

Silyl Enol Ethers as Monomer. I. Radical Copolymerizability of α -Trimethylsilyloxystyrene

KATSUTOSHI NAGAI,* KEISUKE ASADA, KEIJI CHIBA, and
NORIYUKI KURAMOTO, *Department of Polymer Chemistry,
Faculty of Engineering, Yamagata University, Jonan,
Yonezawa 992, Japan*

Synopsis

α -Trimethylsilyloxystyrene (TMSST), the silyl enol ether of acetophenone, was not homopolymerized either by a radical or a cationic initiator. Radical copolymerization of TMSST with styrene (ST) and acrylonitrile (AN) in bulk and the terpolymerization of TMSST, ST, and maleic anhydride (MA) in dioxane were studied at 60°C and the polymerization parameters of TMSST were estimated. The rate of copolymerization decreased with increased amounts of TMSST for both systems. Monomer reactivity ratios were found as follows: $r_1 = 1.48$ and $r_2 = 0$ for the ST (M_1)-TMSST (M_2) system and $r_1 = 0.050$ and $r_2 = 0$ for the AN (M_1)-TMSST (M_2) system. The terpolymerization of ST (M_1), TMSST (M_2), and MA (M_3) gave a terpolymer containing ca. 50 mol % of MA units with a varying ratio of TMSST to ST units and the ratio of rate constants of propagation, k_{32}/k_{31} , was found to be 0.39. Q and e values of TMSST were determined using the values shown above to be 0.88 and -1.13 , respectively. Attempted desilylation by an acid catalyst for the copolymer of TMSST with ST afforded polystyrene partially substituted with hydroxyl groups at the α -position.

INTRODUCTION

Silyl enol ethers can be readily prepared by the reaction of aldehydes and ketones with trialkylsilyl chlorides in the presence of acid scavengers¹ and they have been shown to be useful reagents for various organic syntheses.^{2,3} Some silyl enol ethers can be expected to be susceptible to polymerization and the resulting polymer will be readily transformed to the analogous polymer containing hydroxyl groups through desilylation. However, little has been studied on radical polymerization of such monomers, though some vinyl trialkylsilyl ethers have been used in cationic polymerization⁴ and in aldehyde-catalyzed group-transfer polymerization.⁵

The present paper deals with the copolymerizations of TMSST with ST and AN, and the terpolymerization of TMSST, ST, and maleic anhydride (MA) to determine the polymerization parameters of TMSST. TMSST can be regarded as a derivative of either a vinyl ether or styrene. Therefore, it is of interest to examine which property is predominant for the polymerization.

In addition, an attempt was made to desilylate the copolymer of TMSST with ST using an acid catalyst. On the other hand, the desilylation of copolymer containing AN or MA units under similar conditions was accompa-

*To whom correspondence should be addressed.

nied by lactonization. Details of these reactions will be reported in a subsequent paper.

EXPERIMENTAL

Reagents

TMSST was prepared by the reaction of acetophenone with trimethylsilyl chloride in the presence of NaI in acetonitrile according to the procedure of Walshe et al.⁶ and purified by a fractional distillation under reduced pressure: bp 59°C/2 mm Hg (lit.¹ 89–91°C/12 mm Hg). No contamination of TMSST was detected by gas chromatography or NMR spectroscopy.

ST and AN (both from Wako Pure Chemical Industries, Ltd.) were purified by distillation after removing inhibitor and drying over CaH₂ and P₂O₅, respectively. MA (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized from anhydrous diethyl ether. α, α' -Azobisisobutyronitrile (AIBN, from Tokyo Kasei Kogyo Co. Ltd.) was purified by recrystallization from methanol.

Polymerization

Polymerization was conducted at 60°C in sealed glass tubes under nitrogen atmosphere. The copolymerizations of TMSST with ST and AN were relatively slow even in bulk, so that an initiator was used at concentrations somewhat higher than those commonly used for radical polymerization (1–5 mol %). After definite periods of time, the polymerization mixture was poured into a large volume of methanol containing a small amount of *p*-methoxyphenol to stop the polymerization. The precipitated polymer was filtered off, washed with methanol, and dried in vacuum. In the case of terpolymerization, diethyl ether was used as a nonsolvent to precipitate the terpolymer.

Characterization of Polymers

IR spectra were measured in KBr tablets in a JASCO IR-S1 spectrometer. ¹H-NMR spectra were recorded on a Hitachi R-24B spectrometer in chloroform-*d*₁ for copolymers and acetone-*d*₆ for terpolymer at 35°C. GPC was obtained using tetrahydrofuran as solvent in a Toyo Soda HLC-802A. Molecular weight was estimated based on that of standard polystyrene used as a reference. The copolymer composition was determined from elemental analysis. The terpolymer composition was calculated from both elemental analysis and NMR spectra. The ratio of TMSST to ST unit in the terpolymer was first determined using the ratio of peak areas for the trimethylsilyl and phenyl groups in NMR spectra and then the contents of all three monomer units were estimated based on elemental analysis.

Desilylation of Copolymer

A small amount of concentrated HCl was added to a solution of the copolymer of TMSST with ST, containing ca. 10 mol % of TMSST unit, in dioxane and then the solution was refluxed for 48 h. After evaporating the solvent, methanol was added to the residue, and the product was isolated by filtration, followed by drying.

RESULTS AND DISCUSSION

Copolymerization of TMSST with Styrene

The homopolymerization of TMSST was unsuccessful with both radical and cationic initiators under various conditions. The lack of homopolymerizability of TMSST could be ascribed to a steric effect owing to two bulky substituents at the same carbon atom of the vinyl group. The results of the copolymerization of TMSST with ST in bulk using AIBN are depicted in Figure 1. The rate of copolymerization sharply decreases with increasing feed composition of TMSST and becomes practically nil above 60 mol % of TMSST in the monomer. The weight-average molecular weight of the copolymer also falls considerably as the feed concentration of TMSST increases. Furthermore, the TMSST content in the resulting copolymer is lower than that in the feed. Such copolymerization behavior could result from the failure of TMSST to homopolymerize. Figure 2 shows the time dependences of yield and composition of copolymer at a feed composition of TMSST of 10 mol %. The copolymerization proceeds at a considerable rate at this feed composition to give the copolymer having a composition somewhat lower than the feed composition. The monomer reactivity ratio of TMSST (M_2) is zero (no homopropagation) and hence that of ST (M_1), r_1 , for the copolymerization system can be estimated using a following relation:

$$f = r_1 F + 1 \quad (1)$$

where f and F represent the molar ratio of ST and TMSST in the copolymer and monomer feed, respectively. As depicted in Figure 3 [which includes a similar plot for the copolymerization of TMSST with AN (M_1)], the plot affords a straight line having an intercept of 1; r_1 , estimated from the slope, was 1.48 for the copolymerization with ST.

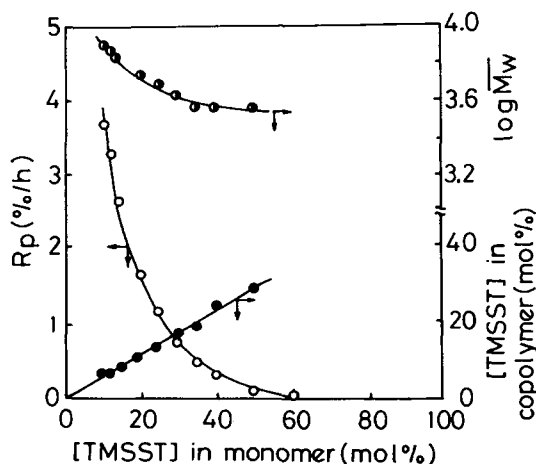


Fig. 1. Copolymerization of TMSST with ST in bulk at 60°C. $[TMSST] + [ST] = 10.0$ mmol; $[AIBN] = 5.0$ mol %. R_p , the rate of copolymerization expressed in %/h.

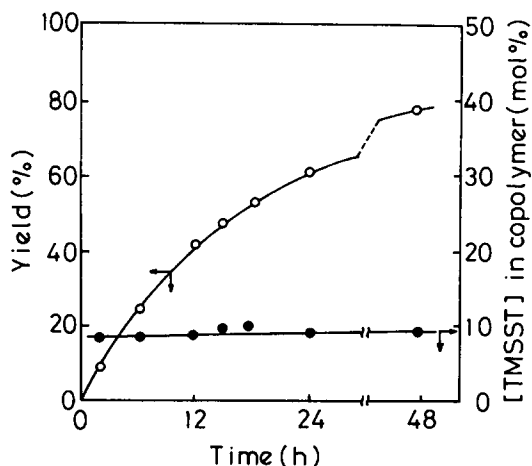


Fig. 2. Copolymerization of TMSST with ST in bulk at 60°C. $[TMSST]/[ST] = 1$ mmol/9 mmol; $[AIBN] = 5.0$ mol %.

The copolymer is a white powder and soluble in a wide range of organic solvents except for petroleum ether and methanol.

Copolymerization of TMSST with Acrylonitrile

As presented in Figure 4, a drop in the rate of copolymerization with increasing feed concentration of TMSST is also observed for the copolymerization with AN. However, copolymerization is possible up to higher TMSST content compared to the copolymerization system involving ST as comonomer. The copolymer having an approximately alternating composition is obtained

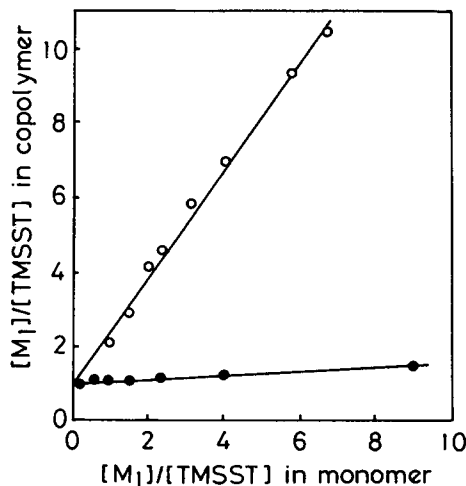


Fig. 3. Plots of molar ratio of $[M_1]/[TMSST]$ in copolymer against that in monomer for the copolymerizations of TMSST with ST and AN: (○) $M_1 = ST$; (●) $M_1 = AN$. Conditions as in Figures 1 and 4.

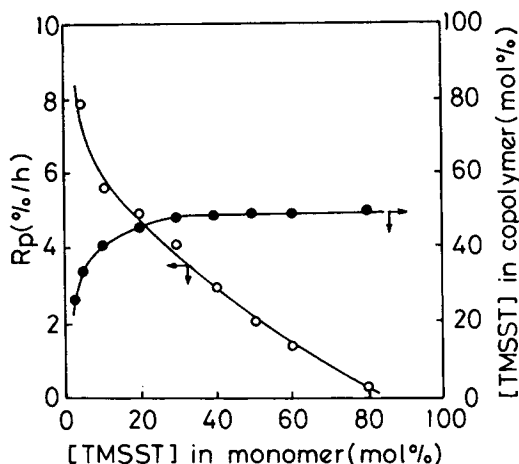


Fig. 4. Copolymerization of TMSST with AN in bulk at 60°C. $[TMSST] + [AN] = 10.0$ mmol; $[AIBN] = 5.0$ mol %. R_p , the rate of copolymerization expressed in %/h.

at a feed composition of TMSST higher than 30 mol %. The monomer reactivity ratio of AN was found to be 0.050 from the slope of the straight line shown in Figure 3, which was in good agreement with the value determined by Kelen-Tüdös method,⁷ indicating that the copolymerization system is of highly alternating character. Figure 5 shows the results on the copolymerization at an equimolar feed composition in bulk. The molecular weight of the copolymer exhibits a gradual increase with time, which is probably due to a gel effect.

The copolymer is a white powder and soluble in various organic solvents other than petroleum ether and methanol.

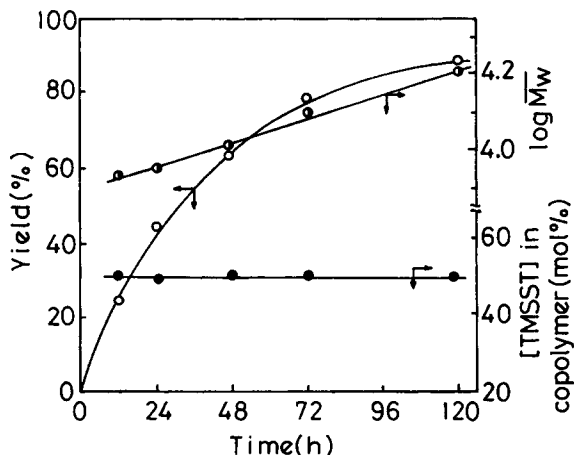


Fig. 5. Copolymerization of TMSST with AN in bulk at 60°C. $[TMSST]/[AN] = 5$ mmol/5 mmol; $[AIBN] = 5.0$ mol %.

Terpolymerization of TMSST, ST and MA

The results on the terpolymerization of ST (M_1), TMSST (M_2), and MA (M_3) in dioxane are presented using triangular coordinates in Figure 6. The resulting terpolymer contains ca. 50 mol % MA units as shown by the broken line, except for those formed at a low concentration of MA in feed. Styrene is known to undergo an alternating copolymerization with MA⁸ and further, the copolymerization of TMSST with MA also gives a copolymer having an alternating composition over a wide range of feed composition.⁹ Therefore, the present terpolymerization system can be regarded as composed of two donor monomers and an acceptor monomer. Accordingly, the cross propagation should be predominant for such a terpolymerization system and the propagation can be represented as follows:



where M and M · represent monomer and propagating radical, respectively. Under steady state conditions, there must be the following relationships between the compositions of the feed and the terpolymer:

$$(d[M_1] + d[M_2])/d[M_3] = 1 \quad (6)$$

$$d[M_1]/d[M_2] = (k_{31}/k_{32})[M_1]/[M_2] \quad (7)$$

where $d[M_1]$, $d[M_2]$, and $d[M_3]$ refer to the concentrations of TMSST, ST, and MA units in terpolymer, respectively. As shown in Figure 6, the relationship represented by eq. (6) is satisfactorily valid except for the terpolymer formed at a low feed composition. Furthermore, the plot of $d[M_1]/d[M_2]$ against $[M_1]/[M_2]$, based on eq. (7), gives a good straight line through the

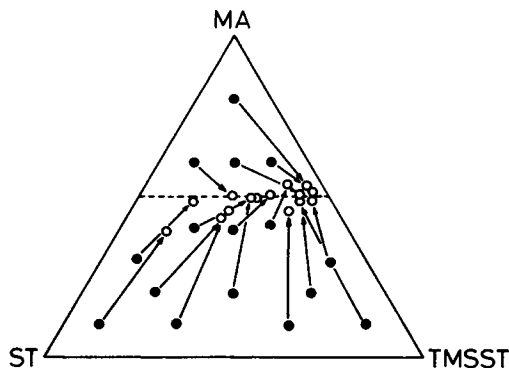


Fig. 6. Terpolymerization of ST, TMSST, MA in dioxane at 60°C: (○) terpolymer composition; (●) monomer composition. $[ST] + [TMSST] + [MA] = 10.0$ mmol; $[AIBN] = 1.0$ mol %.

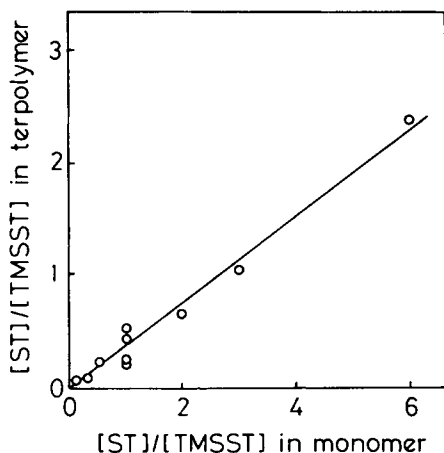


Fig. 7. Plot of molar ratio of $[ST]/[TMSST]$ in terpolymer against that in monomer for the terpolymerization of ST, TMSST, and MA. Conditions as in Figure 6.

origin, as depicted in Figure 7. The ratio, k_{31}/k_{32} , was determined to be 0.39 from the slope of the line.

Determination of Q and e Values of TMSST

Although Q and e values cannot be determined using monomer reactivity ratios obtained for a single copolymerization system because of the failure of TMSST to homopolymerize, these parameters can be estimated by either a combination of the monomer reactivity ratios for ST and AN obtained from the respective copolymerizations with TMSST or a combination of the monomer reactivity ratio of ST and the ratio of rate constants obtained from the terpolymerization. When ST, AN, TMSST, and MA are represented as M_1 , M_1' , M_2 , and M_3 , respectively, the following equations can be obtained:

$$r_1 = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] \quad (8)$$

$$r_1' = (Q_1'/Q_2)\exp[-e_1'(e_1' - e_2)] \quad (9)$$

$$k_{31}/k_{32} = (Q_1/Q_2)\exp[-e_3(e_1 - e_2)] \quad (10)$$

Thus, Q and e values of TMSST can be calculated substituting 1.48, 0.050, and 0.39 for r_1 , r_1' , and k_{31}/k_{32} , respectively, and using Q and e values for ST, AN, and MA. The results are summarized in Table I.

Thus, Q and e values of TMSST calculated using eqs. (8) and (10) are in fairly good agreement with those obtained using eqs. (8) and (9), when Q and e values of MA, revised by Greenley,¹⁰ are employed instead of those recorded in *Polymer Handbook*.¹¹ The Q value of TMSST is somewhat lower than that of ST (1.0) and the e value is close to -1.1.

The Q and e values of α -methoxystyrene (MOST), which has a molecular structure similar to TMSST, were reported to be 0.65 and -1.20, respectively.¹² Thus, substitution at α -position of styrene with alkoxy or silyloxy

TABLE I
 Q and e Values of TMSST^a

	Q	e	Remarks
[I]	0.82	-1.04	Calcd using eqs. (8) and (9)
[II]	0.95	-1.24	Calcd using eqs. (8) and (10)
[III]	0.86	-1.10	Calcd using eqs. (8) and (10)
Av.	0.88	-1.13	

^aThe following Q and e values were used together with those for ST ($Q = 1.0$ and $e = -0.8$)¹¹: [I], $Q = 0.60$ and $e = 1.20$ for AN¹¹; [II], $Q = 0.23$ and $e = 2.25$ for MA¹¹; [III], $Q = 0.86$ and $e = 3.69$ for MA.¹⁰

group seems to lower the Q value, being probably associated with a steric effect of the group. The e value of TMSST is comparable to that of MOST. Most vinyl alkyl ethers have e values ranging from -0.6 to -1.8 , being centered at about -1.2 ¹¹ and hence TMSST can be also regarded as a derivative of vinyl ethers, as judged from its e value. Thus, TMSST is characteristic of a donor monomer, as evidenced by a high copolymerizability with electron-accepting monomers such as MA and fumaronitrile.⁹

Desilylation of the Copolymer of TMSST with ST

Figure 8 represents IR spectra of the copolymer of TMSST with ST containing ca. 10 mol % of TMSST units and the desilylated product. Absorption bands at 830, 1070, and 1250 cm^{-1} , characteristic of the silyloxy group in the copolymer, practically disappear and a small band, assigned to a hydroxyl group, appears near 1640 cm^{-1} . Moreover, disappearance of the silyloxy group was also clearly evidenced by the NMR spectrum of the desilylated product. Thus, polystyrene partially substituted with a hydroxyl group at the α -position can be readily prepared from the copolymer of ST

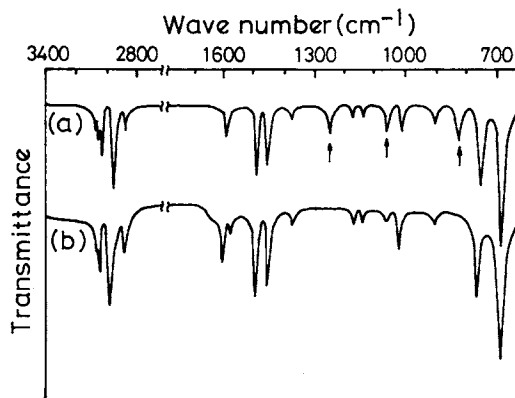
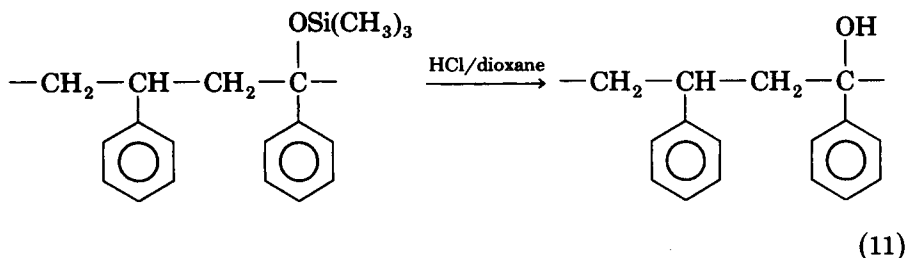


Fig. 8. IR spectra of copolymer of TMSST with (a) ST and (b) the desilylated product.

with TMSST [eq. (11)]:



On the other hand, attempted desilylation of copolymers or terpolymers containing MA or AN units under similar conditions was accompanied by the formation of a lactone ring.⁹ The results on the desilylation for such polymers will be reported in the subsequent paper.

The authors would like to thank Takeyoshi Takahashi for his contribution in elemental analysis.

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Received October 11, 1988

Accepted April 11, 1989