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Chain-Transfer Reaction to Trimethylvinylsilane in the Polymerization of Ring-Substituted Phenylacetylenes by WCl_6–Ph_4Sn

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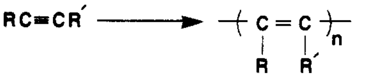
ABSTRACT: Effects of various olefins as chain-transfer agents were examined in the polymerization of phenylacetylenes (PAs) catalyzed by WCl_6–Ph_4Sn (1:1), and it has been found that Si-containing and hydrocarbon-based olefins work as effective transfer agents. In the presence of Si-containing olefins such as trimethylvinylsilane, remarkable molecular weight decreases were observed generally with PAs having electron-withdrawing groups (e.g., [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA) and (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene), while it was not the case with PAs having electron-donating groups (e.g., [*o*-(trimethylsilyl)phenyl]acetylene). The poly(*o*-CF_3PA) obtained in the presence of trimethylvinylsilane contained the trimethylsilyl group. These results indicate that the monomers with electron-withdrawing groups have weak coordinating abilities to the propagating end and hence undergo chain transfer readily and that the metal–carbene mechanism is valid for the present polymerization.

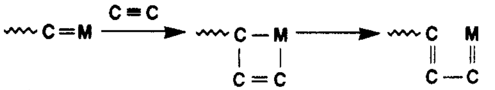
Introduction

Chain-transfer agents are useful for the control of both polymer molecular weight and end group in addition polymerizations. Further, what are effective transfer agents is closely related to the polymerization mechanism itself. Linear olefins are known to work as transfer agents in the ring-opening metathesis polymerization of cycloolefins which proceeds by the metal–carbene mechanism.[1,2]

Thus far we have achieved the synthesis of high molecular weight polymers [weight-average molecular weight ($\bar{M}_w$) $\sim 1 \times 10^6$] from various substituted acetylenes by using group 5 and 6 transition-metal catalysts (eq 1).[3,4]

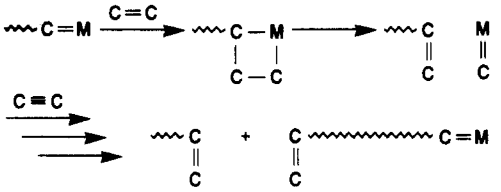


$$RC\equiv CR' \longrightarrow \left[\begin{matrix}C & = & C\\ | & & |\\ R & & R'\end{matrix}\right]_n \qquad (1)$$



(2)

(**M**: metal)



(3)

There have, however, been no studies on transfer agents in the polymerization of substituted acetylenes. The metal–carbene mechanism has been proposed also for this polymerization (eq 2).[5,6] If it is valid, olefins are expected to effect chain-transfer reaction (eq 3) as in the ring-opening metathesis polymerization of cycloolefins.

In the present paper, we report on the effect of various olefins on the polymerization of substituted acetylenes.[7] The monomers used were phenylacetylene (PA) derivatives such as [*o*-(trifluoromethyl)phenyl]acetylene (*o*-CF_3PA),[8] (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene (*p*-BuF_4PA),[9] and [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA)[10] which provide high molecular weight polymers. Consequently, we have found that hydrocarbon-based or Si-containing olefins, especially vinylsilanes, effectively induce chain transfer. Further, it has been revealed that the monomers with electron-withdrawing groups like *o*-CF_3PA and *p*-BuF_4PA readily suffer chain transfer. The chain-transfer mechanism is discussed on the basis of the results obtained.

Experimental Section

Materials. Phenylacetylene (PA) was commercially obtained (Aldrich Chemical Co.), and (*p*-*n*-butyl-*o*,*o*,*m*,*m*-tetrafluorophenyl)acetylene (*p*-BuF_4PA) was offered by the Government Industrial Research Institute, Nagoya. [*o*-(Trifluoromethyl)phenyl]acetylene (*o*-CF_3PA), [*o*-(trimethylsilyl)phenyl]acetylene (*o*-Me_3SiPA), and the other monomers were prepared as described before.[8,10] Aliphatic olefins were purchased from Tokyo Kasei, Japan, while Si-containing olefins were offered by Shin-Etsu Chemicals, Japan. These compounds were all distilled twice from calcium hydride before use. WCl_6 (Strem Chemicals Co.; purity >99.9%), Ph_4Sn (Tokyo Kasei, Japan), and other catalyst components were commercially obtained and used without further purification. Polymerization solvents were washed by conventional methods and distilled twice from calcium hydride before use.

Polymerization. Polymerizations were carried out under dry nitrogen in a prebaked 30-mL flask equipped with a three-way stopcock. A typical procedure of polymerization is as follows (see Table I, row 2 for the results): A monomer solution (2.5 mL) was prepared by mixing *o*-CF_3PA (0.45 mL, 3.1 mmol), trimethylvinylsilane (0.090 mL, 0.62 mmol), chlorobenzene [0.26 mL, internal standard of gas chromatography (GC)], and toluene (1.7 mL). A catalyst solution (3.0 mL) was separately prepared by dissolving WCl_6 (19.8 mg, 0.050 mmol) and Ph_4Sn (21.4 mg, 0.050 mmol) in toluene (3.0 mL) and aging at 30 °C for 15 min. Polymerization was initiated by adding the monomer solution (2.0 mL) to the catalyst solution (3.0 mL) at 30 °C and was continued for 24 h [the remaining monomer solution (0.5 mL) was used for GC]. The reaction was quenched with a toluene/methanol (volume ratio 4:1) mixture (2 mL), and the monomer conversion was measured by GC (silicone DC 3 m, 120 °C). The reaction mixture was diluted with toluene (30 mL), washed with 2% hydrochloric acid and water, and dried over anhydrous Na_2SO_4 overnight. Toluene was evaporated to afford the isolated reaction product.

Polymer Characterization. The number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of polymers were determined by gel permeation chromatography (GPC) by use of a polystyrene calibration. GPC measurements were carried out on a Shimadzu LC-9A liquid chromatograph connected with a Shimadzu C-R4A basic data processor [eluent, $CHCl_3$; columns, a series of Shodex K-805, K-806, and K-807 for high molecular weight polymers ($1 \times 10^5 \leq \bar{M}_n$), Shodex K-803, K-804, and K-805

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Table I
Effects of Various Olefins on the Polymerization of o-CF$_3$PA by WCl$_6$–Ph$_4$Sn (1:1)[a]

olefin	monomer convn, %	polymer $\bar{M}_n/10^3$ [b]	polymer $\bar{M}_w/10^3$ [b]
none	100	182	491
$H_2C{=}CHSiMe_3$	100	29	61
$H_2C{=}CHSiMe_2$-n-C_4H_9	100	23	43
$H_2C{=}CHSiMe_2Ph$	100	51	110
$H_2C{=}CHCMe_3$	100	165	413
$H_2C{=}CH$-n-C_6H_{13}	100	68	162
$MeCH{=}CH$-n-C_5H_{11}	100	104	252

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_o = 0.50$ M, [WCl$_6$] = 10 mM, [C=C] = 0.10 M. [b] Determined by GPC.

for low molecular weight polymers ($1 \times 10^4 \leq \bar{M}_n < 1 \times 10^5$), Shodex K-802, K-803, and K-804 for oligomers ($\bar{M}_n < 1 \times 10^4$); refractive index detector]. IR spectra (KBr pellet) were recorded on a Shimadzu FTIR-8100 spectrophotometer. ^{1}H and ^{13}C NMR spectra were observed on a JEOL GSK-270 spectrometer (270 MHz for ^{1}H) in CDCl$_3$ at 25 °C.

Results and Discussion

Chain Transfer in the Polymerization of o-CF$_3$PA. Table I summarizes effects of various olefin additives on the polymerization of o-CF$_3$PA. This monomer polymerizes quantitatively with WCl$_6$–Ph$_4$Sn (1:1) catalyst under the conditions of Table I irrespective of the absence or presence of olefins. The number-average molecular weight ($\bar{M}_n$) of the formed polymer reaches about 2×10^5 in the absence of an olefin. In contrast, the molecular weight of polymer more or less decreased by addition of Si-containing or hydrocarbon-based olefins ($^1/_5$ equiv to monomer). In particular, trimethylvinylsilane and n-butyldimethylvinylsilane decreased the $\bar{M}_n$ of the polymer to smaller than one-sixth of the value without an olefin. The effectiveness of Si-containing olefins is hence attributable to the suitably electron-donating nature of silyl groups. Olefins with stronger electron-donating groups like isobutyl vinyl ether underwent WCl$_6$-catalyzyed cationic oligomerization. Consequently, trimethylvinylsilane was mainly used in the following experiments.

To the best of our knowledge, trimethylvinylsilane has not been used as a chain-transfer agent in the ring-opening metathesis polymerization of cycloolefins. Related investigations include the following: (i) Trimethylvinylsilane does not undergo self-metathesis in the presence of WCl$_6$–Me$_4$Sn.[11] (ii) Trichlorovinylsilane serves as chain-transfer agent in cyclopentene polymerization by W catalysts.[12] (iii) Dimethylphenylvinylsilane suffers cross-metathesis with various olefins in the presence of Ru catalysts.[13] Thus the behavior of trimethylvinylsilane in metathesis reaction is scarcely known.

Figure 1 demonstrates molecular weight distribution (MWD) curves of the poly(o-CF$_3$PA) obtained in the absence and presence of trimethylvinylsilane. The molecular weight of the polymer clearly decreased when the olefin was added. On the other hand, the MWD of the polymer was hardly affected by trimethylvinylsilane ($\bar{M}_w/\bar{M}_n \sim 3.0$).

Figure 2 shows the effect of trimethylvinylsilane concentration on the polymerization of o-CF$_3$PA. The polymerization proceeded to completion after 24 h under the conditions of Figure 2 even though the olefin concentration is increased up to 0.25 M ($^1/_2$ equiv to monomer). Whereas the $\bar{M}_n$ of the polymer is 18×10^4 in the absence of trimethylvinylsilane, the value for the polymer decreased to no more than ca. 2.0×10^4 when the concentration of trimethylvinylsilane was 0.25 M.

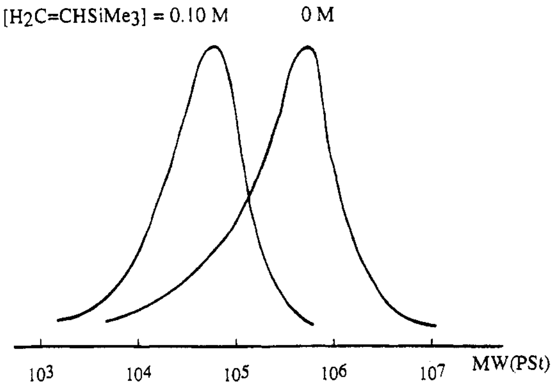


Figure 1. MWD curves for poly(o-CF$_3$PA)s obtained with WCl$_6$–Ph$_4$Sn (1:1) in the absence and presence of trimethylvinylsilane (polymerized in toluene at 30 °C for 24 h; $[M]_o = 0.50$ M, [WCl$_6$] = 10 mM).

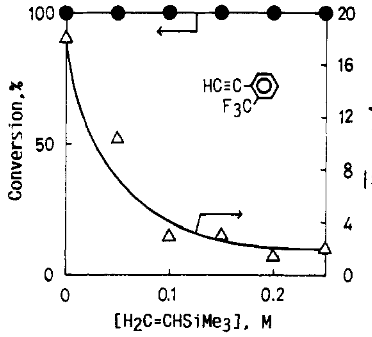


Figure 2. Effect of trimethylvinylsilane concentration on the polymerization of o-CF$_3$PA by WCl$_6$–Ph$_4$Sn (1:1) (in toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, [WCl$_6$] = 10 mM).

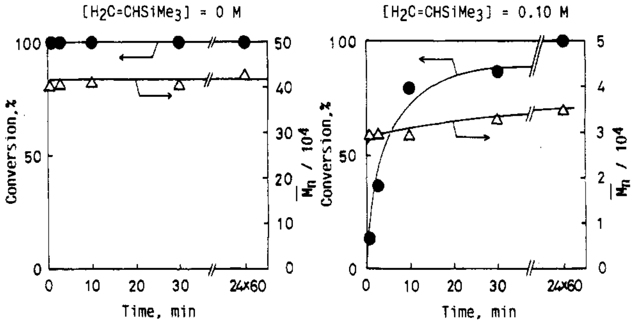


Figure 3. Time course of the polymerization of o-CF$_3$PA by WCl$_6$–Ph$_4$Sn (1:1) (in toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, [WCl$_6$] = 10 mM).

Time dependences of the polymerization of o-CF$_3$PA in the absence and presence of trimethylvinylsilane as transfer agent were compared with each other (Figure 3). Without trimethylvinylsilane, polymerization is completed within a few minutes at 0 °C, and the $\bar{M}_n$ of the polymer is ca. 5×10^5. With trimethylvinylsilane, on the other hand, the $\bar{M}_n$ of the polymer decreased to no more than ca. 3.5×10^4, irrespective of monomer conversion. Deceleration of polymerization suggests that reinitiation, i.e., the reaction of the low molecular weight metal carbene with the acetylene monomer in eq 2, is rather slow. The molecular weight did not decrease even though the polymerization mixture was allowed to stand for 24 h. Thus, unless otherwise specified, polymerizations in the present study were carried out for 24 h for the sake of simplicity.

The polymerization of substituted acetylenes in the presence of trimethylvinylsilane may be accompanied by reactions other than chain-transfer such as self-metathesis of trimethylvinylsilane (eq 4) and metathesis of the formed polymer with the olefin (eq 5). The reaction of eq 4,

$$2CH_2{=}CHSiMe_3 \rightleftarrows Me_3SiCH{=}CHSiMe_3 + H_2C{=}CH_2 \quad (4)$$

$$H_2C{=}CHSiMe_3 + \sim\!C{=}C\!\sim \rightarrow \sim\!C{=}CH_2 + Me_3SiCH{=}C\!\sim \quad (5)$$

however, is denied because trimethylvinylsilane was not consumed in the presence of WCl_6–Ph_4Sn over 24 h under the same conditions as for polymerization. Further, the addition of trimethylvinylsilane to the completely polymerized system did not cause any decrease of polymer molecular weight; this implies that the reaction of eq 5 does not occur, either.

The above-stated findings permit one to apply the Mayo plot of $1/\overline{DP}_n$ vs [transfer agent] corresponding to eq 6 (where $\overline{DP}_n$ and $\overline{DP}_{n,0}$ represent the degrees of polymerization in the presence and absence of a transfer agent, respectively).[14] Figure 4 shows a plot of $1/\overline{DP}_n$ vs [trimethylvinylsilane] for the polymerization of o-CF_3PA. Here, the monomer conversions were kept below 20% on the synthesis of the polymer samples, in order that the concentrations of the monomer and the olefin could be regarded as constant. This plot gives a straight line, from the slope of which the transfer constant ratio, k_{tr}/k_p is calculated as 1.90×10^{-2}.

$$\frac{1}{\overline{DP}_n} = \frac{1}{\overline{DP}_{n,0}} + \frac{k_{tr}}{k_p}\frac{[H_2C{=}CHSiMe_3]}{[M]_0} \quad (6)$$

In the polymerization of o-CF_3PA by WCl_6–Ph_4Sn, the monomer was consumed quantitatively in the temperature range 0 to 50 °C (Figure 5). In the absence of trimethylvinylsilane, the $\bar{M}_n$ of the polymer shows a maximum of 5×10^5 around 0 °C and decreases with increasing temperature. When trimethylvinylsilane was added, the $\bar{M}_n$ values of the polymers formed in the presence of the olefin were almost constant in the range 3×10^4–4×10^4. Eventually, the molecular weight decrease by trimethylvinylsilane is more remarkable at low temperature at which the molecular weight in the absence of trimethylvinylsilane is higher.

o-CF_3PA polymerizes with several types of catalysts.[8] Hence it was examined whether the effect of trimethylvinylsilane would depend on catalyst systems. As catalysts, $MoCl_5$–Ph_4Sn (1:1) and $W(CO)_6$–CCl_4–$h\nu$ were used; the polymerization conditions are the same as in Table I. The polymerizations proceeded quantitatively in both the absence and presence of trimethylvinylsilane. Molecular weight changes with addition of trimethylvinylsilane were as follows: $\bar{M}_n$ from 301×10^3 to 79×10^3 with $MoCl_5$–Ph_4Sn (1:1); 171×10^3 to 39×10^3 with $W(CO)_6$–$h\nu$ in CCl_4 solution. That is, the molecular weight decreases are by about one-fourth, resembling the WCl_6–Ph_4Sn case. This indicates that the polymerization proceeds by the identical mechanism in the presence of all these catalysts.

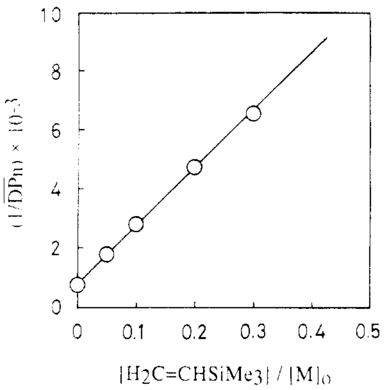


Figure 4. Relationship between the reciprocal $\overline{DP}_n$ of poly(o-CF_3PA) and $[H_2C{=}CHSiMe_3]/[M]_0$ (in toluene, 30 °C, 24 h; $[M]_0$ = 0.50 M, $[WCl_6]$ = 10 mM; conversions <20%).

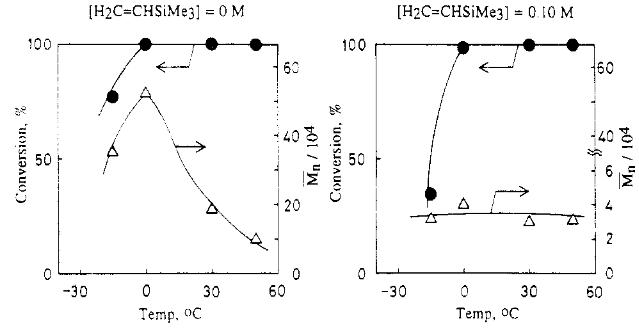


Figure 5. Temperature profile of the polymerization of o-CF_3PA by WCl_6–Ph_4Sn (1:1) (in toluene, 24 h, $[M]_0$ = 0.50 M, $[WCl_6]$ = 10 mM).

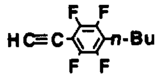
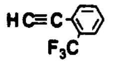
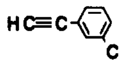
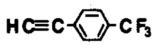
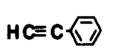
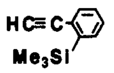
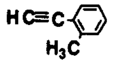
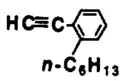
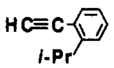
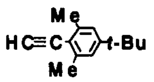
Chain Transfer in the Polymerization of Other Ring-Substituted Phenylacetylenes. Table II shows the effect of trimethylvinylsilane (0.10 M) on the polymerization of various ring-substituted phenylacetylenes by WCl_6–Ph_4Sn. The monomer conversions were quantitative in most cases, irrespective of the absence or presence of the olefin. The $\bar{M}_n$ value of the polymers formed from phenylacetylene in the presence of the olefin was 8×10^3, i.e., ca. one-third the value in the absence of the olefin. In the polymerization of p-BuF_4PA and o-CF_3PA, which have electron-withdrawing fluorines, in contrast, the $\bar{M}_n$ values in the presence of the olefin decreased remarkably to 6×10^3–30×10^3, i.e., about $^1/_{20}$–$^1/_6$ the values in the absence of the olefin. In the polymerization of the monomers with electron-donating groups (e.g., Me_3Si, Me), on the other hand, the ratios of $\bar{M}_n$ values in the presence and absence of the olefin were about $^1/_{1.5}$–$^1/_3$, not so small as with the monomers having electron-withdrawing groups.

The results obtained are explicable in terms of an idea that the monomers with electron-withdrawing fluorine atoms have only weak coordinating ability to the propagating end (a metal carbene) and, in turn, suffer chain-transfer reaction more easily (see eqs 2 and 3). Further, an electron-poor metal carbene will react readily with electron-rich trimethylvinylsilane with good HOMO–LUMO overlap, which is not the case for an electron-rich metal carbene. Anyhow, the relative coordinating ability of monomer and transfer agent should be the most important factor.

It is interesting to study the chain-transfer reaction in the polymerization of p-BuF_4PA which has many electron-withdrawing fluorine atoms. In Table III are shown effects of various olefins ($^1/_5$ equiv to monomer) on the polymerization of p-BuF_4PA. Even in the presence of olefins the conversion exceeded 70%. The $\bar{M}_n$ value of the polymer without an olefin reached about 12×10^4. In contrast, the molecular weight of polymer more or less decreased in the presence of Si-containing or simple hydrocarbon olefins. Obviously, Si-containing olefins are very effective. Though 1-octene was not so effective, a similar extent of molecular weight decrease could be achieved at a higher concentration: $\bar{M}_n$ 7×10^3 at $[H_2C{=}CH\text{-}n\text{-}C_6H_{13}]$ = 1.0 M.

The effect of trimethylvinylsilane concentration on the polymerization of p-BuF_4PA is shown in Figure 6a. The polymerization is completed under the conditions of Figure

Table II
Effect of Trimethylvinylsilane (1) on the Polymerization of Various Acetylenes by WCl_6–Ph_4Sn (1:1)[a]

	$\bar{M}_n/10^3$ [b]		$\bar{M}_w/10^3$ [b]	
monomer	none	1[c]	none	1[c]
	125	6.0[d]	293	14
	182	29	491	61
	28	2.6	64	5.4
	5.4	2.3	6.5	3.3
 [e]	20	7.8	41	12
	180	56	367	150
	16	6.0	28	14
	24	9.0	63	18
	51	44	102	104
	221	127	499	696

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_o = 0.50$ M, $[WCl_6] = [Ph_4Sn] = 10$ mM. The conversions were ≥95% unless otherwise noted. [b] Determined by GPC. [c] [1] = 0.10 M. [d] Conversion 80%. [e] Polymerized for 3 h.

Table III
Effects of Various Olefins on the Polymerization of Phenylacetylenes by WCl_6–Ph_4Sn (1:1)[a]

	$\bar{M}_n/10^3$ [b]		
olefin	p-BuF_4PA	o-CF_3PA	o-Me_3SiPA
none	125	182	180
$H_2C{=}CHSiMe_3$	6.0[c]	29	56
$H_2C{=}CHSiMe_2$-n-C_4H_9	6.3[d]	23	43
$H_2C{=}CHSiMe_2Ph$	4.0[e]	51	75
$H_2C{=}CHCMe_3$	71	180	114
$H_2C{=}CH$-n-C_6H_{13}	21	68	92
$MeCH{=}CH$-n-C_5H_{11}	90	104	111

[a] Polymerized in toluene at 30 °C for 24 h; $[M]_o = 0.50$ M, $[WCl_6] = 10$ mM, [C=C] = 0.10 M. The conversions were 100% unless otherwise noted. [b] Determined by GPC. [c] Conversion 80%. [d] Conversion 75%. [e] Conversion 73%.

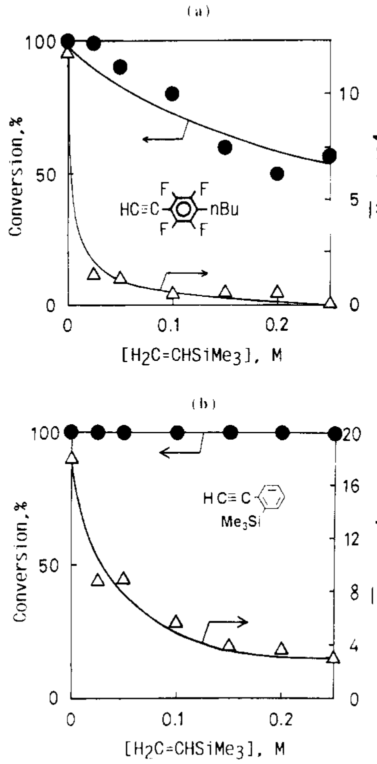


Figure 6. Effect of trimethylvinylsilane concentration on the polymerization of phenylacetylenes by WCl_6–Ph_4Sn (1:1) (in toluene, 30 °C, 24 h; $[M]_o = 0.50$ M, $[WCl_6] = 10$ mM).

6 when the olefin is absent. Whereas the $\bar{M}_n$ of the polymer is 12×10^4 at $[H_2C{=}CHSiMe_3] = 0$ M, the value of the polymer decreased to no more than ca. 3×10^3 at 0.25 M. The monomer conversion, however, somewhat decreased when the concentration of trimethylvinylsilane was 0.25 M, which is attributable to the low reactivity of this monomer.

The data of Table III and Figure 6 are indicative that p-BuF_4PA suffers chain transfer to trimethylvinylsilane more readily than o-CF_3PA and that the former monomer is less reactive in the presence of trimethylvinylsilane (cf. Table I and Figure 2). These results coincide with the notion that p-BuF_4PA has many electron-withdrawing fluorines and therefore less coordinating ability to the propagating end than o-CF_3PA does.

Effects of various olefins ($^1/_5$ equiv to monomer) on the polymerization of o-Me_3SiPA were examined for the sake of comparison (see Table III). The conversions reached 100% even in the presence of olefins. While the $\bar{M}_n$ value of the polymer without an olefin reached about 18×10^4, it decreased to some extent in the presence of Si-containing or simple hydrocarbon olefins. Again, Si-containing olefins are more effective than hydrocarbon olefins. The degree of the molecular weight decrease, however, is much smaller than those in p-BuF_4PA and o-CF_3PA.

Figure 6b depicts the effect of trimethylvinylsilane concentration on the polymerization of o-Me_3SiPA. The polymerization is completed under the conditions of Figure 6b even with olefin concentration up to 0.25 M ($^1/_2$ equiv to monomer). The polymer molecular weight decreased with increasing concentration of trimethylvinylsilane. However, the curve is not so steep as in the polymerizations of o-CF_3PA (Figure 2) and p-BuF_4PA (Figure 6a). These results support the idea that the monomer with the electron-donating silicon atom does not suffer chain transfer easily.

Analyses of the End Groups of Poly(o-CF_3PA) and Poly(p-BuF_4PA). In an attempt to observe the end groups of the polymerization products, we prepared oligomers at high trimethylvinylsilane concentrations, low monomer concentration, and high temperature. The detailed data for the synthesis of oligomers are as follows. Poly(o-CF_3PA): $\bar{M}_n$ 800, conversion 100% ([C=C] = 3.0 M, $[M]_o = 0.10$ M, 50 °C, 24 h). Poly(p-BuF_4PA): $\bar{M}_n$ 600, conversion 100% ([C=C] = 0.50 M, $[M]_o = 0.10$ M, 50 °C, 24 h).

The IR spectra of these oligomers showed Si–C stretchings at 850 and 750 cm^{-1} and SiC–H deformation at 1250 cm^{-1}. In the ^1H NMR spectra methyl protons of the trimethylsilyl group were observed in the range δ +0.3 to −0.1. Comparison of the molecular weight by GPC with the peak ratio in the ^1H NMR spectra suggested that nearly one trimethylsilyl group is present per molecule in both poly(o-CF_3PA) and poly(p-BuF_4PA). The ^{13}C NMR spectra of both oligomers also exhibited several kinds of methyl carbons of the trimethylsilyl group in δ +3 to −3. These results clearly indicate that the trimethylsilyl group exists in these oligomers. Several kinds of methylene groups were observed in the ^{1}H NMR spectra, which is probably attributable to various sequences of the geometric structures of the main chain. The amount of end groups should be examined more quantitatively in the future.

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Registry No. (o-CF$_3$PA) (homopolymer), 96504-22-2; (m-CF$_3$PA) (homopolymer), 96504-21-1; (p-CF$_3$PA) (homopolymer), 96504-19-7; (PA) (homopolymer), 25038-69-1; (o-TMSPA) (homopolymer), 112754-88-8; (o-CH$_3$PA) (homopolymer), 113781-24-1; (o-C$_6$H$_{13}$PA) (homopolymer), 133612-94-9; (o-i-PrPA) (homopolymer), 144467-25-4; (p-BuC$_6$F$_4$C≡CH) (homopolymer), 121134-15-4; (2,6,4-Me$_2$CBu-t-C$_6$H$_2$C≡CH) (homopolymer), 125997-83-3; WCl$_6$, 13283-01-7; Ph$_4$Sn, 595-90-4; Me$_3$SiCH=CH$_2$, 754-05-2; BuMe$_2$SiCH=CH$_2$, 24343-24-6; PhMe$_2$SiCH=CH$_2$, 1125-26-4; (CH$_3$)$_3$CCH=CH$_2$, 558-37-2; 1-octene, 111-66-0; 2-octene, 111-67-1.