The Anionic Polymerization of Trimethylvinylsilane

Gregory K. Rickle[a]

[a] Central Research The Dow Chemical Company, Midland, Michigan

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GREGORY K. RICKLE

Central Research
The Dow Chemical Company
Midland, Michigan 48640

ABSTRACT

Trimethylvinylsilane was found to polymerize anionically in cyclo-hexane much like styrene or dienes, except for the occurrence of a termination step. The propagation and initiation reactions were found to be first order with respect to trimethylvinylsilane and one-half order with respect to the initiator and chain ends initially, but first order after the initiator was consumed. Rate constants for initiation, propagation, and termination were found to increase in the presence of ethers, with the termination rate constant increasing the fastest. In the absence of ethers, the propagation rate constant is small, $1.4 \ mL^{1/2}/(mol^{1/2} \cdot min)$ at 22°C.

INTRODUCTION

Silicon stabilizes α-carbanions due to its vacant d orbitals, making silane-substituted olefins good candidates for anionic polymerizations. However, literature reports of anionic polymerizations of silane-substituted olefins suggest that termination occurs [1].

This report describes the kinetics of initiation, propagation, and termination for the anionic polymerization of trimethylvinylsilane in cyclohexane with organolithium initiators and the effect of ethers upon this polymerization. This study has implications for the synthesis of

1287

block copolymers containing a poly(trimethylvinylsilane) segment. Knowledge of the polymerization kinetics is necessary to synthesize block copolymers and to appreciate the kinetic limitations of the techniques. Synthesis and properties of some block copolymers containing poly(trimethylvinylsilane) will be described in a forthcoming paper.

EXPERIMENTAL

Chemicals

All chemicals were purchased from commercial sources. Cyclohexane was extracted with sulfuric acid, and trimethylvinylsilane was distilled. Both were run through an alumina column prior to use, as were the promoters, tetrahydrofuran and 1,2-dimethoxyethane. The initiators, n-butyllithium or sec-butyllithium, were used as received. In some cases the polymerizations were initiated with polystyryllithium, which was made by addition of styrene to a n-butyllithium solution.

Kinetic Experiments

Trimethylvinylsilane, 1.80-4.00 g, was added to 100.0 g cyclohexane containing 0-500 μL of ether promoter. The polymerizations were initiated with 0.1-5.0 mmol of an organolithium compound. Samples, 0.1 mL, were withdrawn at various time intervals and analyzed by gas-liquid chromatography for trimethylvinylsilane. The reaction mixtures were vacuum degassed before initiation and kept under a blanket of nitrogen for the duration of the experiment. Using this procedure, polystyryllithium solutions (0.10-1.0 mmol/L), orange red in color, did not fade in color over a four-day period. The kinetic experiments were done at $22 \pm 2°C$.

Generally, the experiments were not duplicated, and the numbers reported have a propagated relative error of ± 15-30%. However, when duplicate runs were made in two experiments, the results did agree within experimental error.

RESULTS AND DISCUSSION

Determination of Rate Constants

Reported mechanisms for organolithium-initiated anionic polymerizations of vinyl monomers predict first-order kinetics for the disappearance of trimethylvinylsilane [2]. The initiation and propagation

steps have always been found to be first order with respect to the vinyl monomer concentration, but often a fractional order with respect to the initiator and chain-end concentration [2]. The fractional order is attributed to association of chain ends and initiator in some manner [3, 4]. Thus anionic polymerizations with no termination obey the following rate laws:

$$-\frac{dM}{dt} = k_1(M)(I^-) = K_1 k_1 M (I_0^-)^{1/n} \qquad \text{(initiation)}, \qquad (1a)$$

$$-\frac{dM}{dt} = k_2 M P^- = K_2 k_2 M (I_0^-)^{1/m} \qquad \text{(propagation)}, \qquad (1b)$$

where k_1 = initiation rate constant

M = trimethylvinylsilane monomer concentration
I^- = initiator concentration
k_2 = propagation rate constant
P^- = carbanionic chain end concentration
m and n = 1-6
K_1 and K_2 = equilibrium constants for chain-end and initiator association

If M_0/I_0^- is low ($< \sim 5$), a plot of ln M vs time will show biphasic behavior, unless $K_2 k_2$ is equal to $K_1 k_1$, due to the unequal rates of propagation and initiation. At high M_0/I_0^-, the ln M vs time plot will appear linear with an induction time if $K_1 k_1 < K_2 k_2$.

The plots in Fig. 1 show no induction time and are not linear in the later part of the polymerization. Also, the conversion is not complete, suggesting that the carbanion chain end is undergoing termination. In the early stages of the reaction, when little termination has occurred, and M_0/I_0^- is 3, a semilogarithmic plot of M vs time gives a straight line with an intercept of M_0, indicating that $K_1 k_1 = K_2 k_2$ (Fig. 1, Curve C). Hence the initial slope of the curves in Fig. 1 should give $K_1 k_1$ and $K_2 k_2$.

Termination could be caused by slow reaction of the growing chain ends with impurities in the starting materials. This appears unlikely since termination was observed in an experiment where a large amount of initiator was used (Fig. 1, Curve C). The amount of initiator was sufficient to consume 3 mol%, based on monomer, of an impurity having an equivalent weight of 9, i.e., water. This level of impurity in the reaction mixture is easily detectable, but none was found.
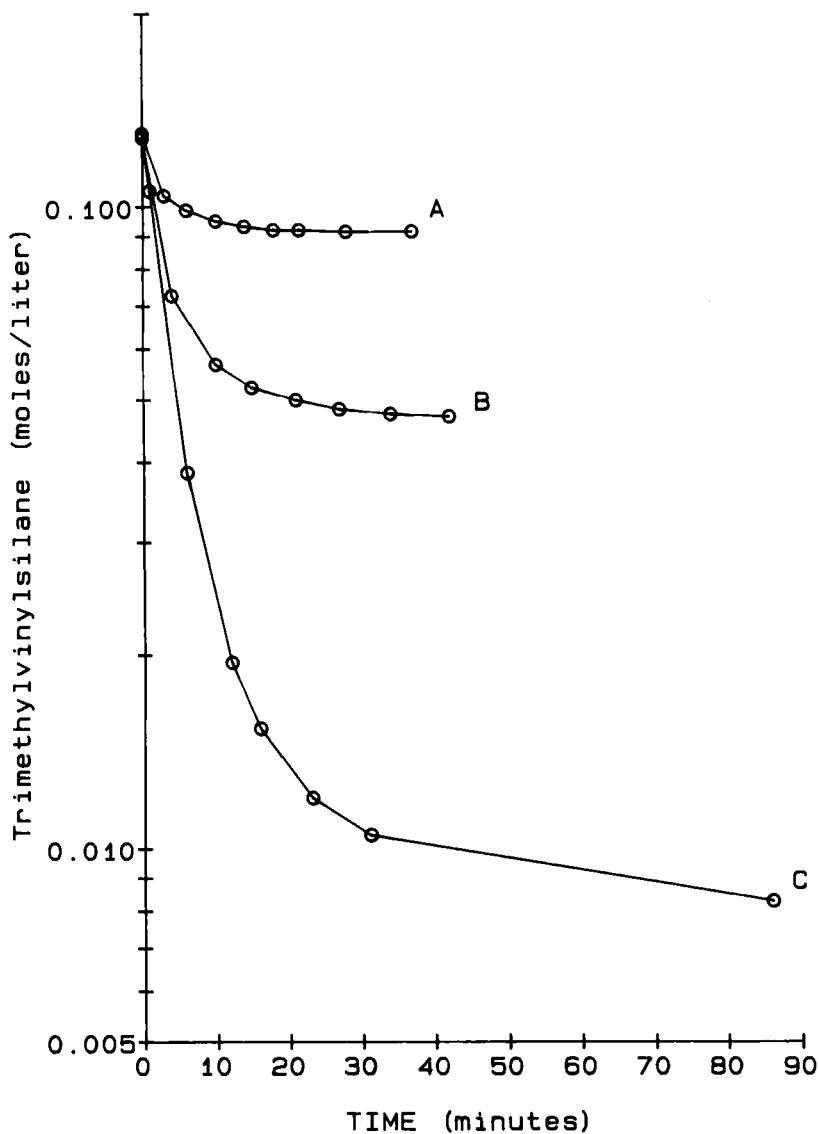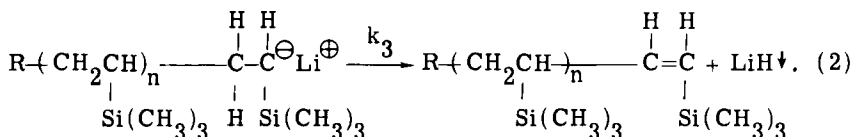
FIG. 1. Trimethylvinylsilane concentration vs time in cyclohexane containing 35.5 mmol/L 1,2-dimethoxyethane initiated with various levels of n-butyllithium. A, 5.34 mmol/L n-butyllithium; B, 15.1 mmol/L n-butyllithium; C, 44.5 mmol/L n-butyllithium.

Another possibility is the termination of the carbanionic chain ends by side reactions with monomer or polymer. Nametkin and coworkers speculated that lithium hydride may be eliminated from the carbanionic chain end according to Eq. (2) [1], in which k_3 is the termination rate constant. In a similar manner, lithium hydride is eliminated in anionic polymerizations of styrene and dienes [5].

$$R \text{\large(} CH_2CH \text{\large)}_n \underset{\underset{Si(CH_3)_3}{|}}{\overset{\overset{H}{|}}{\rule{0pt}{0pt}}} \underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}} \underset{\underset{Si(CH_3)_3}{|}}{\overset{\overset{\ominus}{C} Li^{\oplus}}{\rule{0pt}{0pt}}} \xrightarrow{k_3} R \text{\large(} CH_2CH \text{\large)}_{\overline{n}} \underset{\underset{Si(CH_3)_3}{|}}{\overset{\overset{H}{|}}{C}} = \underset{\underset{Si(CH_3)_3}{|}}{\overset{\overset{H}{|}}{C}} + LiH \downarrow. \quad (2)$$

Indeed, a white-grey precipitate is observed in experiments using high concentrations of initiator. On the assumption that the termination is first order with respect to chain ends after the initiator is consumed, the following integrated rate law can be written:

$$P^- = P_0^- e^{-k_3 t},$$

where $P_0^- = P^-$ when I^- is consumed. After the initiator is consumed, the rate law for polymerization is

$$-\frac{dM}{dt} = k_2 M P^- = K_2 k_2 M (P_0^- e^{-k_3 t})^{1/m}.$$

This rate expression is integrated to give

$$\ln \frac{M}{M_t} = \frac{mK_2 k_2}{k_3} (P_0^- e^{-k_3 t})^{1/m} - \frac{mK_2 k_2}{k_3} (P_0^-)^{1/m}, \quad (3)$$

where M_t = trimethylvinylsilane concentration when I^- is consumed. The final concentration of M, M_f, when $t = \infty$, is given by

$$\ln \frac{M_f}{M_t} = \frac{-mK_2 k_2}{k_3} (P_0^-)^{1/m}. \quad (4)$$

The value of k_2/k_3 can be determined from the initial and final concentration of monomer because the following relation holds:
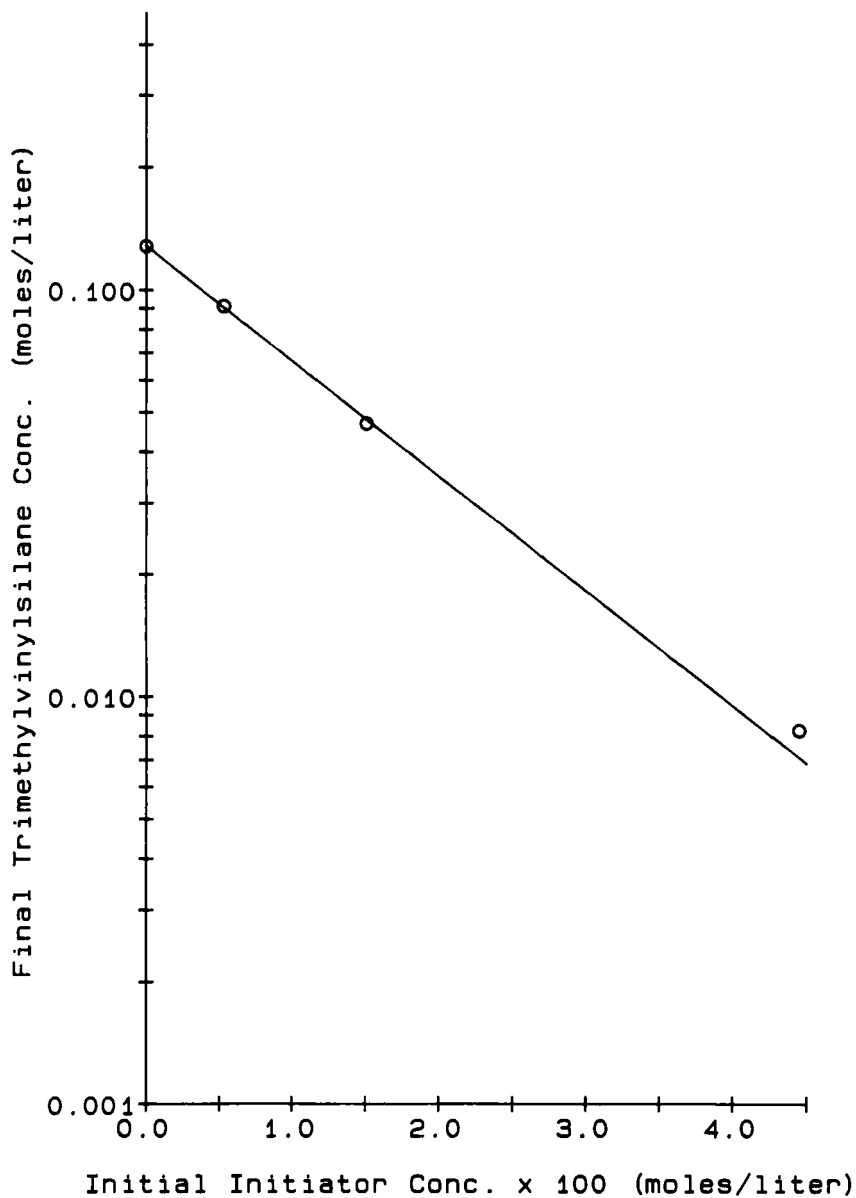
FIG. 2. Final trimethylvinylsilane concentration vs initial n-butyl-lithium level in cyclohexane containing 3.55 mmol/L 1,2-dimethoxy-ethane.

$$\ln \frac{M_0}{M_f} = \lim_{M_t \to M_0} \left[\ln \frac{M_t}{M_f} \right] = \frac{mK_2 k_2}{k_3} (I_0^-)^{1/m}.$$

A semilogarithmic plot of M_f vs I_0^- for a series of experiments at constant M_0 should be a straight line with slope $-k_2/k_3$ if $m = 1$, as is the case in Fig. 2. Because m is 1, there is no association and, therefore, K_2 is also equal to 1. Therefore, it appears the reaction changes from one-half order to first order with respect to chain ends as the initiator is consumed in cyclohexane containing 3.55 mmol/L dimethoxyethane. This change in reaction order is unusual but was predicted by Hsieh for anionic polymerizations [4]. Hsieh's prediction is based on a propagation mechanism involving dimeric chain ends that disassociate at low concentrations to monomeric chain ends. The value for k_2/k_3 obtained from Fig. 2 is 65 L/mol.

Values of k_3 can be determined in the following manner. Equations (3) and (4) can be combined to give

$$\ln \frac{M}{M_f} = \frac{k_2}{k_3} P_0^- e^{-k_3 t}.$$

Thus semilogarithmic plots of $\ln (M/M_f)$ versus time are linear after I^- is consumed, with a slope of $-k_3$ and an intercept of $k_2/k_3 P_0^-$. However, the propagated relative error in k_3 is large for this method (50-150%). The value of k_3 determined by this method is approximately 0.15 min^{-1}. Therefore, the second-order propagation rate constant, k_2, is approximately 10 L/(mol·min) and K_2 is approximately 0.1 (L/mol)$^{1/2}$. Table 1 shows the values of $K_2 k_2$, $K_2 k_3$, and k_2/k_3. At constant initiator concentration and trimethylvinylsilane concentrations below 0.128 mol/L, $K_2 k_2$ and k_2/k_3 are constant, but between 0.128 and 0.281 mol/L trimethylvinylsilane, the termination rate constant increases and k_2/k_3 decreases, indicating that the termination mechanism is more complex at high monomer concentrations.

The molecular weight and yield of polymer are determined largely by k_2/k_3 and M_0. The yield of polymer, C, can be expressed as

$$C = \frac{M_0 - M_f}{M_0} = 1 - e^{(-k_2/k_3)I_0^-}.$$

TABLE 1. Kinetic Data for 1,2-Dimethyoxyethane[a]

Initial initiator concentration, mmol/L	Initial TMVS, mmol/L	$K_1 k_1$, $L^{1/2}/(mol^{1/2} \cdot min)$	$K_2 k_2$, $L^{1/2}/(mol^{1/2} \cdot min)$	$K_2 k_3$, $L^{1/2}/(mol^{1/2} \cdot min)$	$k_2 k_3$, L/mol
44.5	128	0.93	0.93	0.014	62
15.1	128	1.2	1.2	0.018	66
5.34	128	1.0	1.0	0.015	66
13.0	281	1.1	1.1	0.032	34
13.4	73.2	1.0	1.0	0.017	59

[a]35.5 mmol/L.

The number- and weight-average molecular weights, $\overline{M}_n$ and $\overline{M}_w$, and the heterogeneity index, $\overline{M}_w/\overline{M}_n$, are given by

$$\overline{M}_n = \frac{wM_0}{I_0^-}\,(1 - e^{(-k_2/k_3)I_0^-}),$$

$$\overline{M}_w = \frac{wk_2M_0(1 + e^{(-k_2/k_3)I_0^-})}{2k_3},$$

$$\overline{M}_w/\overline{M}_n = \frac{I_0^- k_2}{2k_3}\,\frac{(1 + e^{(-k_2/k_3)I_0^-})}{(1 - e^{(-k_2/k_3)I_0^-})},$$

where w = monomer molecular weight.

Lowering the initiator concentration increases the molecular weight slightly but dramatically lowers the yield of polymer. Increasing the monomer concentration increases the molecular weight, while increasing k_2/k_3 increases both molecular weight and yield.

The concentration of ether has a large effect upon the rate constants. The values of K_2k_2 and K_3k_3 decrease with decreasing ether concentration but K_2k_3 decreases faster, so that the value of k_2/k_3 and the overall yield of polymer increases. Table 2 shows the effect of ether concentration upon k_2/k_3 and conversion to polymer. The reaction rate in the absence of ether is slow, only 46% conversion is achieved after 72 h in cyclohexane at 22°C. The one-half-order rate constant for initiation and propagation is 1.4 mmol$^{1/2}$/(L$^{1/2}$·min) compared to values of 33 and 494 mmol$^{1/2}$/(L$^{1/2}$·min) for 1,3-butadiene and styrene, respectively, at 30°C [4].

SUMMARY

The results reported here for the organolithium-initiated anionic polymerization of trimethylvinylsilane are consistent with the mechanisms proposed for other vinyl monomers such as styrene and 1,3-dienes [2], except that a termination step exists. The reaction is first order with respect to monomer but varies between one-half and first order with respect to initiator and chain ends.

Ethers increase the rates of initiation, polymerization, and termination. However, the termination rate is increased faster by ethers, so

RICKLE

TABLE 2. The Effect of Ether Addition

Ether, mmol/L	Initiator, mmol/L	K_2k_2, $L^{1/2}/(mol^{1/2} \cdot min)$	k_2/k_3, L/mol	K_2k_3, $L^{1/2}/(mol^{1/2} \cdot min)$	Conversion, %
1,2-Dimethoxyethane, 35.5	5.34	1.0	66	1.5×10^{-2}	29
Tetrahydrofuran, 4.08	6.95	ND	122	ND	57
Tetrahydrofuran, 1.67	7.12	6.2×10^{-2}	199	3.1×10^{-4}	75
Tetrahydrofuran, 0.433	7.29	1.5×10^{-2}	195	7.6×10^{-5}	76
None	11.3	1.4×10^{-3}	ND	ND	ND

that high conversions to polymer are obtained at low ether concentrations, where the reaction rate is low but the ratio k_2/k_3 is high.

Kinetics will place limitations upon the synthesis of block copolymers containing trimethylvinylsilane. The sequential addition method, with poly(trimethylvinylsilane) segments being formed last, will be the best way to make such block copolymers. The coupling method would not be effective due to possible termination of poly(trimethylsilane) segments before coupling. Thus block copolymers with high molecular weight poly(trimethylvinylsilane) middle segments would be difficult to make in high yield and purity.

ACKNOWLEDGMENTS

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