.

Polymerzation by $MoCl_5$-Based Catalysts in 1,4-Dioxane

The polymerization by $MoCl_5$-based catalysts in 1,4-dioxane, which provides a high molecular weight polymer, was studied in detail.

Table II shows effects of various organometallic cocatalysts on the polymerization. When $MoCl_5$ alone was used, both monomer conversion and polymer yield were low. In contrast, when suitable cocatalysts such as *n*-Bu_4Sn, Ph_3Bi, and Ph_3Sb were used, the monomer was virtually quantitatively consumed, and the polymer yields are higher than 90%. The $\overline{M}_w$ values of the formed polymer were $6x10^5$–$8x10^5$, the highest value being achieved with *n*-Bu_4Sn.

Figure 1 illustrates temperature dependence of the polymerization. While the polymer yield is moderate at 10 °C, it is as high as ca. 90% at 30–80 °C. In contrast, the $\overline{M}_w$ values of polymer is ca. $80x10^4$ at 10–30 °C but decreases with raising temperature. Hence 30 °C seems most suitable for the preparation of a high molecular weight polymer in high yield.

Under the conditions shown in Figure 2, the polymerization of 2Me5tBuPA is completed after 6 h, at which a methanol-insoluble polymer is obtained in ca. 90% yield. The molecular weight of the formed polymer tends to increase with polymer yield, which suggests the presence of a long-

Table II. Cocatalyst Effects on the Polymerization of 2Me5tBuPA by $MoCl_5$ [a]

Cocatalyst	Monomer convn, %	Polymer [b] Yield, %	$\overline{M}_w/10^3$ [c]	$\overline{M}_n/10^3$ [c]
none	19	3	60	20
n-Bu_4Sn	100	92	830	380
Ph_4Sn	28	2	110	39
Et_3SiH	66	55	430	190
Ph_3SiH	47	5	63	24
Ph_3Bi	95	95	740	310
Ph_3Sb	100	100	610	250

[a] Polymerized in 1,4-dioxane at 30 °C for 24 h; $[M]_0 = 0.50$ M, $[MoCl_5] = [Cocat] = 10$ mM. [b] Methanol-insoluble product.
[c] Determined by GPC.

lived propagating species. Since the polymer molecular weight did not decrease even though the polymerization system was left over 24 h, one can employ any polymerization time of 6 h and longer to achieve both high polymer yield and high molecular weight.

In order to gain knowledge on the reactivity of the present monomer, the copolymerization with *o*-MePA was carried out in 1,4-dioxane at 30 °C; $[M_1]_0 = [M_2]_0 = 0.25$ M, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$ mM. The reaction of 2Me5tBuPA relative to *o*-MePA was 2.4. In the copolymerization with PA, *o*-MePA is less reactive than PA (*o*-MePA : PA = 0.8 : 1) which has been attributed to the steric effect of the *o*-Me group (2). The high reactivity of the present monomer compared with that of *o*-MePA should, therefore, be due to the electron-donating nature of *t*-Bu group rather than its steric effect.

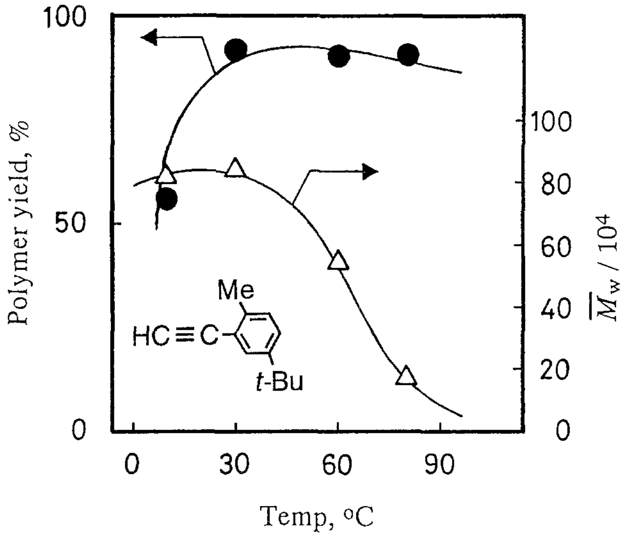


Figure 1. Effect of temperature on the polymerizations of 2Me5tBuPA and by $MoCl_5$–*n*-Bu_4Sn (in 1,4-dioxane, 24 h, $[M]_0 = 0.50$ M, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$ mM).

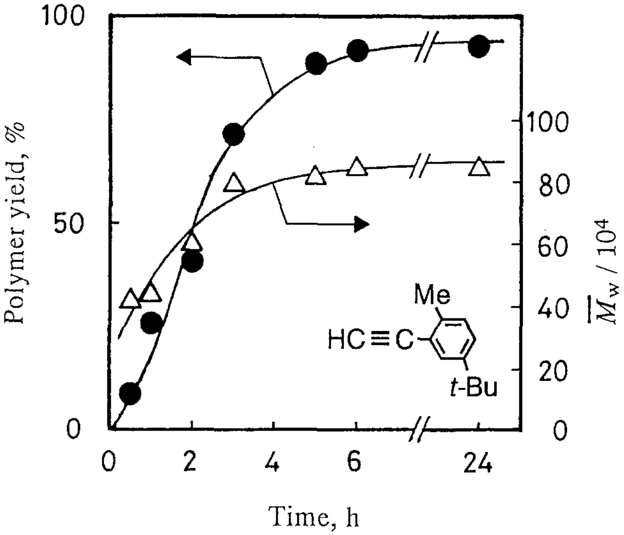


Figure 2. Time profile of the polymerization of 2Me5tBuPA by $MoCl_5$–*n*-Bu_4Sn (in 1,4-dioxane, 30 °C, $[M]_0 = 0.50$ M, $[MoCl_5] = [n\text{-}Bu_4Sn] = 10$ mM).

Polymer Structure

The values of elemental analysis of poly(2Me5tBuPA) agreed well with the calculated values (see the Experimental).

The IR spectrum of the polymer showed absorptions due to a 1,2,4-trisubstituted benzene at 895 and 816 cm^{-1}. The characteristic absorptions of ≡C-H (3293 cm^{-1}) and C≡C (2105 cm^{-1}) stretchings seen in the monomer have completely disappeared in the polymer. Instead, a band due to the C=C stretching is observed at 1607 cm^{-1} in the polymer. In the ^{13}C NMR spectrum, the monomer showed two peaks due to the acetylenic carbons at δ 83.1 and 80.2, which disappeared in the polymer. These spectral data support the idea that the present polymer has alternating double bonds along the main chain.

The UV-visible spectrum of poly(2Me5tBuPA) shows an absorption maximum at 480 nm (ε_{max} 3700 $M^{-1}\cdot cm^{-1}$), which shifts to a long wavelength as compared with that of poly(*o*-MePA) (2).

Polymer Properties

Poly(2Me5tBuPA) is a dark brown solid. It dissolved in toluene, hexane, CCl_4, $CHCl_3$, cyclohexane, tetrahydrofuran, diethyl ether, partly dissolved in $(CH_2Cl)_2$ and methyl benzoate, but did not dissolve at all in 1,4-dioxane, N,N-dimethylformamide, acetophenone, acetone, and methanol. These solubility properties are essentially the same as those of poly(*o*-MePA) (2). A free-standing film could be prepared by casting poly(2Me5tBuPA) from toluene solution, whereas poly(*o*-MePA) does not form a free-standing film. This seems due to a difference in molecular weights.

The onset temperatures of weight loss in air for poly(PA) and poly(*o*-MePA) are 200 and 250 °C, respectively (2). The temperature for the present polymer was 260 °C, being somewhat higher than that of poly(*o*-MePA) (Figure 3).

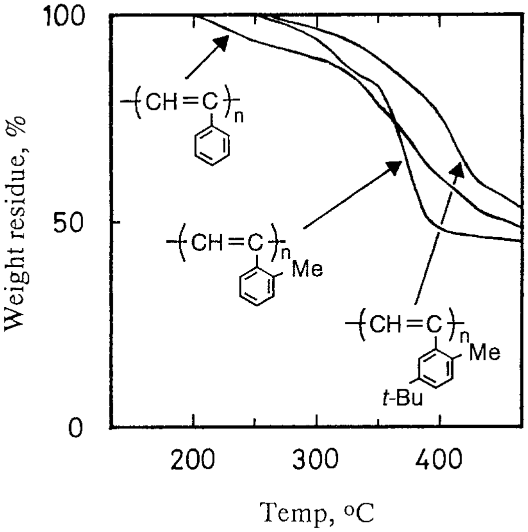


Figure 3. TGA curves of poly(phenylacetylene)s (in air, heating rate 10 °C/min).

The tensile properties of poly(2Me5tBuPA) at 25 °C are as follows: Young's modulus E = 1300 MPa, tensile strength σ_B = 32.9 MPa, elongation at break γ_B = 2.6%; cf. poly(*o*-CF_3PA): E = 1050 MPa, σ_B = 18 MPa, γ_B = 1.7% (8); poly(*o*-Me_3SiPA): E = 700 MPa, σ_B = 23 MPa, γ_B = 4.3% (8). Thus, the present polymer is hard and brittle like other *ortho*-substituted poly(PA)s. The glass transition temperature of the polymer was about 180 °C according to the dynamic viscoelastic measurement. The softening point was around 244 °C.

The oxygen permeability coefficient (P_{O_2}) of the present polymer was 43 barrers (P_{O_2}/P_{N_2} = 2.4; 25 °C), being about twice that of natural rubber (23 barrers). The P_{O_2} value of the present polymer is higher than those of poly(*o*-MePA) (8.1 barrers) and poly(*o*-CF_3PA) (25 barrers) (9). This suggests that the number of available molecular-scale voids is larger owing to the presence of *t*-Bu groups.

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