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DESIGN, SYNTHESIS, AND PROPERTIES OF SUBSTITUTED POLYACETYLENES

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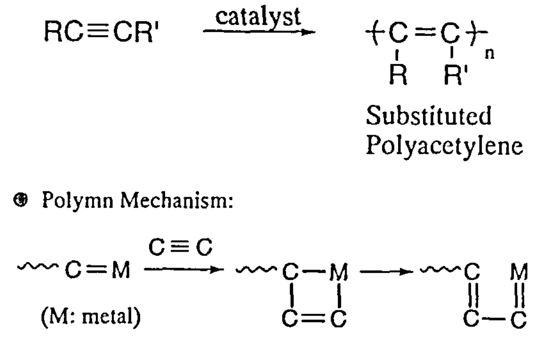
ABSTRACT

This article reviews recent topics on the polymerization of substituted acetylenes, focusing on the synthesis of poly(diphenylacetylenes) and the living polymerization of phenylacetylenes. Diphenylacetylene (DPA) polymerizes with $TaCl_5$–n-Bu_4Sn to give a polymer which is thermally very stable but insoluble in any solvents. DPAs with various groups (e.g., p-Me_3Si, m-Me_3Ge, p-t-Bu, and p-PhO) polymerize similarly. These polymers are soluble and their $\overline{M}_w$'s reach 1×10^6 to 3×10^6. Some of them are more gas-permeable than poly(dimethylsiloxane). Several acetylenes (e.g., $ClC{\equiv}C$-n-C_6H_{13} and $HC{\equiv}C$-t-Bu) have been found to undergo living polymerization with $MoOCl_4$–n-Bu_4Sn–EtOH. Whereas phenylacetylene (PA) does not polymerize in a living fashion, ortho-substituents in PA more or less suppress termination and chain transfer. PAs with bulky ortho groups (e.g., CF_3 and Me_3Ge) especially undergo virtually ideal living polymerization.

INTRODUCTION

Substituted acetylenes can be polymerized by suitable transition-metal catalysts [1–7] (Scheme 1). The polymers produced have alternating double bonds along the main chain and various groups as the side chains. The polymerization of substituted acetylenes by Group 5 and 6 transition metal catalysts is thought to proceed via metal carbenes; i.e., a metal carbene reacts with an acetylene to give a metalla-



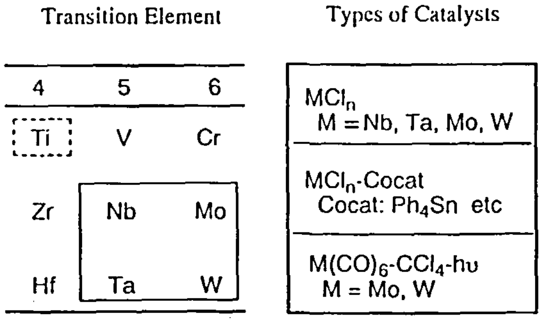
SCHEME 1. Polymerization of substituted acetylenes.

cyclobutene, the ring opening of which regenerates a metal carbene, and thus propagation proceeds. This mechanism resembles that of the ring-opening metathesis polymerization (ROMP) of cycloolefins [8, 9].

Ti catalysts are known to polymerize the unsubstituted acetylene, and the most typical one is $Ti(O\text{-}n\text{-}Bu)_4\text{–}Et_3Al$, the so-called Shirakawa catalyst (Scheme 2). We have found that catalysts containing Group 5 and 6 transition metals such as Nb, Ta, Mo, and W polymerize substituted acetylenes. Some of the catalysts exploited by us are as follows: (i) chlorides of Nb, Ta, Mo, and W; (ii) 1:1 mixtures of those metal chlorides with suitable organometallic cocatalysts; and (iii) catalysts obtained by UV irradiation of CCl_4 solutions of Mo and W hexacarbonyls.

Table 1 shows typical examples of the synthesis of high molecular weight polymers from substituted acetylenes. *tert*-Butylacetylene and various disubstituted acetylenes produce high molecular weight polymers. In general, Group 6 transition metal (Mo and W) catalysts are effective for various monosubstituted and sterically less crowded disubstituted acetylenes, while Group 5 transition metal (Nb and Ta) catalysts are active toward sterically crowded disubstituted acetylenes. Choice of suitable catalysts and solvents accomplishes high yields of polymers. More importantly, the molecular weights of polymers reach 5×10^5 to 2×10^6.

The properties of polyacetylenes with bulky substituents differ remarkably



SCHEME 2. Catalysts for the polymerization of substituted acetylenes.

TABLE 1. Examples of High Polymer Synthesis[a]

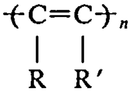
Monomer	Catalyst	Solvent	Temperature, °C	Polymer yield, %	$\overline{M}_w / 10^4$
$HC{\equiv}C\mathit{t}Bu$	$MoCl_5$	Toluene	30	100	75
$CH_3C{\equiv}C\mathit{n}Pr$	$MoCl_5$-Ph_4Sn (1:1)	Toluene	30	90	110
$ClC{\equiv}CPh$	$Mo(CO)_6$-CCl_4-$h\nu$	CCl_4	30	80	200
$CH_3C{\equiv}CPh$	$TaBr_5$	Toluene	80	60	92
$CH_3C{\equiv}CSi(CH_3)_3$	$TaCl_5$	Toluene	80	100	73

[a] Polymerized for 24 hours, $[M]_0 = 1.0\ M$, $[Cat] = 10$-$30\ mM$.

from those of unsubstituted polyacetylene (Table 2). For example, the substituted polyacetylenes are variously colored from white or yellow to brown and further to dark purple. This originates from the fact that their main chain assumes more or less twisted conformations induced by the substituents. Further, they are soluble in many common organic solvents owing to the interaction between substituents and solvent. Unlike polyacetylene, those with bulky substituents are stable in air at room temperature over a long period of time. This is explained by the less easy formation of free radicals due to twisted main-chain structures and by protection of the main chain from oxygen attack by bulky substituents. As typical polymer functions, one can point out electrical conductivity for polyacetylene and gas permeability for substituted polyacetylenes. The latter function stems from the large free volume brought about by the rigid main chain and bulky substituents.

Herein, recent work on the polymerization of substituted acetylenes is introduced, focusing on a couple of topics: (a) synthesis and properties of poly(diphenylacetylenes); and (b) living polymerization of ortho-substituted phenylacetylenes.

TABLE 2. Comparison of Substituted Polyacetylenes with Polyacetylene

	Polyacetylene	Substituted polyacetylene
Structure	$\left(CH{=}CH\right)_n$	 $\left(\underset{R}{C}{=}\underset{R'}{C}\right)_n$
Polymn catalyst	$Ti(OBu)_4$-Et_3Al	Nb, Ta, Mo, W
Molecular weight	$\sim 10^4$	10^5-10^6
Color	Black (powder)	Various colors
Solubility	Insoluble	Soluble
Crystallinity	Crystalline	Amorphous
To air	Unstable	Stable
Typical function	Electrical conductivity	Gas permeability

SYNTHESIS AND PROPERTIES OF POLY(DIPHENYLACETYLENES)

The polymerization of diphenylacetylene (DPA) and its derivatives having Me_3Si, Me_3Ge, *t*-butyl, *n*-butyl, benzyl, and phenoxy groups at the para or meta position has been investigated for the purposes of (i) searching for effective polymerization catalysts for these monomers, (ii) characterization of the polymers formed, and (iii) development of polymer functions.

The polymerization of diphenylacetylene has been examined in toluene at 80°C [10]. Among various Group 5 and 6 transition metal catalysts, $TaCl_5$-based catalysts have proved exclusively effective (Table 3). When $TaCl_5$ alone is used, i.e., no cocatalyst is employed, then the monomer is consumed to some extent, but no methanol-insoluble polymer is formed. In contrast, polymers are obtained in high yields when alkyl-containing Sn and Si compounds are used as cocatalysts. On the other hand, phenyl-substituted cocatalysts are hardly effective, probably owing to steric reasons.

The poly(diphenylacetylene) formed is a yellow solid. This polymer does not dissolve in any solvent and does not melt on heating. Therefore, it is impossible to fabricate a membrane from this polymer. This polymer, however, retains its weight up to 500°C in thermogravimetric analysis (TGA) in air. Thus, high thermal stability is one of its salient features.

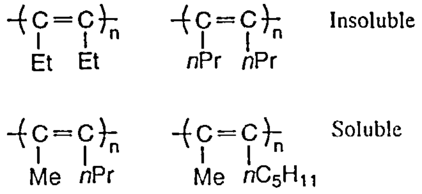
Regarding polymer solubility, there is a tendency for polyacetylenes with two identical alkyl groups in the repeat unit to be insoluble [11] whereas polyacetylenes having a methyl and a long alkyl are soluble in organic solvents [12] (Scheme 3). This is attributable to the difference in polymer surface area between these two types of polymers. Hence, a possible working hypothesis is that if a bulky substituent is introduced into one of the phenyl groups of diphenylacetylene, then the polymer will be soluble.

Therefore, the polymerization of diphenylacetylenes having a Me_3Si group has been examined [13, 14] (Table 4). 1-Phenyl-2-[*p*-(trimethylsilyl)phenyl]acetylene

TABLE 3. Polymerization of Diphenylacetylene by $TaCl_5$–*n*-Bu_4Sn (1:1)[a]

Cocatalyst	Conversion, %	Polymer yield, %
None	53	0
Me_4Sn	100	100
n-Bu_4Sn	87	77
Et_3SiH	100	100
Ph_4Sn	0	0
Ph_3SiH	24	5
Ph_3Bi	0	0

[a] Polymerized in toluene at 80°C for 24 hours, $[M]_0$ = 1.0 M, [Cat] = 20 mM.



SCHEME 3. Solubility of aliphatic polyacetylenes.

(p-Me$_3$SiDPA) polymerizes with TaCl$_5$-n-Bu$_4$Sn catalyst to give a new polymer in high yield (up to 85%). In contrast, TaCl$_5$ alone provides no polymer. Not only is n-Bu$_4$Sn an effective cocatalyst, but Et$_3$SiH and 9BBN are also. In accordance with expectation, the polymer obtained is totally soluble in toluene and chloroform. Quite interestingly, the molecular weight of the polymer reaches about two million. In contrast, the corresponding Nb catalyst does not form any polymer. The m-Me$_3$Si derivative polymerizes similarly to give a polymer in high yield and whose molecular weight exceeds one million.

The polymers from the Si-containing diphenylacetylenes are yellow to orange-colored solids with an alternating double bond structure along the main chain, $[-CPh{=}C(C_6H_4SiMe_3)-]_n$. These polymers exhibit two absorptions around 380 and 430 nm (cutoffs ~500 nm) in the UV-visible spectra. Their solvents include toluene, cyclohexane, carbon tetrachloride, chloroform, anisole, and tetrahydrofuran. Casting toluene solutions of the polymers provides tough films. The onset temperatures (T_0) of weight loss in TGA in air for these polymers are as high as ~400°C, showing excellent thermal stability. Their Young's moduli are 800-1500 MPa, tensile strengths 14-19 MPa, and elongations at break ~2%, indicating that

TABLE 4. Polymerization of Me$_3$Si-diphenylacetylenes[a]

Catalyst	Monomer conversion, %	Polymer[b] Yield, %	Polymer[b] $\overline{M}_w/10^4$ [c]
	p-Me$_3$Si		
TaCl$_5$-n-Bu$_4$Sn	95	85	220
NbCl$_5$-n-Bu$_4$Sn	34	0	—
	m-Me$_3$Si		
TaCl$_5$-n-Bu$_4$Sn	100	87	140
NbCl$_5$-n-Bu$_4$Sn	25	0	—

[a] In toluene, 80°C, 24 hours, $[M]_0 = 0.50$ M, [Cat] = 20 mM, [n-Bu$_4$Sn] = 40 mM.

[b] Methanol-insoluble product.

[c] Determined by GPC (polystyrene calibration).

they are hard and brittle. Their glass transition temperatures are above 200°C according to dynamic viscoelastic measurements.

The polymerization of various para-substituted diphenylacetylenes (Me_3Ge [15], *t*-butyl [16], *n*-butyl [16], benzyl [17], and phenoxy [18]) has been studied by using the $TaCl_5$-*n*-Bu_4Sn catalyst (Table 5). All these monomers yield polymers in good yields over 50%. The product polymers are totally soluble in toluene and chloroform as expected. Their molecular weights, determined by GPC, are as high as a few million. An interesting point is that their absolute $\overline{M}_w$ values measured by light scattering are smaller and ~ ½-⅔ of the values by GPC.

Figure 1 shows TGA curves of various poly(diphenylacetylenes) measured in air. Poly(phenylacetylene) begins to lose weight at around 200°C, being rather unstable. As described above, poly(DPA) retains its weight up to 500°C and is more stable than any other substituted polyacetylenes. Apart from the *n*-alkyl-containing ones, most poly(DPAs) having substituents lose weight above ~400°C, which indicates appreciably high thermal stability.

Gas permeability of the poly(DPA) derivatives has been examined as one of their functions. Figure 2 plots the oxygen permeability coefficient (P_{O_2}) vs the ratio of permeability coefficients of oxygen and nitrogen (P_{O_2}/P_{N_2}; separation factor). Among the conventional polymers, poly(dimethylsiloxane) shows the highest oxygen permeability. It has, however, been found that poly[1-(trimethylsilyl)-1-propyne] shows a value about 10 times higher than that of poly(dimethylsiloxane) [19-21]. Further, as seen in Fig. 2, the Me_3Si-, Me_3Ge-, and *t*-butyl-containing poly(DPAs) are about two times as permeable to oxygen as is poly(dimethysiloxane). In contrast, the P_{O_2} values of *n*-butyl- and phenoxy-carrying poly(DPAs) are much smaller. These findings indicate that not the kind but the round shape of the substituents in poly(DPA) is important to achieve high oxygen permeability. Poly(*t*-BuDPA) is the first example of a hydrocarbon-based polymer that is more permeable to oxygen than is poly(dimethylsiloxane).

Table 6 summarizes the results of the polymerization of diphenylacetylenes. Not only poly(DPA) but also its ring-substituted derivatives can be obtained by the

TABLE 5. Polymerization of Diphenylacetylenes with Para-Substituents ($C_6H_5C{\equiv}CC_6H_4$-*p*-R) by $TaCl_5$-*n*-Bu_4Sn (1:2)[a]

R	Monomer conversion, %	Polymer (MeOH-insoluble product) Yield, %	$\overline{M}_w/10^3$ GPC	$\overline{M}_w/10^3$ LS	$\overline{M}_n/10^3$, GPC
Me_3Si	95	85	2200	–	750
Me_3Ge	100	52	1800	–	530
t-Bu	100	84	3600	1600	1400
n-Bu	100	82	1300	940	460
$PhCH_2$	100	74	870	430	350
PhO	100	69	1700	1200	400

[a] In toluene, 80°C, 3-24 hours, $[M]_0$ = 0.1-0.5 M, $[TaCl_5]$ = 20 mM.

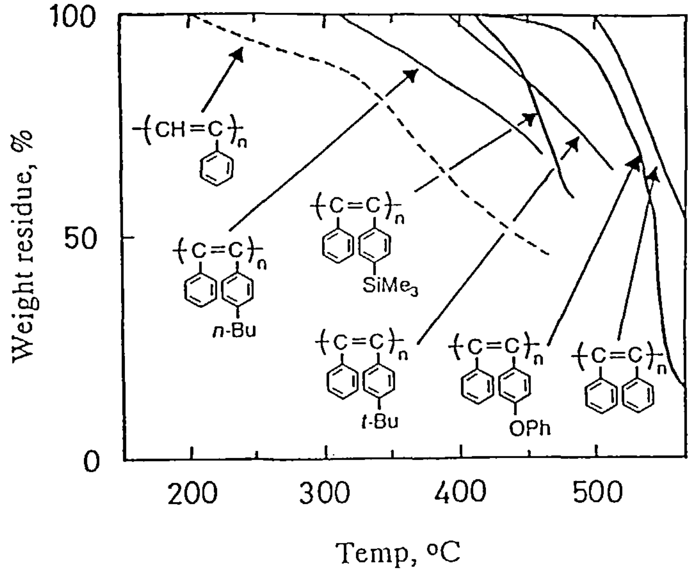


FIG. 1. TGA curves of poly(diphenylacetylenes) (in air, heating rate 10°C/min).

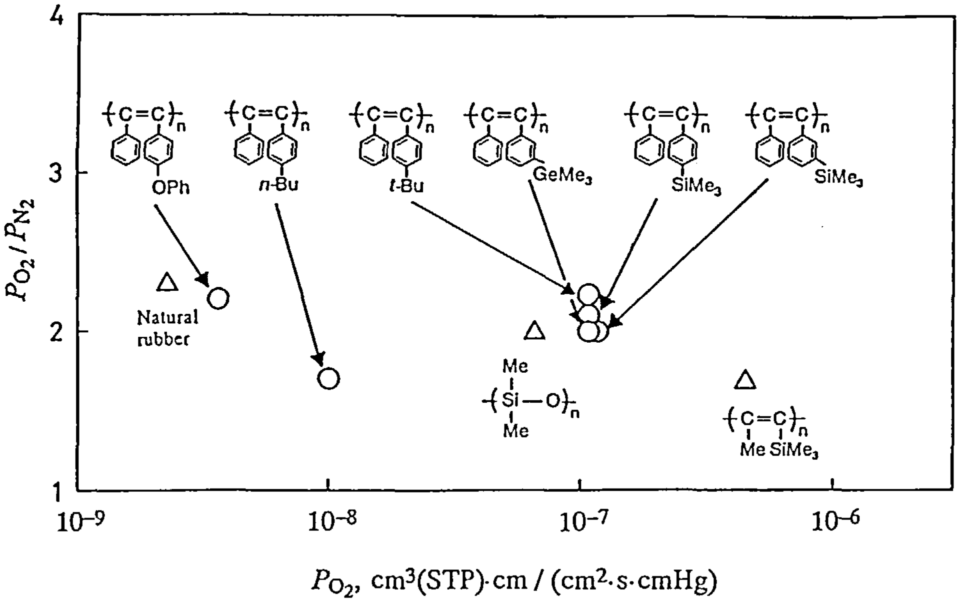
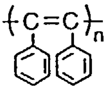
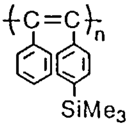
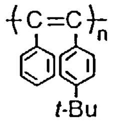
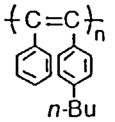
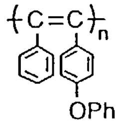


FIG. 2. Plot of oxygen permeability coefficient (P_{O_2}) vs separation factor (P_{O_2}/P_{N_2}) for poly(diphenylacetylenes) and a few other polymers (25°C).

TABLE 6. Polymerization of Diphenylacetylenes and Polymer Properties

					
Polymerization by		TaCl$_5$-n-Bu$_4$Sn (yield >50%)			
$\overline{M}_w/10^3$	–	2200	3600	1300	1700
In toluene	Insoluble	Soluble	Soluble	Soluble	Soluble
T_0, °C[a]	500	420	380	320	420
P_{O_2}, barrer[b]	–	1100	1100	100	37

[a] Onset temperature of weight loss in TGA in air.

[b] Oxygen permeability coefficient (25°C).

polymerization using TaCl$_5$-n-Bu$_4$Sn. Their molecular weights reach a few million. The poly(DPA) derivatives shown in Table 6 are all soluble in toluene and so on. The T_0 values for poly(DPA) and most of its derivatives are 400–500°C, showing high thermal stability. The P_{O_2} values of the polymers having round-shaped substituents like Me$_3$Si and t-butyl are ~1000 barrers, about twice that of poly(dimethylsiloxane). Thus poly(DPA) derivatives are a new class of polyacetylenes featured by interesting properties, and further development of their unique functions is expected.

LIVING POLYMERIZATION OF ORTHO-SUBSTITUTED PHENYLACETYLENES

Living polymerization is one of the most useful means to control both molecular weight and molecular weight distribution (MWD) of polymers. Recently, many living processes have been developed in not only anionic but also in various other types of polymerizations [22]. While the study on the living ROMP of cycloolefins has recently made great progress [8, 9], there have still been only a few reports on the living polymerization of substituted acetylenes; e.g., 2-butyne by a Ta carbene [23], an α,ω-diyne by a Mo carbene [4], 1-(trimethylsilyl)-1-propyne by NbCl$_5$ in cyclohexane [24], and several substituted acetylenes by MoOCl$_4$ (or MoCl$_5$)-n-Bu$_4$Sn-EtOH [25–32].

Figure 3 shows molecular weight distribution (MWD) curves of the polymers formed from 1-chloro-1-octyne [25]. The polymerizations have been carried out with MoOCl$_4$-based catalysts in toluene at 30°C, and the monomer feed has been supplied three times every 5 minutes. In the polymerization by MoOCl$_4$ alone, the polymer molecular weight increases progressively, but the MWDs are rather broad. The MoOCl$_4$-n-Bu$_4$Sn catalyst fairly narrows the MWD, but the polydispersity ratio ($\overline{M}_w/(\overline{M}_n)$ is 1.3–1.5 and not very close to unity. In contrast, MoOCl$_4$-n-Bu$_4$Sn-EtOH (mole ratio 1:1:1), a MoOCl$_4$-based ternary catalyst, decreases the polydispersity ratio to 1.1–1.2. Here the polymer molecular weight increases progressively with each further supply of monomer, whereas the MWD remains narrow throughout

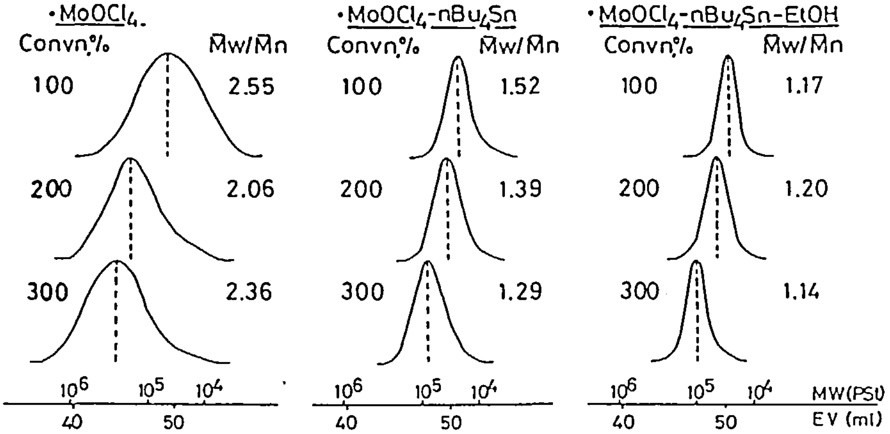
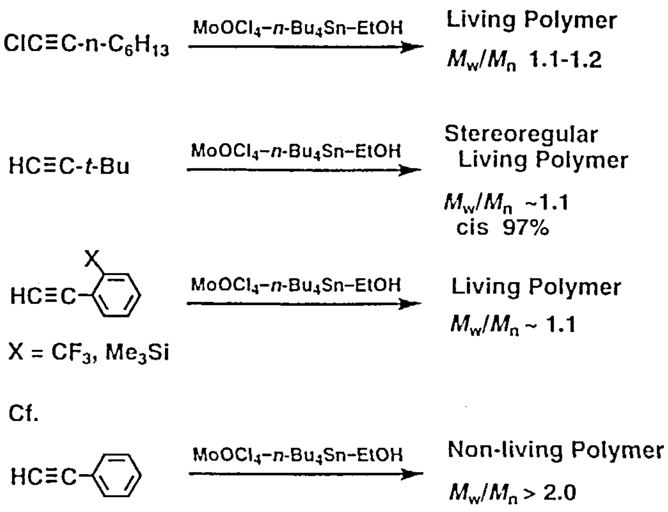


FIG. 3. MWD curves of poly(1-chloro-1-octyne)s formed with $MoOCl_4$-based catalysts (in toluene, 30°C, $[M]_0 = 0.10$ M, $[MoOCl_4] = 10$ mM).

this procedure. These results manifest that this polymerization is a living polymerization. The corresponding $MoCl_5$-based catalyst ($MoCl_5$-n-Bu_4Sn-EtOH) is also effective in the polymerization of 1-chloro-1-octyne, but the MWD of the polymer is somewhat broader ($\overline{M}_w/\overline{M}_n = 1.2$–$1.3$) [26].

Several other acetylenes also undergo living polymerization in the presence of the $MoOCl_4$-based ternary catalyst (Scheme 4). As demonstrated in Fig. 3, 1-chloro-1-octyne provides a living polymer whose polydispersity ratio is 1.1–1.2. Quite interestingly, *tert*-butylacetylene produces a stereoregular living polymer, that is, a polymer having 97% cis and a polydispersity ratio of 1.1 [27]. Such stereospecific



SCHEME 4. Living polymerization of substituted acetylenes by $MoOCl_4$-n-Bu_4Sn-EtOH (1:1:1).

living polymerizations are rare, even when one considers all the known polymerization mechanisms. Further, phenylacetylenes having ortho substituents also polymerize in a living fashion; examples of such monomers include phenylacetylenes with *o*-CF_3 [28], *o*-Me_3Si [29], and *p*-butyl-*o*,*o*,*m*,*m*-F_4 groups [30]. This result is noteworthy because phenylacetylene itself does not give a living polymer with this catalyst. The synthesis of block copolymers from 1-chloro-1-octyne and other acetylenes has been achieved through their sequential living polymerization by $MoOCl_4$-*n*-Bu_4Sn-EtOH [31].

The above-stated, fragmentary but interesting results on the polymerization of phenylacetylenes prompted us to study in detail the effect of various ortho substituents on the living polymerization of phenylacetylene [32, 33]. The ortho substituents examined were H, F, CH_3, Cl, *i*-Pr, CF_3, and Me_3Ge, in the order of increasing bulkiness. The polymerizations were carried out with the $MoOCl_4$-based ternary catalyst in toluene at 30°C.

Figure 4 shows time profiles of the polymerization of phenylacetylenes having no or a sterically small substituent at the ortho position, specifically phenylacetylene, *o*-F- and *p*-CH_3-phenylacetylenes. The monomer conversions reach 35–45% within 10 minutes but then level off, and the monomers are not completely consumed even after 24 hours.

Figure 5 illustrates GPC curves of the products obtained after 10 minutes reaction in the above-stated polymerizations. The MWD of poly(phenylacetylene) is very broad, and a considerable amount of cyclotrimers is formed as by-products. This means that not only termination and chain transfer, but also cyclotrimerization has occurred. The PA derivatives with the *o*-CF_3 or *p*-CH_3 group also show broad MWDs and the formation of cyclotrimers. Thus, the phenylacetylenes with no or a small substituent at the ortho position do not polymerize in a living manner.

The polymerization of phenylacetylenes having medium-sized ortho-substituents have been examined; the monomers are *o*-CH_3-, *o*-Cl-, and *o*-*i*Pr-phenyl-

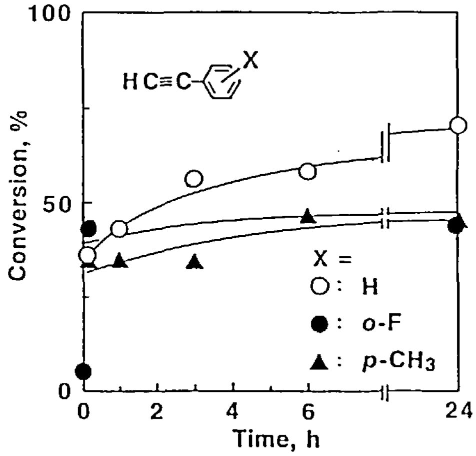


FIG. 4. Time conversion curves for the polymerization of ring-substituted phenylacetylenes (*o*-X: none or small) by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1) (in toluene, 30°C, $[M]_0$ = 0.10 M, $[MoOCl_4]$ = 10 mM).

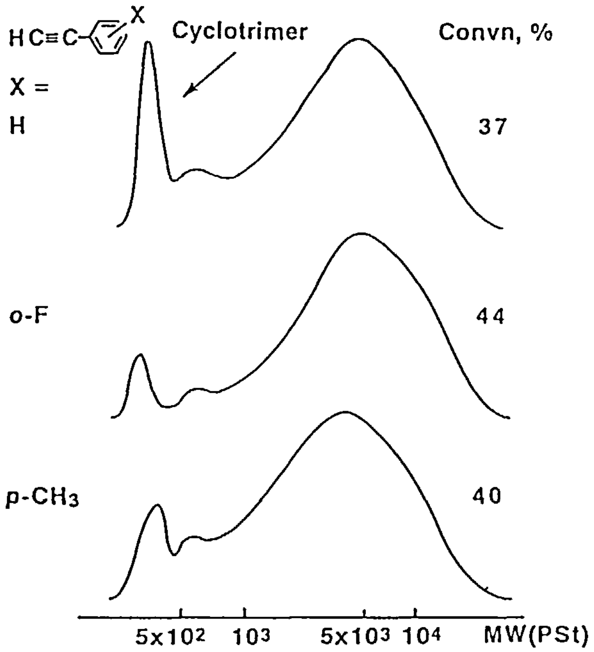
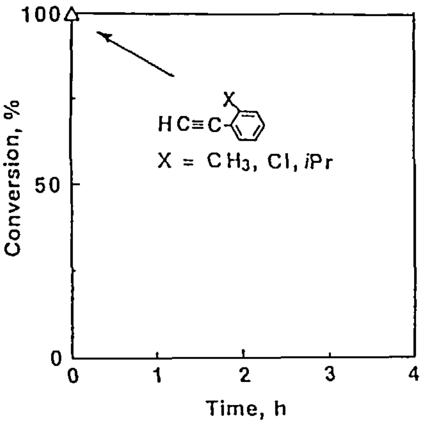


FIG. 5. MWD curves of the ring-substituted poly(phenylacetylenes) (*o*-X: none or small) obtained with $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1) (in toluene, 30°C, $[M]_0 = 0.10$ M, $[MoOCl_4] = 10$ mM).



X	$\bar{M}_n$	$\bar{M}_n/\bar{M}_w$
CH_3	16,000	1.31
Cl	13,200	1.30
*i*Pr	24,500	1.23

FIG. 6. Time profiles of the polymerization of ortho-substituted phenylacetylenes (*o*-X: medium size) by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1) (in toluene, 30°C, $[M]_0 = 0.10$ M, $[MoOCl_4] = 10$ mM).

acetylenes (Fig. 6). Unlike the previous case, all these monomers completely polymerize within 1 minutes. The polydispersity ratios of the formed polymers are 1.2–1.3, indicating fairly narrow MWDs. These values suggest living polymerization.

Two-stage polymerization is useful to clarify whether a polymerization is living or not. In two-stage polymerization, a new monomer feed is added to a completely polymerized system, and changes of molecular weight and molecular weight distribution are examined. Figure 7 shows MWD curves for the two-stage polymerization of phenylacetylenes with medium-sized ortho substituents. After the second-stage polymerization, no dead polymers are formed and the molecular weights of polymers are directly proportional to monomer consumption. This clearly shows that these polymerizations are living polymerizations, though the MWDs are not very narrow.

The third type of polymers examined are phenylacetylenes having bulky ortho substituents like *o*-CF_3 and *o*-Me_3Ge groups (Fig. 8). These polymerizations proceed smoothly without an induction phase to reach 100% conversion finally. The $\overline{M}_n$ of both polymers increases in direct proportion to monomer conversion, while the polydispersity ratio remains as small as 1.1. Thus, these monomers undergo virtually ideal living polymerization.

Table 7 summarizes the polymerization of various ortho-substituted phenylacetylenes by $MoOCl_4$-based ternary catalyst. When the ortho substituents are none or small, the polymerizations level off halfway and give broad MWDs. On the other hand, phenylacetylenes having medium-sized substituents polymerize almost instantaneously to 100% to provide living polymers having polydispersity ratios of 1.2–1.3. Further, the monomers having bulky CF_3 and Me_3Ge groups polymerize

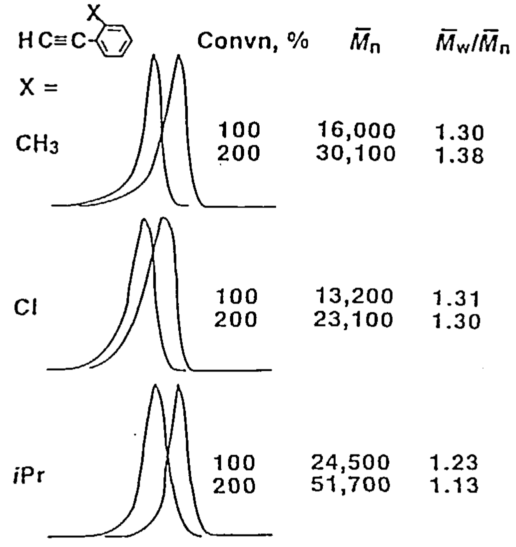


FIG. 7. MWD curves of the ortho-substituted poly(phenylacetylenes) (*o*-X: medium size) formed in the two-stage polymerization using $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1) (in toluene, 30°C, $[M]_0$ = 0.10 M, $[MoOCl_4]$ = 10 mM).

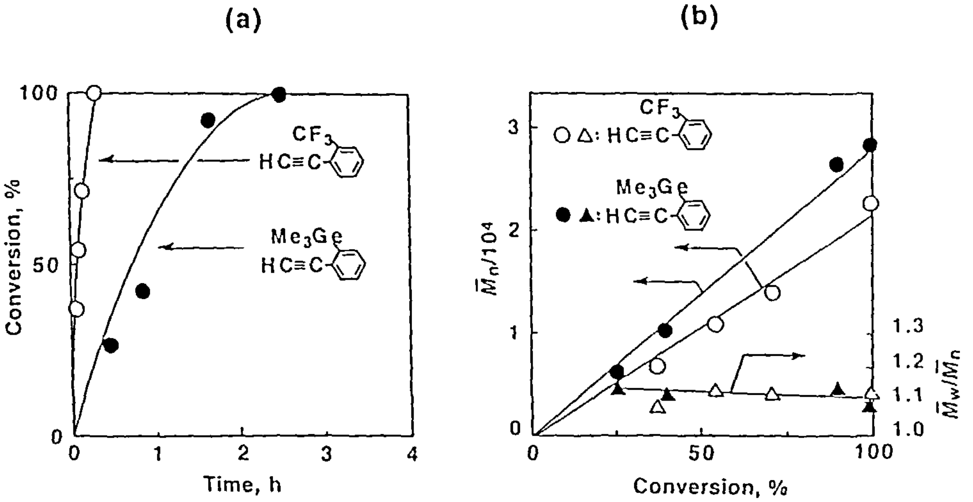


FIG. 8. Polymerization of ortho-substituted phenylacetylenes (*o*-X: bulky) by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1) (in toluene, 30°C, $[M]_0$ = 0.10 M, $[MoOCl_4]$ = 10 mM).

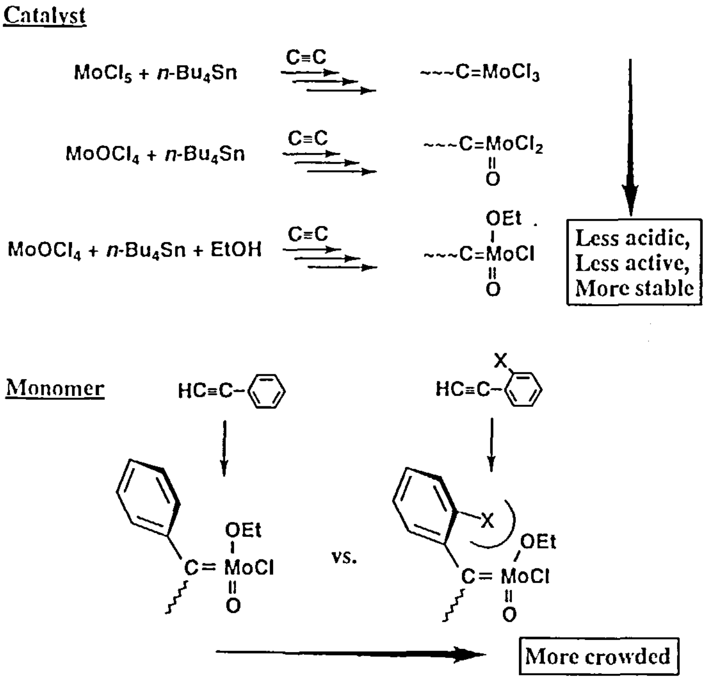
smoothly and exhibit an excellent living nature with small polydispersity ratios of ~1.1. Based on these results, one can conclude that it is not the electronic effect but the steric effect of ortho substituents, that plays an important role in achieving the living polymerization of phenylacetylenes.

The factors controlling the present living polymerization are discussed (Scheme 5). The binary catalyst comprising $MoCl_5$ and tetrabutyltin is assumed to generate a Mo carbene that contains three chlorines as the propagating species. Similarly, a mixture of $MoOCl_4$ and tetrabutyltin will produce a Mo carbene having two chlorines. On the other hand, the addition of ethanol as the third component to this catalyst system will presumably form a species having an ethoxy group instead of a chlorine. This species should be less electrophilic, less active, but more stable than the species formed from $MoCl_5$- and $MoOCl_4$-based binary catalysts; this seems to lead to living polymerization.

TABLE 7. Polymerization of Ortho-Substituted Phenylacetylenes by $MoOCl_4$-*n*-Bu_4Sn-EtOH (1:1:1)[a]

Ortho-Substituent			
Bulkiness	Example	$\bar{M}_w/\bar{M}_n$	Livingness
Small	H, F	>2.0	No
Medium	CH_3, Cl, *i*Pr	1.2-1.3	Yes
Large	CF_3, Me_3Ge	~1.1	Yes

[a] In toluene, 30°C, $[M]_0$ = 0.10 M, $[MoOCl_4]$ = 10 mM.



SCHEME 5. Factors for living polymerization.

Regarding the effect of ortho-substituent, ortho-substituted phenylacetylenes are thought to produce sterically crowded propagating species. It seems that such steric crowding prohibits chain transfer (e.g., intermolecular secondary metathesis) and termination (e.g., formation of binuclear complexes).

CONCLUDING REMARKS

This article has reviewed recent advances in the design, synthesis, and properties of substituted polyacetylenes. The conclusions are: (a) the synthesis of various poly(diphenylacetylene) derivatives which are completely soluble, of high molecular weight, thermally fairly stable in air, and highly gas permeable has been achieved; and (b) the $MoOCl_4$-n-Bu_4Sn-EtOH catalyst induces the living polymerization of ortho-substituted phenylacetylenes, where not the electronic effect but the steric effect of ortho substituents plays an important role.

Apart from high gas permeability, various functions of substituted polyacetylenes are being developed extensively. Examples include separation of ethanol-water mixture by pervaporation [34], photoconductivity which might be applicable to photosensors [35], electrochromism (reversible color change with electricity) [36], and third-order nonlinear optical properties [37].

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