Polymerization

Cyclic silyl pinacole ethers*
A new class of multifunctional free radical initiators

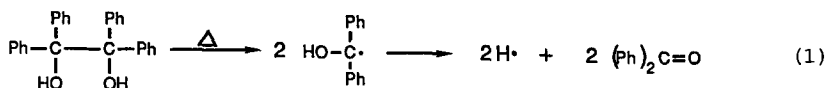**J.V. Crivello, J.L. Lee, and D.A. Conlon**

General Electric Corporate Research and Development Center, P.O. Box 8,
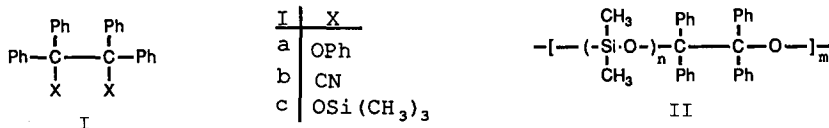Schenectady, NY 12301, USA

Summary

Cyclic silyl pinacole ethers are a new class of difunctional free
radical initiators which have been prepared and characterized. On the
basis of their first order kinetic rates of dissociation and half-lives,
these compounds are high temperature initiators useful generally above
120°C. The unusual difunctional character of these initiators suggests
some rather interesting applications for their use.

Introduction

It is well known that sterically hindered carbon-carbon single bonds
such as those found in hexaphenylethane are easily thermally cleaved to
produce trityl radicals (GILMAN and DUNN 1951). Subsequently, it was found
that the tetraarylethane, benzopinacole, could also be used to initiate
free radical polymerization (BRAUN and BECKER 1969; 1971). Braun and
Becker were able to demonstrate that initiation results from hydrogen
transfer from the initially formed diarylhydroxymethyl radical to the mono-
mer as shown in equation 1.

$$ Ph-\underset{\underset{HO}{|}}{\overset{\overset{Ph}{|}}{C}}-\underset{\underset{OH}{|}}{\overset{\overset{Ph}{|}}{C}}-Ph \xrightarrow{\Delta} 2\ HO-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{C}}\cdot \longrightarrow 2H\cdot\ +\ 2\ (Ph)_2C=O \qquad (1) $$
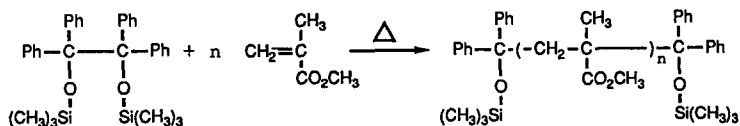
More recently, the related initiators Ia and Ib (BLEDZKI and BRAUN
1981a; 1981b) have been reported in the literature as useful free radical
initiators. Of particular interest to our research group are the trialkyl-
silyl ether derivatives of benzopinacole, Ic, which have been disclosed in
two patents (RUDOLPH and TRAENCKNER 1976; VIO 1974) and the related oligo-
meric silyl pinacole ethers having the general structure II (WOLFERS,
RUDOLPH and ROSENKRANZ 1978; REUTER and DHEIN 1983) which have also been
found to be active initiators of free radical polymerization.

$$ Ph-\underset{\underset{X}{|}}{\overset{\overset{Ph}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{Ph}{|}}{C}}-Ph $$

I

I	X
a	OPh
b	CN
c	OSi(CH₃)₃

$$ -[-(-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}\cdot O}-)_n-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{C}}-\underset{\underset{Ph}{|}}{\overset{\overset{Ph}{|}}{C}}-O-]_m- $$

II

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* The proper IUPAC name for these compounds is 1,3-dioxa-2-siloles; however, for brevity in this paper they will be referred
to as cyclic silyl pinacole ethers

Unlike benzopinacole, its bistrialkylsilylether derivatives do not initiate polymerization by the hydrogen transfer reaction as shown above. Instead, the diaryltrialkylsiloxymethyl radicals directly add to vinyl monomers to initiate their polymerization and in addition, function as terminating agents for the growing polymer chains (BLEDZKI, BRAUN and TITZSCHKAU 1983) as indicated in equation 2.

$$Ph-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Si(CH_3)_3}{|}}{\underset{\displaystyle O}{|}}{C}}-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Si(CH_3)_3}{|}}{\underset{\displaystyle O}{|}}{C}}-Ph \;+\; n \;\; CH_2{=}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle}{}}{\underset{\displaystyle CO_2CH_3}{|}}{C}} \;\xrightarrow{\;\Delta\;}\; Ph-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle (CH_3)_3Si}{|}}{\underset{\displaystyle O}{|}}{C}}-(\text{-}CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle}{}}{\underset{\displaystyle CO_2CH_3}{|}}{C}}\text{---})_n-\overset{\overset{\displaystyle Ph}{|}}{\underset{\underset{\displaystyle Si(CH_3)_3}{|}}{\underset{\displaystyle O}{|}}{C}}-Ph$$

We have recently made use of the ability of these types of initiators to behave both as initiators and terminating agents for the preparation of polydimethylsiloxane-vinyl block polymers (CRIVELLO, CONLON and LEE 1986a; CRIVELLO, LEE and CONLON 1986b). To carry out this synthesis, polydimethyl-siloxane macroinitiators having benzopinacole bissilyl ether groups along the chain backbone were prepared which were then thermolyzed in the presence of vinyl monomers. During the course of this latter investigation, several novel cyclic analogs of the open chain benzopinacole bissilyl ethers were prepared. Accordingly, it was decided to undertake a study of their synthesis, characterization and their ability to initiate free radical polymerization.

Experimental

All of the aromatic ketones and silanes were used as purchased from commercial sources. Tetrahydrofuran (THF) was purified by first drying over CaH_2 then fractionally distilling under nitrogen from sodium naphthalene complex. N,N,N',N'-Tetramethylurea (TMU) was dried over CaH_2 then fractionally distilled, while hexamethylphosphoramide (HMPA) was used as received. Magnesium metal was employed as 30 mesh shot. The monomers used during the course of this work were purchased from commercial sources. Prior to use, the monomers were freed of inhibitors by washing with a 5% aqueous NaOH solution, dried over anhydrous $MgSO_4$, and then fractionally distilled under reduced pressure. 2,3,5,6-Tetrachloro-1,4-benzoquinone used in the kinetic studies was recrystallized from acetone prior to use.

Molecular weight measurements were made in $CHCl_3$ with the aid of a Waters 244 gel permeation chromatograph and are based on polystyrene standards. A Varian XL 200-MHz spectrometer was used to conduct the ^{13}C and ^{29}Si NMR measurements while a Varian EM 390 90-MHz spectrometer was used for the ^{1}H NMR spectra. Mass spectra were recorded on a Varian MAT 731 spectrometer. Melting points were determined on a Thomas-Hoover Melting Point Apparatus and are uncorrected.

Kinetic determinations of the dissociation constants and half-lives were made using an adaptation of the method of Ziebarth and Neumann (ZIEBARTH and NEUMANN 1978) and are described in a previous communication (CRIVELLO, CONLON and LEE 1986a).

General Procedures for the Synthesis of Cyclic Benzopinacole Silyl Ethers

The following general procedures for the synthesis of 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silole, III, are illustrative of the methods which were used to prepare the cyclic benzopinacole silyl ethers.

Method A

Into a 500 mL round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and nitrogen inlet were placed 18.2 g (0.1 mol) benzophenone, 50 mL THF, 12.9 g (0.1 mol) dimethyldichlorosilane, 1.2 mg magnesium metal, and 5 mL HMPA. After 15 minutes an exothermic reaction ensued with the formation of a brown solution color. Within 30 minutes, the color had become yellow and the reaction mixture was allowed to stir overnight at room temperature. The THF was removed with the aid of a rotary evaporator and approximately 100 mL CH_2Cl_2 were added and the solution filtered through a sintered glass filter to remove the magnesium salts. The filtrate was stripped of solvent under reduced pressure leaving a solid residue. The residue was crystallized from absolute ethanol giving a colorless crystalline product in 36% yield having a m.p. of 134-136°C after drying at 60°C in vacuo for 16 hours. The product was identified as 2,2-dimethyl-4,4,5,5-tetraphenyl-1.3-dioxa-2-silole by its ^{29}Si and ^{13}C-NMR spectra (Figure 1) as well as by the parent peak at M/e = 435 in the mass spectrum and its elemental analysis shown in Table 1.

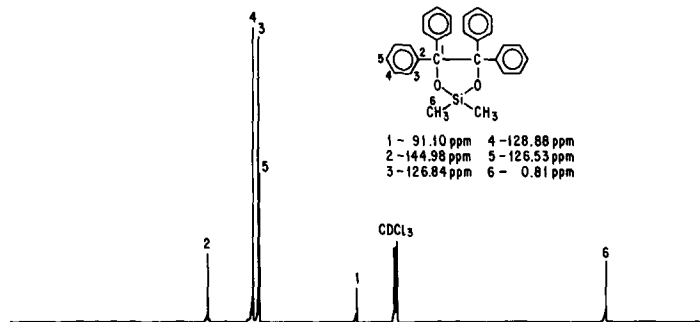Figure 1. ^{13}C-NMR Spectrum of 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silole (III) in CDCl₃.

Method B

To a 250 mL round-bottomed three-neck flask there were added 1.2 g (0.05 mol) magnesium metal, 18.2 g (0.1 mol) benzophenone, 5 mL HMPA and 50 mL dry THF. The reaction flask was fitted with a stirrer, condenser, nitrogen inlet, thermometer and a dropping funnel, and there were added dropwise with cooling 9.45 g (0.1 mol) dimethylchlorosilane. During the addition the temperature rose to 60°C and was held at that temperature for 2 h after addition was complete. The reaction mixture was cooled, and excess silane and THF were removed using a rotary evaporator, and approximately 50 mL CH_2Cl_2 were added. The solution was filtered to remove the inorganic magnesium salts and the solvent once again removed under reduced pressure. A pale yellow solid was obtained which after recrystallization from hot abs. ethanol gave 7 g dry colorless crystals, m.p. 134-136°C. The ^{1}H NMR and ^{13}C NMR of this product correspond in all respects with those obtained by the previous method for the pure 1,3-dioxa-2-silole.

Method C

There were added to a 250 mL round-bottomed flask equipped with a reflux condenser, dropping funnel, thermometer, and nitrogen inlet, 18.3 g

Table 1

Characteristics of Cyclic Silyl Pinacole Ether Initiators

$$(C_6H_5)_2C\underset{\underset{\underset{R_1}{\diagup}\underset{\diagdown}{Si}\underset{R_2}{\diagdown}}{\underset{O}{\diagup}\underset{O}{\diagdown}}}{\underline{\hspace{1cm}}}C(C_6H_5)_2$$

	R_1	R_2	m.p. (°C)[a]	δ ^{29}Si (ppm)[b]	Elemental Analysis				Method (yield%)
						%C	%H	%Si	
III	CH_3	CH_3	134–136	20.82	Calc:	79.58	6.20	6.64	A(36), B(33), C(59)
					Fnd:	79.31	6.5	6.7	
IV	C_2H_5	C_2H_5	123–125	19.16	Calc:	79.95	6.71	6.23	A(54)
					Fnd:	79.77	6.67	6.2	
V	C_6H_5	C_6H_5	>200	−9.51	Calc:	83.48	5.53	5.14	A(35)
					Fnd:	83.38	5.47	4.97	
VI	CH_3	$CH_2=CH$	135–137	4.68	Calc:	80.14	6.03	6.46	A(36)
					Fnd:	79.97	6.09	6.34	
VII	CH_3	C_6H_5	150–151	5.22	Calc:	81.82	5.79	5.74	C(45)
					Fnd:	81.16	5.76	5.80	
VIII	$(CH_3)_3C$	$(CH_3)_3C$	185–199	12.59	Calc:	80.58	7.56	5.53	A(13)
					Fnd:	80.16	7.41	5.03	

$$IX \quad \underset{(C_6H_5)_2C}{(C_6H_5)_2C}\underset{\diagdown O}{\overset{\diagup O}{\underset{\diagdown}{\overset{\diagup}{}}}}Si\underset{\diagdown O}{\overset{\diagup O}{\underset{\diagdown}{\overset{\diagup}{}}}}\underset{C(C_6H_5)_2}{\overset{C(C_6H_5)_2}{}}$$

IX			240	−45.5	Calc:	82.45	5.29	3.70	A(24)
					Fnd:	79.2	5.30	3.65	

a) Melting is accompanied by decomposition

b) ^{29}Si NMR run in $CLCl_3$

(0.05 mol) benzopinacole, 4.7 g (0.05 mol) dimethylchlorosilane and 50 mL $CHCl_3$. To this mixture there was added dropwise 5.05 g (0.05 mol) tri-ethylamine. An exothermic reaction was observed with the temperature rising to 50°C accompanied by the vigorous evolution of gas. After the addition had been completed, the reaction mixture was stirred for an additional 2 hours. The solvent was removed under reduced pressure yielding a white solid which was slurried with 100 mL n-hexane and the mixture filtered through a sintered glass filter. The filtrate was collected and the solvent stripped off under reduced pressure to give after drying 12.5 g (59.2% yield) of pure 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silole.

Preparation of 2,2,3,3,7,7,8,8-Octaphenyl-1,4,6,9-tetraoxa-5-sila[4.4]
Spirononane (IX)

　　To the usual apparatus there were added 4.8 g (0.2 mol) magnesium
metal, 9.1 g (0.05 mol) benzophenone, 2.4 g (0.009 mol) mercuric chloride,
and 50 mL THF. The exothermic reaction which took place was controlled by
placing the reaction flask in a water bath. To the blue solution which was
formed after 15 minutes reaction there were added 2.1 g (0.0125 mol) sili-
con tetrachloride. Rapid discharge of the blue color was noted with the
formation of a yellow solution. The mixture was allowed to stir for
approximately 20 minutes and then filtered using a sintered glass filter.
The white inorganic solids were washed with fresh THF and the organic solu-
tions combined and then stripped under reduced pressure. A white solid was
obtained which was dissolved in acetone and triturated with water. Final
recrystallization from hot CCl_4 gave 2.6 g (24%) of the pure spiro com-
pound, IX, whose m.p. 240-245°C corresponded with that reported in the lit-
erature (KIPPING and ABRAMS 1944).

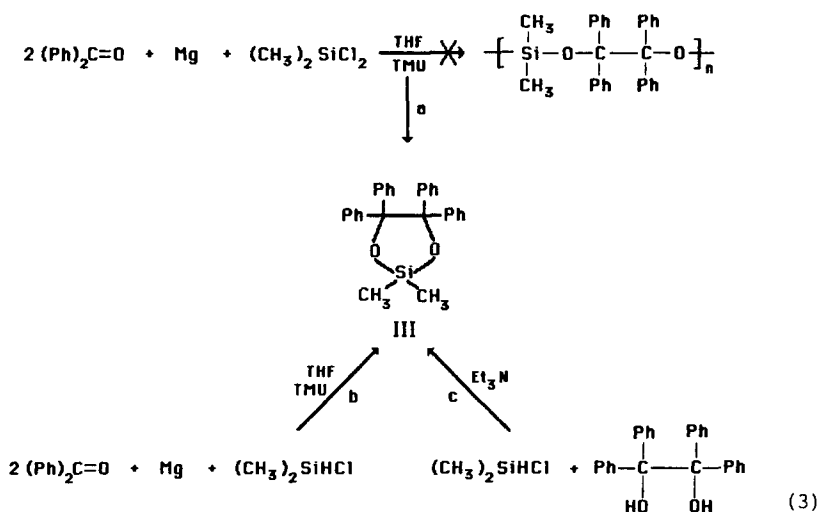Polymerization of Styrene Using Mono, Di and Tetrafunctional Initiators

　　Into separate cleaned and dried glass polymerization tubes were
placed 2 x 10^{-4} mole of one of the following initiators: Ic (0.1224 g),
III (0.1013 g), and IX (0.1814 g). To each tube there was then added 5.0 g
freshly distilled and dry styrene monomer and the reaction mixture thor-
oughly deoxygenated by flushing with nitrogen. The tubes were sealed using
rubber serum caps and then immersed into an oil bath at 100°C. After 1
hour, the polymerizations were terminated by pouring the contents of the
tubes into 100 mL methanol. The polymers were isolated by suction filtra-
tion, washed with fresh methanol and then dried overnight at 60°C in vacuo.
Initiator Ic gave a polymer (0.66 g) having a $\bar{M}_n$ of 19,000, while III,
(0.55 g) and IX, (0.40 g) gave $\bar{M}_n$ values of 91,000 and 250,500 g/mol,
respectively.

Results and Discussion

　　Several years ago, Calas and his coworkers (CALAS et al 1968) reported
that diarylketones could be reduced in the presence of magnesium metal in
the presence of a trimethylchlorosilane and a promoter such as TMU to give
bistrimethylsilyl ethers of the corresponding pinacole. Recently, it was
observed in our laboratories that when dimethyldichlorosilane was substi-
tuted for trimethylchlorosilane in this reaction, with benzophenone that
instead of the expected linear polymeric species, the novel cyclic di-
methylsilyl ether of benzopinacole, III, shown in Scheme 1 was obtained.

　　Subsequently, it was observed that the same compound could be pre-
pared by two additional routes which are also shown in Scheme 1. When
dialkylchlorosilanes are used in the diarylketone reduction reaction, the
formation of cyclic III is accompanied by the elimination of hydrogen (path
b). An additional entry into the synthesis of this compound is via the
direct condensation of benzopinacole with dimethylchlorosilanes in the
presence of a trialkylamine acid acceptor (path c). Further investigations
showed that the preparative methods shown in Scheme 1 are general and could
be used to synthesize a variety of analogous cyclic bissilyl pinacole
ethers (1,3-dioxa-2-siloles).

Scheme 1

$$2 (Ph)_2 C=O \; + \; Mg \; + \; (CH_3)_2 SiCl_2 \xrightarrow[TMU]{THF} \; \cancel{\;} \; \left[\begin{matrix} CH_3 & Ph & Ph \\ | & | & | \\ Si-O-C & -C-O \\ | & | & | \\ CH_3 & Ph & Ph \end{matrix} \right]_n$$

$$\Big\downarrow a$$

III

THF / TMU b   Et_3N c

$$2 (Ph)_2 C=O \; + \; Mg \; + \; (CH_3)_2 SiHCl \qquad (CH_3)_2 SiHCl \; + \; \underset{HO}{\overset{Ph}{Ph-C}} \underset{OH}{\overset{Ph}{-C-Ph}} \qquad (3)$$

The structures and properties of a number of cyclic silyl pinacole ethers prepared by these methods are shown in Table 1. All the compounds shown in this table with the exception of the spirocyclic compound, IX, are new compounds. The latter compound was previously reported by Kipping and Abrams (KIPPING and ABRAMS 1944) who isolated it in very low yield from the reaction of silicon tetrachloride with magnesium in the presence of benzophenone. Using essentially the same method, but with the addition of mercuric chloride to activate the magnesium, the desired compound was readily obtained in good yield. To confirm the structures to be the five membered rings shown and to exclude the possibility that these compounds could be higher order cyclics, mass spectra were obtained on the dimethyl, diethyl, and diphenyl substituted compounds. Well characterized spectra were obtained by field desorption mass spectrometry for these particular compounds having parent peaks at 422, 450, and 546, respectively, for the above compounds which correspond in all cases to the cyclic five membered ring structures given in Table 1. Finally, ^{13}C-NMR spectra give definitive evidence for the structures of these compounds. For example, Figure 1 gives the spectrum of 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silole, III, while Figure 2 shows the corresponding spectrum of the 2-methyl-2-vinyl substituted compound.
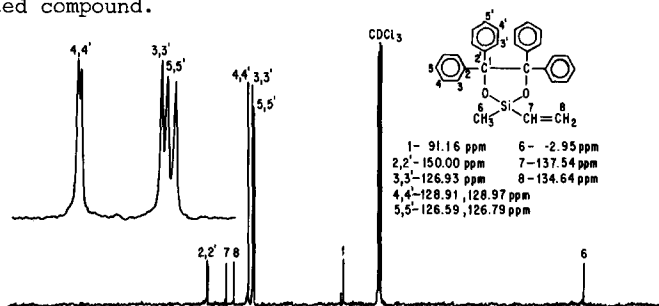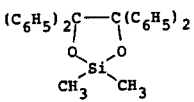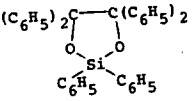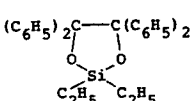
Figure 2. ^{13}C-NMR Spectrum of 2-methyl-2-vinyl-4,4,5,5-tetraphenyl-1,3-dioxa-2-silole (VI) in CDCl$_3$.

Since all of the compounds shown in Table 1 contain a highly strained carbon-carbon bond, it was decided to investigate the kinetics of the thermolysis of these compounds and to access their potential ability to initiate free radical polymerization. In Table 2 are given the pseudo first order rate constants and the half-lives for three typical cyclic silyl ethers of benzopinacole determined at 120°C. Compared to their open chain analogs (CRIVELLO, CONLON and LEE 1986a), these compounds are considerably more stable toward homolytic dissociation of their tetraarylethane carbon-carbon bonds. The data in this table would suggest (and we have observed) that they are a new class of high temperature initiators most effective at temperatures above 120°C. As such, they are particularly useful for curing unsaturated polyesters and for polymer grafting reactions. In addition, they are photochemically inactive, nonexplosive, do not give gaseous by-products on thermolysis and can be stored indefinitely at room temperature without decomposition.
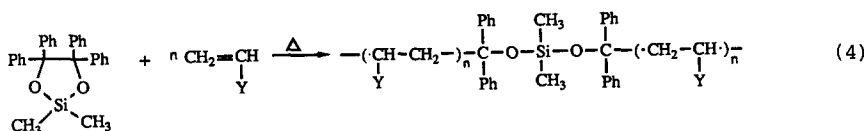
Table 2

Kinetics of Thermolysis of Cyclic Silyl Pinacolate Initiators[a]

Compound	k_1 (sec^{-1})	$t_{\frac{1}{2}}$ (hr)
$(C_6H_5)_2C\text{—}C(C_6H_5)_2$, O-Si-O, CH_3 CH_3	4.4×10^{-6}	43.8
$(C_6H_5)_2C\text{—}C(C_6H_5)_2$, O-Si-O, C_6H_5 C_6H_5	5.04×10^{-6}	38.2
$(C_6H_5)_2C\text{—}C(C_6H_5)_2$, O-Si-O, C_2H_5 C_2H_5	10.2×10^{-6}	18.9

a) Determined at 120°C

Cyclic silyl ethers of tetraaryl pinacoles are a new, interesting class of free radical initiators since on thermolysis, the five membered ring is cleaved to give biradical species. Thus, as shown in equation 4, these cyclic initiators initiate the polymerization of vinyl monomers to

$$Ph\text{—}Ph\ (Ph,Ph)\ O\ O\ Si\ CH_3\ CH_3\ +\ n\ CH_2\text{=}CH\ (Y)\ \xrightarrow{\Delta}\ \text{—}(\cdot CH\text{-}CH_2\text{-})_n\text{-}\underset{Y}{C}\text{-}O\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}\underset{Ph}{\overset{Ph}{C}}\text{-}(\cdot CH_2\text{-}CH\cdot)_n\text{-}Y \quad (4)$$

produce macrodiradicals. These macrodiradicals can undergo further chain growth either by addition of more monomer to the chain ends or by radical-radical coupling with other macrodiradicals present in the reaction mixture. In effect, the initiator fragments become incorporated into the backbone of the polymer rather than at the chain ends as is the case when conventional monofunctional initiators are employed. In this respect, these cyclic silyl pinacole ethers uniquely display the characteristics of

both monomers and initiators. The spirocyclic silyl ortho ester, IX, is in analogy to the above five-membered ring cyclics, a tetrafunctional initiator capable of initiating four chains which emanate from the same silicon atom. In Figure 3 is shown the linear dependence of the molecular weights
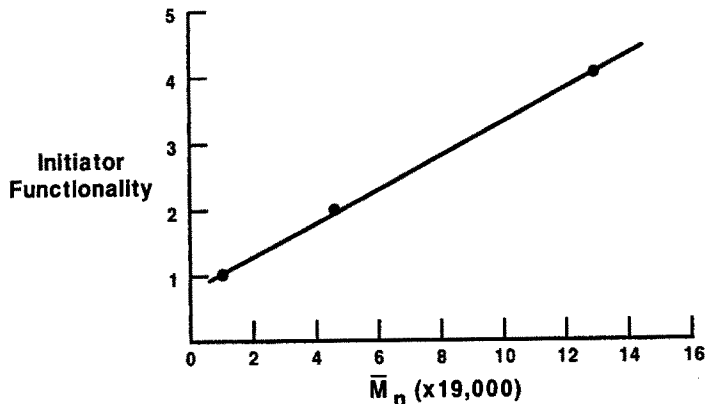

Initiator Functionality (vertical axis, values 1–5)

$\bar{M}_n$ (x19,000) (horizontal axis, values 0–16)

Figure 3. Variation of Mol. Wt. as a function of initiator functionality for polystyrenes produced using initiators Ic, III and IV with functionality, respectively, of 1, 2 and 4

-obtained in the polymerization of styrene on the functionality of the initiator which was used. In this study, monofunctional, Ic, difunctional, III, and tetrafunctional, IX, initiators were employed in equimolar amounts. In agreement with the above mentioned concepts, the cyclic initiators are much more effective in producing higher molecular weight polymers than their non-cyclic analogs. The above experiments were carried only to low conversions (8-13%). Due to the dominance of radical-radical coupling reactions as the primary mode of termination for styrene, network polymers should be produced when the tetrafunctional initiator is used. Indeed, when the polymerization was carried to high conversion using this initiator, crosslinked polymers were obtained. Thus, by selection of the appropriate cyclic initiator, one can obtain linear or crosslinked polymers even with simple monofunctional vinyl monomers.

References

BRAUN, D. and BECKER, K.H.: Angew. Makromol. Chem., 6, 186 (1969)
BRAUN, D. and BECKER, K.H.: Makromol. Chem., 147, 91 (1971)
BLEDZKI, A. and BRAUN, D.: Makromol. Chem., 182, 1047 (1981a)
BELDZKI, A. and BRAUN, D.: Madromol. Chem., 182, 3195 (1981b)
BLEDZKI, A., BRAUN, D. and TITZSCHKAU, K.: Makromol. Chem., 184, 745 (1983)
CALAS, R., DUFFAUT, N., BIRAN, C., BOURGEOIS, M.P., PISCIOTTI, F., and DUNOGUES, M.J.: C.R. Acad. Sci. Paris, 267, 322 (1968)
CRIVELLO, J.V., CONLON, D.A. and LEE, J.L.: J. Polym. Sci., Polym. Chem. Ed., 24, 1197 (1986a)
CRIVELLO, J.V., LEE, J.L. and CONLON, D.A.: J. Polym. Sci., Polym. Chem. Ed., 24, 1251 (1986b)
GILMAN, H. and DUNN, G.E.: J. Am. Chem. Soc., 73, 5077 (1951)
KIPPING, F.S. and ABRAMS, J.T.: J. Chem. Soc., 81 (1944)
REUTER, K. and DHEIN, R.: Ger. Offen. 3,151,444 (July 7 1983) to Bayer
RUDOLPH, H. and TRAECKNER, H.-J.: U.S. Patent 3,931,355 (1/6/76) to Bayer
VIO, L.: U.S. Patent 3,792,126 (2/12/74) to Societe Nationale des Petroles d'Aquitaine
WOLFERS, H., RUDOLPH, H. and ROSENKRANZ, H.J.: Ger. Offen. 2,632,294 (January 19, 1978) to Bayer
ZIEBARTH, M. and NEUMANN, W.P.: Liebigs Ann. Chem., 1765 (1978)

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