wavelength (460–478 nm). For ratios $[M]/[HA]_0 > 3$, more carbocations are formed, and the increase of the optical density at 478 nm is proportional to that of the first maximum at 382.5 nm. This observation confirms that these two absorption bands correspond to the isomerized species (M_{3i}^+ or M_{ni}^+). If this is assumed the extinction coefficient at 478 nm is found to be equal to 5600 L·mol^{-1}·cm^{-1}.

In a following article we shall report on the cationic polymerization of *p-tert*-butyl-α-methylstyrene, *p*-methyl-α-methylstyrene, and α-methylstyrene and compare them with *p*-methoxy-α-methylstyrene.[20]

References and Notes

(1) Sauvet, G.; Vairon, J. P.; Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 52*, 173.
(2) Nguyen, A. H.; Subira, F.; Cheradame, M.; Sigwalt, P. *Tetrahedron* **1978**, *34*, 335.
(3) Leborgne, A.; Souverain, D.; Sauvet, G.; Sigwalt, P. *Eur. Polym. J.* **1980**, *16*, 865; **1980**, *16*, 861.
(4) Cotrel, R.; Sauvet, G.; Vairon, J. P.; Sigwalt, P. *Macromolecules* **1976**, *9*, 931.
(5) Subira, F.; Sauvet, G.; Vairon, J. P.; Sigwalt P. *J. Polym. Sci., Polym. Symp.* **1976**, *No. 56*, 221.
(6) Lorimer, J. P.; Pepper, D. C. *Proc. R. Soc. London, A* **1976**, *351*, 551.
(7) Kunitake, T.; Takarabe, K. *Macromolecules* **1979**, *12*, 1061.
(8) Olah, G. A.; Pittman, C. U.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488.
(9) Teyssie, D.; Villesange, M.; Vairon, J. P. *Polym. Bull. (Berlin)* **1984**, *11*, 459.
(10) Ritchie, C. O.; Sager, W. F. *Prog. Phys. Org. Chem.* **1964**, *2*, 323.
(11) Sauvet, G.; Vairon, J. P.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1975**, 4031.
(12) Gourdenne, A.; Sigwalt, P. *Bull. Soc. Chim. Fr.* **1967**, 2249.
(13) Olah, G. A.; Comisarow, M. B.; Kim, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 1458.
(14) Svob, A.; Cernicki, B. *Chimia* **1968**, *22*(11), 434.
(15) Curtis, R. F. *Chem. Ind.* **1960**, 928.
(16) Arnett, E. M.; Petro. C. *J. Am. Chem. Soc.* **1978**, *100*, 5402.
(17) Fleischfresser, B. E.; Cheng, W. J.; Pearson, J. M.; Szwarc, M. *J. Am. Chem. Soc.* **1968**, *90*, 2172.
(18) Higashimura, T.; Kanoh, N.; Okamura, S. *J. Macromol. Sci.—Chem.* **1966**, *1*, 109.
(19) Sawamoto, M.; Higashimura, T. *Macromolecules* **1979**, *12*, 581.
(20) Matyjaszewski, K.; Sigwalt, P., to be published.

New Electrophilic Olefin Initiators for Cationic Polymerization

Myoung Seon Gong and H. K. Hall, Jr.*

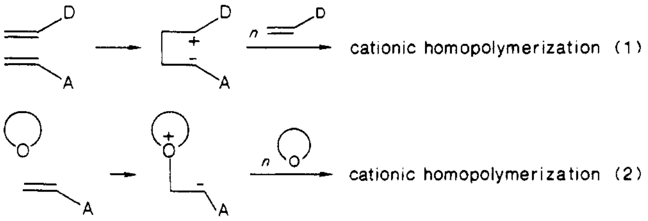
Department of Chemistry, C. S. Marvel Laboratories, University of Arizona, Tucson, Arizona 85721.

Received November 25, 1986

ABSTRACT: Four electrophilic olefins containing β-*p*-toluenesulfonate or β-trifluoroacetate groups were synthesized as new initiators for cationic polymerizations. These were 2,2-dicyanovinyl *p*-toluenesulfonate (**1**), 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate (**2**), 2,2-dicyanovinyl trifluoroacetate (**3**), and 2-cyano-2-carbomethoxyvinyl trifluoroacetate (**4**). They function by forming zwitterionic intermediates which expel the leaving group to form a carbenium–gegenion pair. They were active initiators for the cationic polymerization of electron-rich vinyl monomers and oxacyclic monomers. Moreover, **1** and **2** but not **3** and **4** displayed suitable stability by being insensitive to water, thus excluding adventitious polymerizations by *p*-toluenesulfonic acid.

Introduction

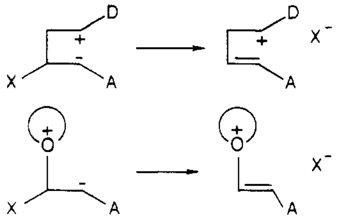
In past research we have shown that electrophilic multisubstituted ethylenes can initiate cationic vinyl and ring-opening polymerizations by forming reactive zwitterions with the monomers.[1] These zwitterions are the true initiating species.[2,3]



D = donor substituent
A = one to four acceptor substituents

However, the presence of the carbanion center limits such cationic polymerizations to those of the most electron-rich monomers.

The efficiency of such zwitterionic initiators was greatly increased if they possessed a leaving group at the β-position.[3-5] Its expulsion leaves a carbenium–gegenion pair which initiates and propagates more effectively.



The choice of the leaving group X in these initiators requires careful consideration. First, the monomer must be more nucleophilic than X^-, or high polymer cannot be formed. When X was Cl^- or I^-, the very electron-rich monomers *N*-vinylcarbazole and *N*-ethyl-3-vinylcarbazole polymerized successfully, but the less nucleophilic *p*-methoxystyrene gave only low polymers.[4,6] Chloride ion also interfered with 1,3-dioxolane.[3] In this latter case, 1,3-dioxolane polymerization initiated by β,β-dicyanovinyl chloride, oligomers could be isolated in which the presence of the head group (dicyanovinyl) and end group (chloride) was proven by NMR spectroscopy.

When X was $^-O_3SCF_3$ (triflate), *p*-methoxystyrene, trioxane, and tetrahydrofuran could be polymerized successfully, but now another complication arose.[5] The initiators β,β-dicyanovinyl triflate and tricyanovinyl triflate

Table I
Synthesis of Initiators

initiator	chloride	silver salt	acetonitrile, mL	temp, °C	time, h	purification method	yield, %
1	2,2-dicyanovinyl chloride (1.12 g, 10 mmol)	silver *p*-toluenesulfonate (2 g, 8 mmol)	20	40	2	recrystallization in CCl_4	53
2	2-cyano-2-carbomethoxyvinyl chloride (4:1 mixture of isomers, 1.45 g, 10 mmol)	silver *p*-toluenesulfonate (2 g, 8 mmol)	20	40	3	recrystallization in CCl_4	60
3	2,2-dicyanovinyl chloride (1.12 g, 10 mmol)	silver trifluoroacetate (2 g, 9.1 mmol)	40	28	1	sublimation	76
4	2-cyano-2-carbomethoxyvinyl chloride (1.45 g, 10 mol)	silver trifluoroacetate (2 g, 9.1 mmol)	40	28	2	sublimation	71

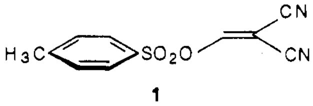
Table II
Properties of Initiators

initiator	mp, °C	properties	NMR, ppm ($CDCl_3$)[b]	IR, cm^{-1} (KBr)	elemental analysis
1	84	stable to water at room temp turns yellow on standing in air	8.0 (s, vinyl, 1 H) 7.8–7.2 (m, arom, 4 H) 2.5 (s, ϕ-CH_3, 3 H)	3062 (=CH) 2237 (C≡N) 1612 (C=C) 1590 (arom) 1406 (arom) 1354 (S=O)	calcd 53.22% C, 3.22% H, 11.29% N found 52.43% C, 3.16% H, 10.92% N
2	113	stable to water at room temp	8.2 (s, vinyl, 1 H) 7.7–7.1 (m, arom, 4 H) 3.8 (s, OCH_3, 3 H) 2.5 (s, ϕ-CH_3, 3 H)	3071 (=CH) 2244 (C≡N) 1719 ($COOCH_3$) 1613 (C=C) 1592 (arom) 1400 (arom) 1172 ($COOCH_3$) 1361 (S=O) 1195 (S=O)	calcd 51.20% C, 3.9% H, 4.98% N found 50.53% C, 3.93% H, 4.85% N
3	114[a]	dec.[c] in moisture	8.4 (s, vinyl, 1 H)	3050 (=CH) 2225 (C≡N) 1750 (CO) 1655, 1630 (C=C) 1198 (COO)	*a*
4	67[a]	dec.[c] in moisture	8.3 (s, vinyl, 1 H) 3.9 (s, OCH_3, 3 H)	3058 (C=CH) 2223 (C≡N) 1752–1705 (several absorptions, $COOCH_3$, CF_3CO 1620 (C=C) 1208–1169 (several absorptions, COO)	*a*

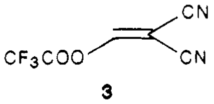
[a] Decomposed. [b] arom = aromatic. [c] dec. = decomposed.

were so reactive to water that they hydrolyzed very easily to triflic acid, CF_3SO_3H. This Brønsted acid might then contribute to the observed cationic polymerizations, although we excluded this side reaction under our experimental conditions.

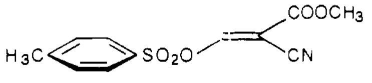
It appeared that initiators containing leaving groups X of intermediate stability would be best. Two which suggested themselves were arenesulfonates and trifluoroacetate. Sulfonic acids have often been used to initiate cationic polymerization,[7] while Szwarc and co-workers, among others, used trifluoroacetic acid for styrene polymerization.[8] Accordingly we wished to synthesize electrophilic olefins of the following types:



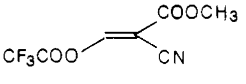
1



3

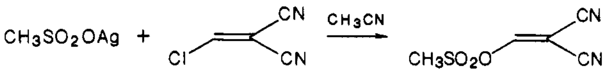


2



4

Padias[6] already synthesized β,β-dicyanovinyl *p*-toluenesulfonate (1) from the reaction of tosyl bromide with the silver derivative of hydroxymethylenemalononitrile. It was an active initiator and was also stable to water. However, the yield by this route was too small for extensive investigation. Rappoport and Topol reported[9] that silver methanesulfonate and β,β-dicyanovinyl chloride gave the methanesulfonate derivative:



(5)

We have used this reaction to synthesize new electrophilic initiators and studied their ability to initiate cationic polymerization.

Results

Synthesis. Reactions of silver *p*-toluenesulfonate with β,β-dicyanovinyl chloride or with β-cyano-β-carbomethoxyvinyl chloride in acetonitrile proceeded very well (Table I). The products 1 and 2 were crystalline and possessed clean NMR spectra (Table II). In contrast, silver *p*-toluenesulfonate and also silver triflate failed to react with β,β-dicarbomethoxyvinyl chloride. It appears that the presence of cyano is necessary for the success of this reaction.

The corresponding trifluoroacetates 3 and 4 were synthesized by analogous reactions using silver trifluoroacetate. They were also crystalline at room temperature.

Table III
Cationic Polymerizations of Electron-Rich Monomers by Initiators 1–4

monomer	concn, mol/L	initiator[j]	mol %	temp, °C	time, h	yield, %	MW[g]	η
N-vinylcarbazole[a]	0.5	**1**	1.0	-78	2[d]	~100	155000	0.41[h]
	0.5	**2**	1.0	-78	2[d]	92	90000	0.35[h]
	0.5	**3**	1.0	-78	2[d]	85	58000	0.25[h]
	0.5	**4**	1.0	-78	2[d]	54	21500	0.14[h]
p-methoxystyrene[b]	1.0	**1**	1.0	28	4	~100	91000	0.27[h]
	1.0	**2**	1.0	28	4	~100	47000	0.17[h]
	1.0	**3**	1.0	28	4	~100	62000	0.22[h]
	1.0	**4**	1.0	28	4	20	44000	0.16[h]
	1.0	**1**	1.0	-10	22	~100	86000	0.25[h]
	1.0	**2**	1.0	-10	22	94	31000	0.14[h]
	1.0	**3**	1.0	-10	22	61	140000	0.40[h]
	1.0	**4**	1.0	-10	22	<5		
	1.0	**1**	5.0	-10	24	~100	79000	0.24[h]
	1.0	**2**	5.0	-10	24	~100	37000	0.15[h]
	1.0	**3**	5.0	-10	24	~100	120000	0.34[h]
	1.0	**4**	5.0	-10	24	42	90000	0.27[h]
styrene[b]	1.0	**1**	5.0	28	72	trace		
	1.0	**3**	5.0	28	72	trace		
trioxane[c]		**1**	1.0	65	22	97[e]		0.51[i]
		2	1.0	65	22	92[f]		0.48[i]
		3	1.0	65	22	95[e]		0.60[i]
		4	1.0	65	22	91[f]		0.42[i]
cyclohexene oxide[c]		**1**	3.0	28	24	22		0.12[h]
		2	3.0	28	24	0		
		3	3.0	28	24	19		0.11[h]
		4	3.0	28	24	0		
1,3-dioxolane[c]		**1**	5.0	28	48	20		0.09[h]
		2	5.0	28	48	0		
		3	5.0	28	48	25		0.06[h]
		4	5.0	28	48	0		

[a] Solvent: dichloromethane–nitromethane (2:1). [b] Solvent: dichloromethane–nitromethane (1:1). [c] Bulk polymerization. [d] Polymerizes instantaneously. [e] Polymerizes within 5 min. [f] Polymerizes within 2 h. [g] Determined by SEC. [h] Determined in $CHCl_3$, 1 g/100 mL, 28 °C. [i] Determined in *p*-chlorophenol, 1 g/100 mL, 60 °C. [j] **1** = 2,2-dicyanovinyl *p*-toluenesulfonate, **2** = 2-cyano-2-carbomethoxyvinyl *p*-toluenesulfonate, **3** = 2,2-dicyanovinyl trifluoroacetate, and **4** = 2-cyano-2-carbomethoxyvinyl trifluoroacetate.

Polymerizations. Polymerizations were carried out with various electron-rich vinyl and cyclic monomers. The data are collected in Table III.

Ready cationic vinyl polymerizations proceeded with very electron-rich monomers. Initiators **1–4** polymerized *N*-vinylcarbazole in dichloromethane within minutes at -78 °C. Yield and molecular weights were high.

p-Methoxystyrene was less reactive, requiring room temperature (28 °C) to polymerize within hours. Even then only **1–3** gave quantitative yields, while **4** was less reactive. At -10 °C, the relative reactivity of the different initiators could be determined from the polymer yields: **1** > **2** > **3** > **4**.

Styrene gave only traces of polymer even after 72 h at room temperature.

Cationic ring opening of molten trioxane proceeded well during 22 h to give >90% yields of high polymer. 1,3-Dioxolane and cyclohexene oxide gave only ~20% yields of polymer with **1** and **3** and none with **2** and **4**.

Stability to Water. Derivatives **1** and **2** were stable when stirred with water at room temperature. In contrast, **3** and **4** reacted rather quickly under these conditions. This may involve reaction with water at the carbonyl group, rather than at the double bond.

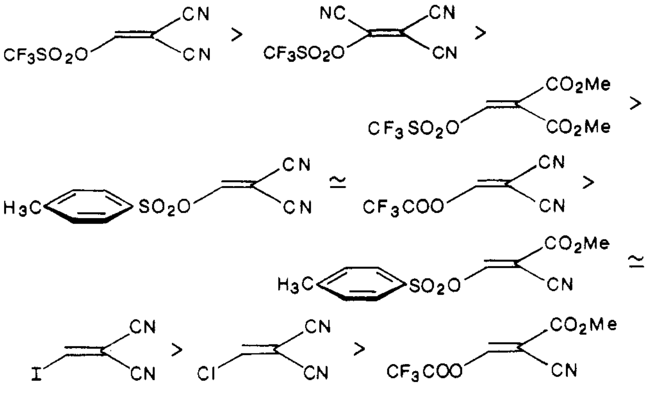
Discussion

Our results establish electrophilic olefins containing β-leaving groups as a new general class of cationic initiators. Initiators **1** and **2** displayed suitable stability by being insensitive to water, thus excluding adventitious polymerization by *p*-toluenesulfonic acid. Initiators **3** and **4** were susceptible to hydrolysis, but extreme care was taken to exclude all moisture from the polymerization.

High molecular weights prevented us from observing the head groups in these polymerizations, but on the basis of our present and earlier results,[3] we propose that the mechanism described in eq 3 and 4 is valid for these initiators. Assuming the absence of chain transfer, these initiators open the possibility of introducing reactive head groups in polymers, which can then be used in polycondensation reactions.

As far as the synthesis of these compounds is concerned, the reaction of silver tosylate or trifluoroacetate with a vinyl chloride derivative is very effective in the case of β,β-dicyanovinyl chloride and β-cyano-β-carbomethoxyvinyl chloride. The reaction does not proceed if β,β-dicarbomethoxyvinyl chloride is used. Normally we do not think of cyano as stabilizing a carbenium ion, the presumed intermediate in a silver-ion-promoted dechloridation. However, Gassman[10] has shown that back-donation from the lone pair electrons of nitrogen can offset the unfavorable inductive effect of cyano.

We can offer the following reactivity series on the basis of present and earlier results:



This sequence is reasonable in terms of greater stabilization

Macromolecules 1987, *20*, 1467–1472

of negative charge by cyano over ester and in terms of the stabilities of the various leaving groups.

Experimental Section

Methods. NMR spectra are recorded with an EM-360 Varian 60-MHz nuclear magnetic resonance spectrometer. The infrared data are obtained from a Perkin-Elmer Model 983 spectrometer. Melting points are measured with a Thomas-Hoover capillary melting point apparatus without any correction. Chemical analyses are performed by MicAnal, Tucson, AZ.

Size exclusion chromatography was carried out with three columns: Du Pont Zorbax PSM 300S and IBM GPC/SEC pore type A column, calibrated with polystyrene standards, chloroform as eluent, and a Spectra Physics detector at 254 nm.

Materials. Dichloromethane was purified by consecutive washing with sulfuric acid, water, aqueous sodium hydroxide, and water and then dried over calcium chloride and distilled from calcium hydride and sodium. Silver *p*-toluenesulfonate and silver trifluoroacetate (Aldrich Chemical Co.) were used without further purification.

All monomers were purified by literature methods.

Representative Synthesis of Initiator. 2,2-Dicyanovinyl chloride (1.12 g, 10 mmol) was added to a solution of silver *p*-toluenesulfonate (2 g, 8 mmol) in 20 mL of dry acetonitrile. The mixture was stirred at 40 °C in the dark for 2 h and cooled. The silver chloride was filtered off, the solvent was evaporated, the residue was dissolved in hot carbon tetrachloride, and the remaining silver chloride was filtered off. On cooling, crude needle-type crystals were obtained. The product was purified by two recrystallizations from carbon tetrachloride.

Polymerization. Polymerizations were performed on a 1-g scale under dry nitrogen in septum-capped polymerization tubes at the required temperature.

The polymers were precipitated from methanol or petroleum ether and dried in vacuo at 50 °C. Yields were determined gravimetrically.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. **1**, 97056-16-1; **2**, 97056-16-1; **3**, 108347-13-3; **4**, 108347-14-4; $ClCH{=}C(CN)_2$, 10472-09-0; 4-$MeC_6H_4SO_3Ag$, 16836-95-6; $ClCH{=}CCN(CO_2Me)$, 57337-96-9; F_3CCO_2Ag, 2966-50-9; *N*-vinylcarbazole (homopolymer), 25067-59-8; *p*-methoxystyrene (homopolymer), 24936-44-5; 1,3-dioxolane (homopolymer), 25067-64-5; cyclohexene oxide (homopolymer), 25702-20-9; cyclohexene oxide (SRU), 32146-09-1; poly(oxymethylene), 9002-81-7.

References and Notes

(1) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.
(2) Gotoh, T.; Padias, A. B.; Hall, H. K., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 4920.
(3) Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 944.
(4) Abdelkader, M.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 949.
(5) Hall, H. K.; Jr.; Rasoul, H. A. A. In *Contemporary Topics in Polymer Science*; Bailey, W. J., Tsuruta, T., Eds.; Plenum: New York, 1984; Vol. 4, p 295.
(6) Padias, A. B.; Hall, H. K., Jr. *Polym. Bull.* **1985**, *13*, 329.
(7) (a) Masuda, T.; Sawamoto, M.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2981. (b) Sawamoto, M.; Masuda, T.; Higashimura, T. *Makromol. Chem.* **1976**, *177*, 2995. (c) Sawamoto, M.; Higashimura, T. *Macromolecules* **1978**, *11*, 501. (d) Sawamoto, M.; Higashimura, T. *Macromolecules* **1978**, *11*, 328. (e) Sawamoto, M.; Higashimura, T. *Polym. Bull.* **1978**, *1*, 11. (f) Kunitake, T.; Takarabe, K. *Polym. J.* **1978**, *10*, 105.
(8) (a) Throssel, J. J.; Sood, S. P.; Szwarc, M.; Stannett, V. *J. Am. Chem. Soc.* **1956**, *78*, 1122. (b) Obrecht, W.; Plesch, P. H. *Makromol. Chem.* **1981**, *182*, 1459.
(9) Rappoport, Z.; Topol, A. *J. Chem. Soc., Perkin Trans.* **1972**, *2*, 1823.
(10) Gassman, P. *Acc. Chem. Res.* **1970**, *3*, 26.

Synthesis and Properties of Poly[3-(trimethylsilyl)-1-alkynes][1]

Toshio Masuda,* Hiroshi Tajima, Toshio Yoshimura, and Toshinobu Higashimura*

Department of Polymer Chemistry, Kyoto University, Kyoto 606, Japan.
Received October 16, 1986

ABSTRACT: 3-(Trimethylsilyl)-1-alkynes [$HC{\equiv}CCH(SiMe_3)R$; R = CH_3, *n*-C_3H_7, *n*-C_5H_{11}, and *n*-C_7H_{15}] were polymerized in high yields with Mo, W, and Nb catalysts to give new high molecular weight polymers. The polymers whose R was CH_3 or *n*-C_3H_7 were partly or totally insoluble in any organic solvents, whereas those whose R was *n*-C_5H_{11} or *n*-C_7H_{15} were totally soluble in solvents such as toluene and $CHCl_3$. Maximum weight-average molecular weights of poly[3-(trimethylsilyl)-1-octyne] were 4.5×10^5 with Mo catalysts, 1.6×10^5 with W catalysts, and 1.0×10^5 with Nb catalysts. All the product polymers possessed the structure $-[CH{=}CCH(SiMe_3)R]_n-$ according to spectroscopic analyses and were yellow solids. Poly[3-(trimethylsilyl)-1-octyne] and poly[1-(trimethylsilyl)-1-decyne] were soluble in many low-polarity solvents, film-forming, thermally relatively stable in air, and amorphous. Their electrical conductivities were $\sim 10^{-18}$ S·cm^{-1} and unpaired-electron densities were $<1 \times 10^{15}$ spin·g^{-1}.

Introduction

Si-containing polyacetylenes, which possess alternating double bonds along the main chain and Si-containing groups in the side chain, are expected to show properties not seen in conventional polymers because of their unique structure. In fact, poly[1-(trimethylsilyl)-1-propyne], one example of such polymers, is known to be extremely permeable to oxygen.[3]

So far, polymerization of (trimethylsilyl)acetylene[4] and its derivatives[2] ($HC{\equiv}CSiMe_2R$; R = Me, *n*-C_6H_{13}, CH_2CH_2Ph, CH_2Ph, Ph, and *t*-Bu) as Si-containing monosubstituted acetylenes has been studied. These monomers polymerize in the presence of W catalysts. Though the polymers with flexible R groups (R = *n*-C_6H_{13}, CH_2CH_2Ph, and CH_2Ph) are soluble, their molecular weights are no more than $\sim 1 \times 10^4$. In contrast, 1-(trimethylsilyl)-1-propyne[5] and its derivatives[6] ($MeC{\equiv}CSiMe_2R$; R = Me, *n*-C_6H_{13}, Ph, $SiMe_2CH_2SiMe_3$, and $SiMe_2CH_2CH_2SiMe_3$), which are disubstituted acetylenes, produce with Ta catalysts polymers whose molecular weights reach $\sim 1 \times 10^6$.

Such a large difference in the polymerization behavior of mono- and disubstituted Si-containing acetylenes is quite interesting. We sought the reason for this and searched for Si-containing monosubstituted acetylenes that afford soluble, high molecular weight polymers. Eventu-