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Polymerization of (Pentafluorophenyl)acetylene and (*p*-Butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene and Polymer Properties

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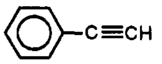
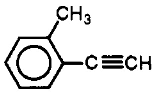
ABSTRACT: (Pentafluorophenyl)acetylene (F_5PA) and (*p*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene (*p*-BuF_4PA) were polymerized in high yields in the presence of W catalysts. Poly(F_5PA) was soluble only in C_6F_6; its intrinsic viscosity was 0.2–0.6 dL/g. In contrast, poly(*p*-BuF_4PA) was totally soluble in toluene, $CHCl_3$, C_6F_6, etc.; its maximum weight-average molecular weight reached ca. 2×10^6. Both polymers were dark brown solids, whose main-chain structure consisted of alternating double bonds. These polymers were thermally fairly stable in air (their weight loss starts at ~250 °C), amorphous, and electrically insulating. Poly(*p*-BuF_4PA) was film-forming, and its P_{O_2} and P_{O_2}/P_{N_2} values were 200 barrer and 3.5, respectively.

Introduction

A number of substituted polyacetylenes have been synthesized by using group 5 and 6 transition-metal catalysts.[1] It has recently been found that ortho-substituted derivatives of phenylacetylene (PA) such as (*o*-methylphenyl)acetylene[2] (*o*-MePA), [*o*-(trifluoromethyl)phenyl]acetylene[3] (*o*-CF_3PA), and [*o*(trimethylsilyl)-phenyl]acetylene[4] (*o*-Me_3SiPA) polymerize with W and Mo catalysts. The poly(*o*-MePA), poly(*o*-CF_3PA), and poly(*o*-Me_3SiPA) obtained have very high molecular weights [weight-average molecular weights ($\bar{M}_w$) 2×10^5–2×10^6]. This is quite interesting because the $\bar{M}_w$ of poly(PA) itself is usually no more than 3×10^4. These results suggest that the ortho substituents favor the increase of polymer molecular weight owing to its steric effect.


PA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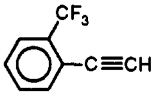
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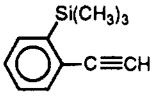
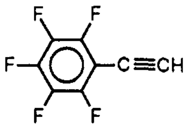
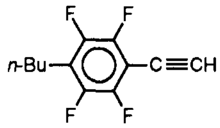

o-Me_3SiPA

Fluorine-containing polymers have drawn much attention because of their unique properties. Only a few fluorine-containing poly(PA) derivatives, however, have been synthesized; e.g., poly(*o*-CF_3PA)[3] ($\bar{M}_w$ ~1×10^6), poly[1-(pentafluorophenyl)-1-alkynes][5] (insoluble in organic solvents), poly[[2,5-bis(trifluoromethyl)phenyl]acetylene][6] (intrinsic viscosity, [η], 0.35 dL/g in *p*-$(CF_3)_2C_6H_4$).

(Pentafluorophenyl)acetylene[7] (F_5PA) and (*p*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene[7] (*p*-BuF_4PA) are new monomer candidates among fluorine-containing phenylacetylenes. They can be regarded as *o*,*o*-difluoro-substituted derivatives of PA, and the fluorines are expected to show steric and electronic effects. Thus it is interesting to study their polymerization behavior.


F_5PA


p-BuF_4PA

The present paper deals with the polymerization of F_5PA and *p*-BuF_4PA. High molecular weight polymers have been successfully obtained from F_5PA and *p*-BuF_4PA, and the structure and properties of the produced polymers have been determined.

Results and Discussion

Polymerization of F_5PA. Table I gives results on the polymerization of F_5PA in the presence of various catalysts. W catalysts produced methanol-insoluble poly(F_5PA)s. Since the polymers formed were soluble only in hexafluorobenzene (C_6F_6), their molecular weights were estimated from their [η] values which can be easily measured. When WCl_6 alone was used as a catalyst, poly(F_5PA) was obtained

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Table I
Polymerization of F_5PA by Various Catalysts[a]

catalyst	monomer convn, %	polymer[b] yield, %	polymer[b] $[\eta]$,[c] dL/g
WCl_6	56	55	0.30
WCl_6–Ph_4Sn (1:1)	98	96	0.21
$W(CO)_6$–$h\nu$[d]	97	92	0.49
$MoCl_5$	26	13	
$MoCl_5$–Ph_4Sn (1:1)	56	40	0.29
$Mo(CO)_6$–$h\nu$[d]	67	5	
$NbCl_5$[e]	97	0	
$TaCl_5$[e]	33	0	
$Ti(OBu)_4$–Et_3Al (1:4)	89	5[f]	
$Fe(acac)_3$–Et_3Al (1:3)	30	23[f]	

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [Cat.] = 20 mM. [b] Methanol-insoluble product. [c] Intrinsic viscosity measured in C_6F_6 at 30 °C. [d] Polymerized in CCl_4; $[M(CO)_6] = 10$ mM. [e] Polymerized at 80 °C. [f] Insoluble in any solvent.

Table II
Solvent Effects on the Polymerization of F_5PA by WCl_6–Ph_4Sn (1:1)[a]

no.	solvent	monomer convn, %	polymer[b] yield, %	polymer[b] $[\eta]$,[c] dL/g
1	toluene	98	96	0.21
2	C_6F_6	100	93	0.61
3	m-$(CF_3)_2C_6H_4$	100	95	0.28
4	CCl_2FCClF_2	100	100	0.25
5	1,4-dioxane	0	0	

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 0.50$ M, $[WCl_6] = 20$ mM. [b] Methanol-insoluble product. [c] Intrinsic viscosity measured in C_6F_6 at 30 °C.

Table III
Cocatalyst Effects on the Polymerization of F_5PA by WCl_6[a]

cocatalyst	monomer convn, %	polymer[b] yield, %	polymer[b] $[\eta]$,[c] dL/g
none	56	49	0.33
Ph_4Sn	100	93	0.61
n-Bu_4Sn	95	64	0.27
Et_3SiH	100	90	0.26
Ph_3Bi	59	53	0.29
Ph_3Sb	86	82	0.38
n-BuLi	54	47	0.25
Et_3Al	41	21	0.19

[a] Polymerized in C_6F_6 at 30 °C for 24 h; $[M]_0 = 0.50$ M, $[WCl_6]$ = [Cocat.] = 20 mM. [b] Methanol-insoluble product. [c] Intrinsic viscosity measured in C_6F_6 at 30 °C.

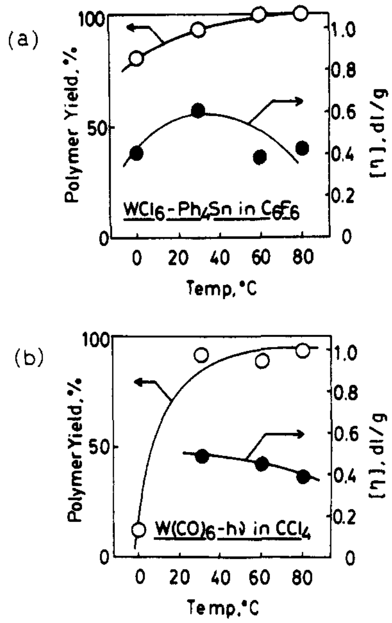


Figure 1. Temperature dependences of the polymerization of F_5PA (24 h, $[M]_0 = 0.50$ M, $[WCl_6] = [Ph_4Sn] = 20$ mM, $[W(CO)_6] = 10$ mM).

with moderate yield, whose $[\eta]$ was 0.3 dL/g. The catalyst composed of equimolar WCl_6 and Ph_4Sn (an organometallic cocatalyst[1b]) yielded a polymer virtually quantitatively but did not increase the $[\eta]$. The catalyst obtained by UV irradiation of the CCl_4 solution of $W(CO)_6$ achieved a higher $[\eta]$ of around 0.5 dL/g. The polymerization by WCl_6–Ph_4Sn was finished after about 20 min, being fairly rapid; the polymerizations by WCl_6 alone and $W(CO)_6$–$h\nu$ were slower.

The three corresponding Mo catalysts were less active than the W catalysts (Table I). $NbCl_5$ and $TaCl_5$, which are effective for the polymerization of disubstituted acetylenes,[1] afforded only methanol-soluble oligomers; the main products were cyclotrimers according to gel permeation chromatography (GPC) and IR spectroscopy. Ziegler catalysts such as $Ti(OBu)_4$–Et_3Al (1:4) and $Fe(acac)_3$–Et_3Al (1:3), which are capable of polymerizing primary or secondary alkylacetylenes, produced poly(F_5PA)s insoluble in any solvent. Hence, the effect of reaction conditions was examined below by using W catalysts, aiming at the increase of polymer molecular weight.

Effects of solvents on the polymerization of F_5PA were studied with use of a WCl_6–Ph_4Sn catalyst (Table II). When polymerization was carried out in C_6F_6, which is the only good solvent of poly(F_5PA), the $[\eta]$ of the polymer considerably increased. Other fluorine-containing solvents such as m-$(CF_3)_2C_6H_4$ and CCl_2FCClF_2, which partly dissolve this polymer, hardly enhanced the $[\eta]$. It is known that a high molecular weight poly(PA) ($\bar{M}_n \sim 1 \times 10^5$) is obtained with WCl_6–Ph_4Sn in 1,4-dioxane;[8] polymerization of F_5PA, however, did not proceed in 1,4-dioxane.

Effects of various organometallic cocatalysts on the polymerization of F_5PA by WCl_6 were studied with C_6F_6 as solvent (Table III). The polymer yield more or less increased in the presence of organometallic cocatalysts involving group 4 and 5 main-group metals. The $[\eta]$ value clearly increased only when Ph_4Sn was employed as a cocatalyst.

Figure 1 illustrates the effect of temperature on the polymerizations by WCl_6–Ph_4Sn and $W(CO)_6$–$h\nu$. The polymer yield with WCl_6–Ph_4Sn as catalyst was fairly high even at 0 °C and quantitative at 60 °C and above. The $[\eta]$ value showed a maximum at 30 °C. Therefore, 30 °C is favorable to obtain high molecular weight poly(F_5PA) with this catalyst. On the other hand, the $W(CO)_6$–$h\nu$ catalyst provided the polymer in about 90% at 30 °C and above, being somewhat less active than WCl_6–Ph_4Sn. The $[\eta]$ value of the polymer obtained at 30 °C was ca. 0.5 dL/g and decreased slightly with increasing temperature.

Polymerization of p-BuF_4PA. The polymer formed from p-BuF_4PA, which has a long alkyl group, proved to dissolve not only in C_6F_6 but also in many common organic solvents such as toluene and $CHCl_3$. This enabled us to measure the polymer molecular weight by GPC, and it seemed to us that this monomer would behave differently in polymerization owing to the polymer solubility. Hence, its polymerization was also studied in detail. Toluene was used as the polymerization solvent unless otherwise stated.

At first, polymerization was examined in the presence of various catalysts (Table IV). All three W catalysts in the table polymerized p-BuF_4PA in over 90% yields. The poly(p-BuF_4PA)s obtained with WCl_6 and WCl_6–Ph_4Sn possessed $\bar{M}_w$'s around 2×10^5. The $W(CO)_6$–$h\nu$ catalyst

Table IV
Polymerization of p-BuF$_4$PA by Various Catalysts[a]

catalyst	monomer convn, %	polymer[b]		
		yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
WCl$_6$	100	95	140[g]	69
WCl$_6$–Ph$_4$Sn (1:1)	100	100	220	110
W(CO)$_6$–$h\nu$[d]	100	91	900	570
MoCl$_5$	37	25	83	38
MoCl$_5$–Ph$_4$Sn (1:1)	59	57	230	120
Mo(CO)$_6$–$h\nu$[d]	13	3		
NbCl$_5$[e]	100	0		
TaCl$_5$[e]	92	0		
Ti(OBu)$_4$–Et$_3$Al (1:4)	100	76[f]		
Fe(acac)$_3$–Et$_3$Al (1:3)	88	85[f]		

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [Cat.] = 20 mM. [b] Methanol-insoluble product. [c] Determined by GPC. [d] Polymerized in CCl$_4$; $[M(CO)_6] = 10$ mM. [e] Polymerized at 80 °C. [f] Partly insoluble in any solvent. [g] $[\eta] = 0.23$ dL/g (measured in toluene at 30 °C).

Table V
Cocatalyst Effects on the Polymerization of p-BuF$_4$PA by WCl$_6$[a]

no.	cocatalyst	monomer convn, %	polymer[b]		
			yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
1	none	100	95	140	69
2	Ph$_4$Sn	100	100	220	110
3	n-Bu$_4$Sn	100	92	260[d]	120
4	Et$_3$SiH	100	96	96[e]	45
5	Ph$_3$Bi	100	100	400	220
6	Ph$_3$Sb	100	94	850	470
7	n-BuLi	100	100	660	230
8	Et$_3$Al	65	35	200	16

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_0 = 0.50$ M, [WCl$_6$] = [Cocat.] = 20 mM. [b] Methanol-insoluble product. [c] Determined by GPC. [d] $[\eta] = 0.47$ dL/g. [e] $[\eta] = 0.23$ dL/g.

Table VI
Solvent Effects on the Polymerization of p-BuF$_4$PA by WCl$_6$–Ph$_3$Sb (1:1)[a]

solvent	monomer convn, %	polymer[b]		
		yield, %	$\bar{M}_w/10^3$ [c]	$\bar{M}_n/10^3$ [c]
toluene	100	94	85	47
C$_6$F$_6$	94	93	53	20
m-(CF$_3$)$_2$C$_6$H$_4$	100	100	63	36
CCl$_2$FCClF$_2$	100	90	77	46
1,4-dioxane	27	0		

[a] Polymerized at 30 °C for 24 h; $[M]_0 = 0.50$ M, [WCl$_6$] = 20 mM. [b] Methanol-insoluble product. [c] Determined by GPC.

gave a polymer with a high molecular weight up to 9×10^5. The polymerization by WCl$_6$–Ph$_4$Sn was completed in ca. 15 min, being similar to that of F$_5$PA in reaction rate. Mo catalysts, in contrast, produced polymers in lower yields. NbCl$_5$ and TaCl$_5$ afforded only methanol-soluble oligomers. Ziegler catalysts yielded poly(p-BuF$_4$PA)s partly insoluble in any solvents. It can be said from these results that p-BuF$_4$PA polymerizes best with W catalysts like F$_5$PA.

Polymers were obtained in high yields both in the absence and in the presence of cocatalysts except for Et$_3$Al (Table V); thus no clear cocatalyst effect is seen with respect to polymer yield. However, the $\bar{M}_w$ of the polymer increased by addition of several cocatalysts. Especially, Ph$_3$Sb increased the $\bar{M}_w$ up to ca. 9×10^5.

Effects of solvents on polymerization were studied with use of the WCl$_6$–Ph$_3$Sb catalyst which provides high molecular weight poly(p-BuF$_4$PA). Polymerization proceeded in high yields not only in toluene but also in fluorine-containing solvents (Table VI). The $\bar{M}_w$ of the polymer, however, took the highest value in toluene, and hence there is no advantage in using fluorine-containing solvents for this monomer.

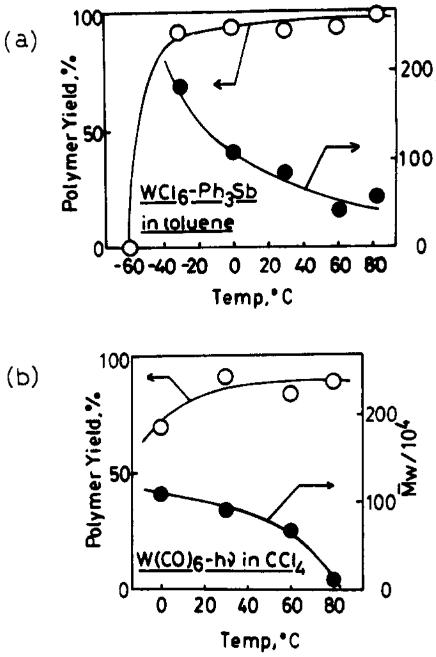


Figure 2. Temperature dependences of the polymerization of p-BuF$_4$PA (24 h, $[M]_0 = 0.50$ M, [WCl$_6$] = [Ph$_3$Sb] = 20 mM, [W(CO)$_6$] = 10 mM).

Figure 2 shows the effect of temperature on the polymerizations by WCl$_6$–Ph$_3$Sb and W(CO)$_6$–$h\nu$. The polymer yield with WCl$_6$–Ph$_3$Sb was almost quantitative at −30 °C and above, indicating a high activity of this catalyst. The $\bar{M}_w$ of poly(p-BuF$_4$PA) sharply increased with decreasing temperature. Eventually, the $\bar{M}_w$ reached ca. 2×10^6 at −30 °C. In the case of the W(CO)$_6$–$h\nu$ catalyst, a polymer formed in over 70% yield at 0 °C and above. The $\bar{M}_w$ of the polymer at 0 °C was about 1×10^6 and decreased with increasing temperature. It is noted that p-BuF$_4$PA is polymerizable at lower temperature, as compared with F$_5$PA. The highest $\bar{M}_n$ values of poly(p-BuF$_4$PA) obtained in Figure 2 are estimated to be 5×10^5–1×10^6 from the $\bar{M}_w/\bar{M}_n$ ratios in Tables IV and V. This means that the concentration of the propagating species is no more than $^1/_{50}$–$^1/_{100}$ that of the catalysts.

Polymerization of substituted acetylenes by group 5 and 6 transition-metal catalysts, including the polymerization in the present study, is thought to proceed via the metal carbene owing to the following reasons: (i) metal carbenes initiate the polymerization;[9a] (ii) linear olefins serve as chain-transfer agents;[9b] (iii) random copolymerization of PA with norbornene is possible.[9c] A recent study has achieved the living polymerization of p-BuF$_4$PA by using a three-component catalyst composed of MoOCl$_4$, n-Bu$_4$Sn, and EtOH (mole ratio 1:1:0.5);[10] $\bar{M}_n \propto$ conversion, polydispersity ratio 1.1–1.2.

Polymer Structure. The analytical data of poly(F$_5$PA) and poly(p-BuF$_4$PA) did not depend on the polymerization conditions. The data stated below have been obtained with the polymer samples from Table II, no. 2 (catalyst: WCl$_6$–Ph$_4$Sn), and Table V, no. 6 (catalyst: WCl$_6$–Ph$_3$Sb).

The elemental analysis data of poly(F$_5$PA) and poly(p-BuF$_4$PA) agreed well with their theoretical values. Poly(F$_5$PA). Calcd for (C$_8$HF$_5$)$_n$: C, 50.02; F, 49.45. Found: C, 49.85; F, 49.22. Poly(p-BuF$_4$PA). Calcd for (C$_{12}$H$_{10}$F$_4$)$_n$: C, 62.61; H, 4.38; F, 33.01. Found: 62.35; H, 4.19; F, 33.01.

IR spectral data of the polymers are as follows. Poly(F$_5$PA): IR (KBr pellet) 1650 (m), 1490 (vs), 1100 (s), 990

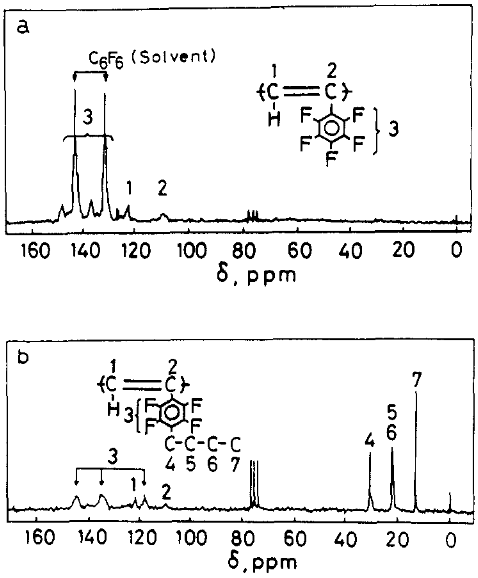


Figure 3. ^{13}C NMR spectra of poly(F$_5$PA) (C$_6$F$_6$ solution) and poly(*p*-BuF$_4$PA) (CDCl$_3$ solution).

(s), 895 (s) cm^{-1}. Poly(*p*-BuF$_4$PA): IR (KBr pellet) 2950 (m), 2860 (m), 1490 (vs), 1100 (m), 980 (s), 910 (m) cm^{-1}. While both monomers (F$_5$PA and *p*-BuF$_4$PA) showed bands at 3350 cm^{-1} due to ≡CH, these bands are absent in the polymers. Strong absorptions characteristic of C–F stretching were present at ca. 1000 cm^{-1} in both monomers and polymers.

In the ^{13}C NMR spectra of monomers were observed two acetylenic carbons at δ 68.1 and 89.9 (F$_5$PA) and at δ 69.2 and 88.9 (*p*-BuF$_4$PA). Instead, two olefinic carbons appear at δ 111.1 and 124.4 (F$_5$PA) and at δ 112.5 and 124.5 (*p*-BuF$_4$PA) in the polymers (Figure 3).

The ^{1}H NMR spectra of poly(F$_5$PA) and poly(*p*-BuF$_4$PA) exhibited rather broad signals of olefinic proton at δ 8.0–6.8 (F$_5$PA) and at δ 7.3–6.6 (*p*-BuF$_4$PA). Besides, aliphatic protons (δ 3.0–0.8) were seen in the ^{1}H NMR spectrum of poly(*p*-BuF$_4$PA). No other unexpected protons appeared. The ^{13}C NMR and ^{1}H NMR spectra of poly(F$_5$PA) and poly(*p*-BuF$_4$PA) obtained with Mo catalysts were virtually identical to those with W catalysts.

The IR, ^{13}C NMR, and ^{1}H NMR spectra thus support the idea that the polymers possess alternating double bonds in the main chain as shown in Figure 3. No information about the geometric structure of the main chain, however, could be obtained from these spectra.

In the UV–visible spectra of poly(F$_5$PA) and poly(*p*-BuF$_4$PA), absorption maxima are seen at 380 nm (ϵ_{max} 5200 M^{-1} cm^{-1}) and 430 nm (ϵ_{max} 5300 M^{-1} cm^{-1}), respectively, while that the poly(PA) is below 300 nm (Figure 4). Other ortho-substituted poly(PA)s such as poly(*o*-MePA),[2] poly(*o*-CF$_3$PA),[3b] and poly(*o*-Me$_3$SiPA)[4] show absorption maxima above 450 nm. Thus it seems a general tendency that introduction of ortho substituents into poly(PA) brings about red shifts of the absorption maximum. This, however, does not agree with the idea that if the ortho substituent hampers the conjugation between the main chain and phenyl group, then the maxima should shift to shorter wavelengths by ortho substitution; the cause why ortho substituents give rise to the red shift is not clear at present.

The data of X-ray diffraction analysis (Cu Kα radiation) are as follows: poly(F$_5$PA), 2θ (Δ2θ/2θ) = 8.0° (0.288), 9.8° (0.204), 12.5° (0.248), 25.4° (0.181); poly(*p*-BuF$_4$PA), 2θ (Δ2θ/2θ) = 5.7° (0.772), 8.8° (0.420), 24.1° (0.232). These data show the presence of only broad peaks, leading to a conclusion that the present polymers are amorphous.

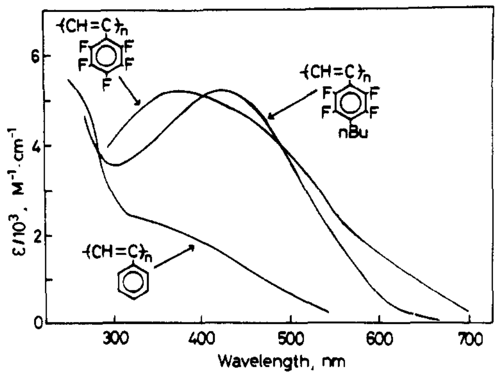


Figure 4. UV–visible spectra of poly(F$_5$PA), poly(*p*-BuF$_4$PA), and poly(PA) (measured in C$_6$F$_6$ [poly(F$_5$PA), poly(*p*-BuF$_4$PA)] or in THF [poly(PA)]).

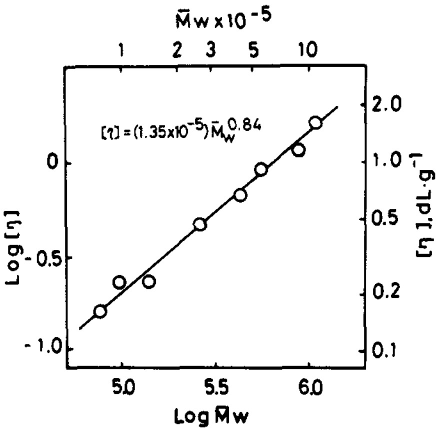


Figure 5. [η] vs $\bar{M}_w$ plot for poly(*p*-BuF$_4$PA) (samples with polydispersity ratios of around 2.5 were used; [η] measured in toluene at 30 °C, and $\bar{M}_w$ determined by GPC).

Polymer Properties. Both poly(F$_5$PA) and poly(*p*-BuF$_4$PA) have the form of dark brown solid irrespective of polymerization conditions. Properties of these polymers are described below; the samples used are from Table II, no. 2, and Table V, no. 6, unless otherwise stated.

Poly(F$_5$PA) completely dissolved only in C$_6$F$_5$ and partly dissolved in CCl$_2$FCClF$_2$ and *m*-(CF$_3$)$_2$C$_6$H$_4$. Its nonsolvents include benzene, toluene, cyclohexane, CCl$_4$, and CHCl$_2$. These solubility properties are in sharp contrast to those of poly(PA), which is insoluble in C$_6$F$_6$ and soluble in toluene, CHCl$_3$, etc. Poly(*p*-BuF$_4$PA), on the other hand, is soluble in many organic solvents such as benzene, toluene, hexane, CCl$_4$, CHCl$_3$, tetrahydrofuran, acetone, ethyl acetate, C$_6$F$_6$, etc.; this excellent solubility is attributable to the *p*-*n*-butyl group.

A logarithmic plot of the [η] vs $\bar{M}_w$ of poly(*p*-BuF$_4$PA) is shown in Figure 5. The plot can be represented by a good linear relationship, leading to the following equation:

$$[\eta] = K\bar{M}_w^{\ a} \quad (K = 1.35 \times 10^{-5} \quad a = 0.84)$$

The value of exponent *a* is relatively close to those of poly(*o*-CF$_3$PA)[3a] (*a* = 0.59) and poly(*o*-Me$_3$SiPA)[4] (*a* = 0.76) and not so large as those for disubstituted acetylene polymers[1] [e.g., (–CCH$_3$=CSi(CH$_3$)$_3$–), *a* = 1.04; (–CCl=CPh–), *a* = 1.07]. This is probably because monosubstituted acetylene polymers assume less expanded conformations in solution than do disubstituted acetylene polymers.

A tough, free-standing film is accessible from poly(*p*-BuF$_4$PA) by casting its toluene solution as in the cases of

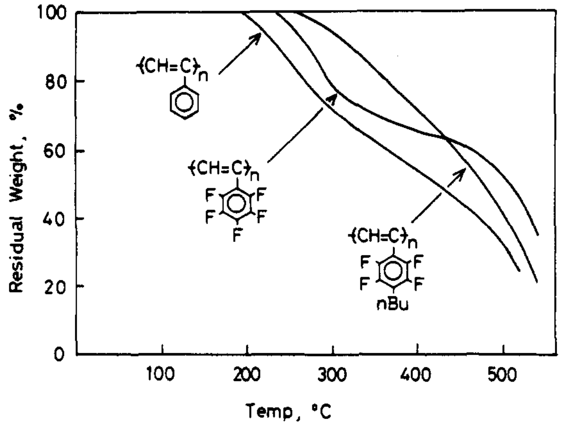


Figure 6. Thermogravimetric analysis of poly(F_5PA), poly(p-BuF_4PA), and poly(PA) (measured in air at a heating rate of 10 °C/min).

poly(o-CF_3PA) and poly(o-Me_3SiPA). In contrast, the film of poly(F_5PA) is rather brittle, and poly(PA) is too brittle to form a film. The film-forming property of poly(p-BuF_4-PA) is attributable to its high molecular weight.

Poly(F_5PA) and poly(p-BuF_4PA) began to lose weight at about 240 and 260 °C, respectively, in thermogravimetric analysis (TGA) in air (Figure 6). These temperatures are higher than that of poly(PA)[11] (200 °C) and lower than those of poly(o-CF_3PA)[3b] (300 °C) and poly(o-Me_3SiPA)[4] (280 °C). None of these ortho-substituted poly(PA)s suffers any molecular weight decrease or oxidation even though they are left in air at room temperature ove a few months, while poly(PA) gradually undergoes a molecular weight decrease owing to oxidative degradation. Thus ortho substituents prove effective in enhancing the stability of poly(PA).

The mechanical properties of poly(p-BuF_4PA) are as follows:[12] Young's modulus 530 MPa, tensile strength 21 MPa, elongation at break 8.1% at 25 °C; glass transition temperature (by dynamic viscoelasticity) 110 °C. These data show that poly(p-BuF_4PA) is hard and rather brittle.

The electrical conductivities of poly(F_5PA) and poly(p-BuF_4PA) at 25 °C were 1×10^{-16} and 2×10^{-16} $S \cdot cm^{-1}$, respectively; i.e., these polymers are typical insulators like poly(PA), poly(o-CF_3PA), and poly(o-Me_3SiPA).

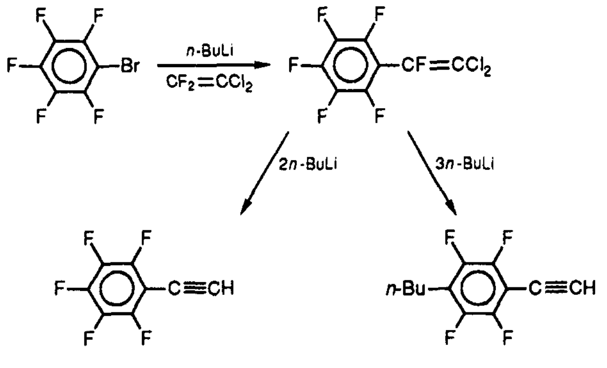
The data of electron spin resonance (solid state; power level 1 mW) are as follows: poly(F_5PA) singlet (line width 5.8 G, g value 2.0028), spin density 5.6×10^{18} g^{-1}; poly(p-BuF_4PA) singlet (line width 9.9 G, g value 2.0027), spin density 2.0×10^{17} g^{-1}. The spin densities of poly(o-CF_3-PA) and poly(o-Me_3SiPA) are 6.1×10^{17} and 7.3×10^{17} g^{-1}, respectively.[3b,4] Further, the values of polyacetylene, poly(PA), and disubstituted acetylene polymers with bulky groups are 10^{18}–10^{19}, 10^{16}–10^{17}, and $<10^{15}$ (i.e., lower than detection limit) g^{-1}, respectively.[1b] Thus the present polymers as well as other ortho-substituted poly(PA)s possess fairly high concentrations of unpaired electron.

The oxygen permeability coefficient (P_{O_2}) of a poly(p-BuF_4PA) membrane at 25 °C was 200 barrer (1 barrer = 1×10^{-10} cm^3 (STP)$\cdot cm \cdot cm^{-2} \cdot s^{-1} \cdot cmHg^{-1}$), and the separation factor of oxygen and nitrogen (P_{O_2}/P_{N_2}) was 3.5. This P_{O_2} value is about $^1/_2$ that of poly(dimethylsiloxane), being very large among those of glassy polymers.[13] Further, the fairly large separation factor may be associated with the affinity between fluorine and oxygen.

Experimental Section

Materials. The monomers were prepared by Okuhara's method[7] (Scheme I); i.e., F_5PA and p-BuF_4PA were prepared by addition of 2 and 3 equiv, respectively, of n-butyllithium to ether solutions of $C_6F_5CF{=}CCl_2$, which in turn was prepared by portionwise addition of cooled ethereal pentafluorophenyllithium to a solution of 1,1-dichloro-2,2-difluoroethylene in ether. Experimental details of these preparations will be described elsewhere.[7a] $C_6F_5CF{=}CCl_2$: yield 66%. F_5PA: yield 63%; purity >99% [gas chromatography (GC)]; bp 66 °C (95 mmHg); d_4^{20} 1.435. p-BuF_5PA: yield 86%; purity 98.3% (GC); bp 80 °C (5 mmHg); d_4^{20} 1.162.

Scheme I



Transition-metal compounds and organometallic cocatalysts were all commercially obtained and used without further purification; care was taken that they would not be decomposed by moisture and/or air. Solvents for polymerization were purified by the standard methods.

Polymerization. Polymerizations were performed in prebaked glass vessels under dry nitrogen. Catalyst systems composed of a transition-metal chloride and an organometallic cocatalyst were allowed to stand (age) in solution at 30 °C for 15 min before use. Metal carbonyl based catalysts were prepared by irradiation of CCl_4 solution of a metal carbonyl with UV light (200-W high-pressure Hg lamp, distance 5 cm) at 30 °C for 1 h.

The following polymerization procedure is exemplary (see Table II, no. 2, for the result): In a Schlenk tube equipped with a three-way stopcock, a monomer solution was prepared by mixing F_5PA (3.0 mmol, 0.58 g, 0.40 mL), chlorobenzene (0.10 mL; internal standard for GC), and C_6F_6 (1.90 mL). In another Schlenk tube, WCl_6 (0.10 mmol, 40 mg) and Ph_4Sn (0.10 mmol, 43 mg) were dissolved in C_6F_6 (3.0 mL), and this catalyst solution was aged at 30 °C for 15 min. Then 2.0 mL of the monomer solution was added to the catalyst solution. After polymerization at 30 °C for 24 h, the reaction was quenched by addition of a mixture (5 mL) of CCl_2FCClF_2 and methanol (4:1 volume ratio). Monomer conversion was determined by GC (silicone DC550 3 m, 90 °C). The reaction mixture was diluted with CCl_2FCClF_2 (10 ml) and poured into methanol (1 L) under stirring. The precipitated polymer was washed with methanol, filtered, and dried to a constant weight. Polymer yield determined by gravimetry.

Characterization. Intrinsic viscosities ($[\eta]$) of polymers were measured in C_6F_6 [poly(F_5PA)] or in toluene [poly(p-BuF_4PA)] at 30 °C by using a Ubbelohde-type viscometer in the concentration (c) range 0.1–0.4 g/dL. The plots of η_{sp}/c vs c were all linear.

Molecular weights of poly(p-BuF_4PA) were determined by GPC with use of a polystyrene calibration. GPC curves were observed with a Jasco Trirotar liquid chromatograph [eluent, $CHCl_3$; columns, Shodex A805, A806, and A807 polystyrene gels (Showa Denko, Co., Japan)]. Monodisperse polystyrene samples with $\bar{M}_n$'s of 1.1×10^5, 3.0×10^5, 6.5×10^5, 1.8×10^6, 2.0×10^6, 3.8×10^6, 6.8×10^6, and 2.0×10^7 were used for calibration. A liquid chromatograph equipped with columns of Shodex A802, A803, and A804 was used for the analysis of oligomeric products.

^{13}C NMR spectra were observed with a JEOL FX90Q spectrometer. IR spectra and UV–visible spectra were recorded with Shimadzu IR435 and UV190 spectrophotometers, respectively. Other analyses were carried out as described before.[2,3b,4]

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