

Silyl Enol Ethers as Monomer. III. Radical Polymerization and Copolymerizations of 2-Trimethylsilyloxy-1,3-Butadiene and Desilylation of the Resulting Polymers

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Synopsis

2-Trimethylsilyloxy-1,3-butadiene (TMSBD), the silyl enol ether of methyl vinyl ketone, was homopolymerized with a radical initiator to afford polymers with a molecular weight of ca. 10^4 . Radical copolymerizations of TMSBD with styrene (ST) and acrylonitrile (AN) in bulk or dioxane at 60°C gave the following monomer reactivity ratios: $r_1 = 0.64$ and $r_2 = 1.20$ for the ST (M_1)-TMSBD (M_2) system and $r_1 = 0.036$ and $r_2 = 0.065$ for the AN (M_1)-TMSBD (M_2) system. The Q and e values of TMSBD determined from the reactivity ratios for the former copolymerization system were 2.34 and -1.31 , respectively. The resulting polymer and copolymers were readily desilylated with hydrochloric acid or tetrabutylammonium fluoride as catalyst to yield analogous polymers having carbonyl groups in the polymer chains.

INTRODUCTION

The silylation of aldehydes and ketones with silylating agents such as trimethylsilyl chloride and trimethylsilyl trifluoromethanesulfonate gives silyl enol ethers which are useful for various organic syntheses.¹⁻⁶ On the other hand, only a few studies have been undertaken on the polymerization and copolymerization of the silyl enol ethers having a vinyl or dienyl group.⁷⁻⁹ We have recently disclosed that α -trimethylsilyloxystyrene (TMSST), the silyl enol ether of acetophenone, undergoes radical copolymerizations with various vinyl monomers and especially exhibits a high copolymerizability toward electron-accepting monomers.^{10,11} Furthermore, the acid-catalyzed desilylation of the resulting copolymers having polar groups such as acid anhydride or nitrile groups has been found to give the polymers containing lactone rings.¹¹

TMSBD is a conjugated diene having the silyl ether group at the 2-position and hence it will afford the polymers still involving the silyl enol ether groups. The polymers containing TMSBD units will not only give analogous polymers having carbonyl groups through the desilylation, but also the silyl enol ether groups in the polymers will be applicable to various reactions based on their nucleophilicity, e.g., reactions with electrophiles such as carbonyl compounds, nitro-olefins, acetals in the presence of Lewis acid.^{5,6} Furthermore, we have recently found that the silyl enol ether derivatives have also an ability to initiate

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the polymerization of AN in the presence of a catalytic amount of tetrabutylammonium fluoride in a similar manner as group transfer polymerization using ketene silyl acetals as initiators^{12,13} and that the copolymers containing TMSBD units cause graft copolymerization of AN.¹⁴ Thus, TMSBD will be used as a monomer giving various, reactive polymers.

The present study deals with the radical polymerization of TMSBD and the copolymerizations with ST and AN to determine polymerization parameters of TMSBD. Furthermore, the desilylation of the resulting polymer and copolymers were studied using hydrochloric acid or tetrabutylammonium fluoride as catalyst.

EXPERIMENTAL

Reagents

TMSBD was prepared by the reaction of methyl vinyl ketone with trimethylsilyl chloride in the presence of triethylamine in dimethylformamide according to the procedure of Jung et al.⁴ and purified by a fractional distillation under reduced pressure after dehydration over CaH_2 : bp, 46°C/51 mm Hg (lit.⁴ 50–55°C/50 mm Hg). No contamination of TMSBD was detected by gas chromatography and NMR spectroscopy.

Methyl vinyl ketone was used as received from Tokyo Kasei Kogyo Co., Ltd. Styrene (ST), methyl methacrylate (MMA), and acrylonitrile (AN), received from Wako Pure Chemical Industries, Ltd., were distilled after drying. Maleic anhydride (MA, Wako Pure Chemicals Industries, Ltd.) and α, α' -azobisisobutyronitrile (AIBN, Tokyo Kasei Kogyo Co., Ltd.) were recrystallized from anhydrous diethyl ether and methanol, respectively. Tetrabutylammonium fluoride (TBAF, 1 M in tetrahydrofuran) was used as received from Tokyo Kasei Kogyo Co., Ltd.

Polymerization and Copolymerization

Polymerization and copolymerization were conducted at 60°C in sealed glass tubes (ca. 10 mL) under nitrogen atmosphere. To the polymerization tubes were added TMSBD, comonomer for the copolymerization, AIBN, and dioxane. The tubes were degassed by freeze–thaw technique, sealed, and placed in a constant temperature bath thermostatted at 60°C. After an appropriate time, the contents of the tubes were poured into a large volume of nonsolvent containing a small amount of *p*-methoxyphenol as an inhibitor. The nonsolvents used were methanol for the homopolymer of TMSBD and the copolymers with ST and MMA and petroleum ether for the copolymer with AN. The precipitated polymer or copolymer was filtered off, washed with the nonsolvent, and then dried in vacuum.

Characterization of Polymer and Copolymers

IR and ¹H-NMR spectra were measured in JASCO IR-S1 and Hitachi R-24B spectrometers, respectively. GPC was obtained using tetrahydrofuran as solvent in a Toyo Soda HLC-802A. Molecular weight was estimated based on that of standard polystyrenes as references. The composition of the copolymers

with ST and MMA was determined using ^1H -NMR spectra and confirmed by elemental analysis and that of the copolymers with AN was calculated from elemental analysis.

Desilylation

An appropriate amount of concentrated hydrochloric acid or acetic acid as catalyst was added to a solution prepared by dissolving the polymer or copolymer in acetone and then the solution was stirred at room temperature or 50°C . Tetrahydrofuran was used as solvent for the reaction in the presence of TBAF as catalyst. To the solution concentrated by evaporation was added a large volume of methanol. The precipitated product was filtered, washed with methanol, and then dried in vacuum.

RESULTS AND DISCUSSION

Polymerization of TMSBD

As shown in Figure 1, TMSBD undergoes the homopolymerization with a radical initiator to yield the polymer having a weight-average molecular weight of the order of 10^4 (Table I), being in contrast to 1-trimethylsilyloxy-1,3-butadiene.¹⁵ The resulting polymer is tacky solid and soluble in various organic solvents except for methanol.

The IR spectrum of the polymer, shown in Figure 2(a), exhibits absorptions for silyl groups at 840 and 1250 cm^{-1} and carbon-carbon double bond at 1660 and 3060 cm^{-1} . There are four possible configurations in the structural units of the polymer: 1,2-, 3,4-, cis-1,4-, and trans-1,4-structures. However, the 1,2-structures could not be present, as judged by the failure of TMSST to homopolymerize.¹⁰ Although the IR spectroscopy has been employed to characterize the microstructure of polyisoprene¹⁶⁻¹⁸ and polychloroprene,¹⁹ no clear information on the microstructure of the polymers of TMSBD was obtained from the IR spectra and, in particular, strong absorption of the silyl groups at 840 cm^{-1} interferes with a determination of the 3,4-structures. On the other hand, the ^1H -NMR spectrum, shown in Figure 2(b), exhibits two peaks at 4.0–4.2

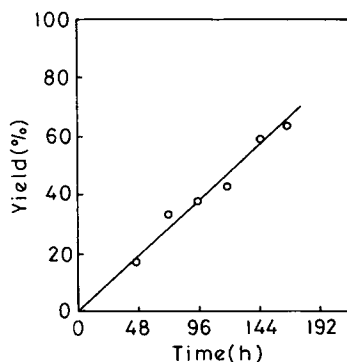


Fig. 1. Polymerization of TMSBD in bulk at 60°C . $[\text{TMSBD}] = 5.0\text{ mmol}$; $[\text{AIBN}] = 5.0\text{ mol \%}$.

TABLE I
 Copolymerization of TMSBD with Various Comonomers^a

Run no.	Comonomer ^b	AIBN (mol %)	Time (h)	Copolymer		
				Yield (%)	TMSBD (mol %)	MW × 10 ^{-4c}
01	None	5.0	120	42.1	100.0	1.12
02	ST	5.0	36	81.7	57.3	1.84
03	MMA	5.0	24	41.6	53.6	3.74
04	AN	1.0	9	52.3	52.5	8.93
05 ^d	MA	1.0	3	67.4 ^e	50.1	28.00

^a [TMSBD] = [comonomer] = 5.0 mmol; temperature 60°C.

^b ST, styrene; MMA, methyl methacrylate; AN, acrylonitrile; MA, maleic anhydride.

^c Weight-average molecular weight, determined by GPC.

^d Dixane (5 mL) was used as solvent.

^e Diels–Alder adduct was formed in 28.2% yield.

and 4.3–4.9 ppm, which can be assigned to olefinic protons in the 3,4- and 1,4-structures, respectively, by reference to the assignment of ¹H-NMR spectra of polyisoprene.^{20,21} The ratio of these peak areas gave a proportion of 18.6% 3,4-structures and 81.4% 1,4-structures, though a ratio of cis-1,4- to trans-1,4-structures could not be determined.

Copolymerization of TMSBD with Various Comonomers

The results of the copolymerization of TMSBD with various comonomers using AIBN as initiator are presented in Table I. TMSBD exhibits a high copolymerizability toward the comonomers used here. In particular, the copolymerizations with the comonomers having high positive e values such as AN and MA proceed with a considerable rate to afford the copolymers having

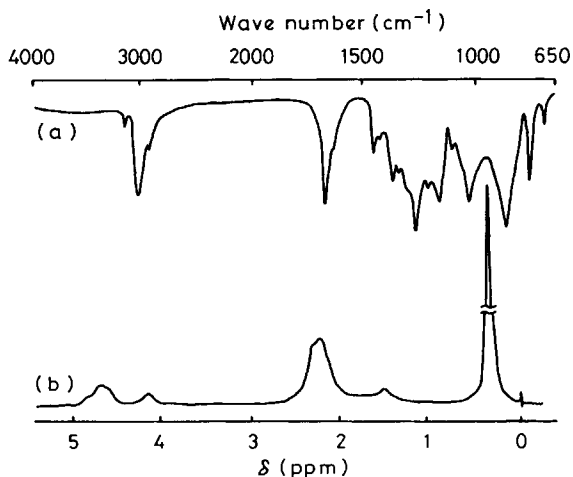


Fig. 2. IR and ¹H-NMR spectra of poly(TMSBD): (a) IR spectrum, (b) NMR spectrum.

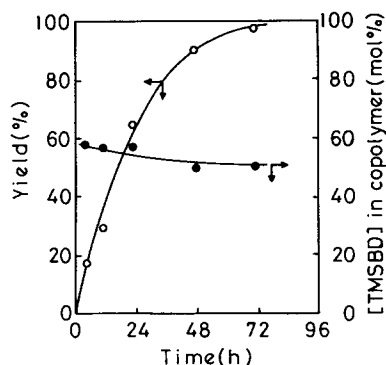


Fig. 3. Copolymerization of TMSBD with ST in bulk at 60°C. $[TMSBD] = [ST] = 5.0$ mmol; $[AIBN] = 5.0$ mol %.

a relatively high molecular weight. The solution of TMSBD containing AN or MA assumed a light yellow color and a small amount of the copolymer was also formed in the absence of initiator for the system involving MA. Such features will be ascribed to a high donor property of TMSBD.

Copolymerization of TMSBD with ST

The results of the copolymerization of TMSBD with ST are depicted in Figures 3 and 4. As illustrated in Figure 3, the copolymerization gives the copolymer in a nearly quantitative yield after 72 h under the conditions shown in the figure, being indicative of no side reactions. Furthermore, the copolymers having TMSBD content slightly higher than 50 mol % corresponding to the composition in monomers are formed at an initial stage, suggesting that TMSBD has a reactivity higher than that of ST. This is also evidenced by the composition curve shown in Figure 4, where the copolymer composition is determined for the copolymers formed in a yield below 10%. The monomer reactivity ratios of ST (M_1) and TMSBD (M_2), estimated by the Kelen-Tüdös method²² using the results of the copolymer composition shown in Figure 4, were presented in

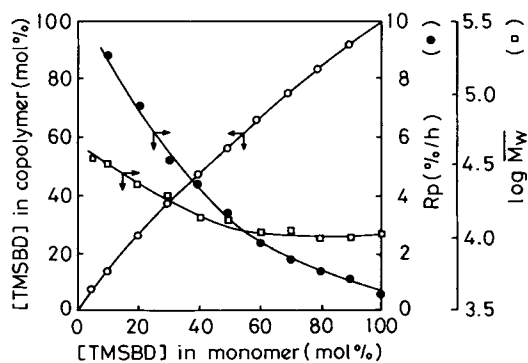


Fig. 4. Copolymerization of TMSBD with ST in bulk at 60°C. $[TMSBD] + [ST] = 10.0$ mmol; $[AIBN] = 5.0$ mol %. R_p , the rate of copolymerization expressed in %/h.

Table II, together with Q and e values calculated on the reactivity ratios. The Q value is comparable to that of 1,3-butadiene,²³ whereas the e value is slightly larger than that of isoprene.²⁴ Consequently, the trimethylsilyloxy group of TMSBD appears to exert little resonance effect but an inductive effect.

As can be seen from Figure 4, the rate of copolymerization and the molecular weight decrease with increasing amounts of TMSBD in monomers, similarly to the copolymerization of TMSST with ST.¹⁰ However, such decrease in the rate of copolymerization is not so steep compared to the latter copolymerization system where no homopropagation of TMSST takes place.

The kinetic features of the copolymerization as a function of monomer composition can be interpreted by assuming that the termination exclusively occurs between the propagating TMSBD radicals. The rate of copolymerization (R_p) for such copolymerization system is represented as follows:

$$R_p = KT[r_1(1 - X)^2X^{-1} + 2(1 - X) + r_2X] \quad (1)$$

where K is a constant including the rate of initiation, T a total monomer concentration ($= [M_1] + [M_2]$), and X a mole fraction of M_2 in monomers. The r_1 and r_2 refer to the monomer reactivity ratios of M_1 and M_2 , respectively. When ST and TMSBD are taken as M_1 and M_2 , respectively, eq. (1) indicates that R_p decreases with increasing X for the r_1 and r_2 values obtained here, being in agreement with the results shown in Figure 4. Consequently, the propagating TMSBD radicals will predominantly participate in the termination for the copolymerization of TMSBD with ST.

Copolymerization of TMSBD with AN

Figures 5 and 6 represent the results of the copolymerization of TMSBD with AN. The copolymerization with AN proceeds with a considerable rate even under the conditions where the concentrations of the initiator and the monomers are lower than those for the copolymerization with ST. Although it has been reported that the copolymerization of 1-ethoxy-1,3-butadiene or 1-diethylamino-1,3-butadiene with AN is accompanied by the formation of appreciable amounts of Diels–Alder adducts,²⁴ no detectable amounts of adducts were formed for the present copolymerization system. As shown in Figure 6, the resulting copolymers have a high degree of alternation of monomer units in the chain. The monomer reactivity ratios of AN (M_1) and TMSBD (M_2) were estimated by the Kelen–Tüdös method²² and presented in Table II, to-

TABLE II
Copolymerization Parameters

M_1	M_2	r_1	r_2	Q_2	e_2
ST	TMSBD	0.64	1.20	2.34	-1.31
AN	TMSBD	0.036	0.065	0.86	-1.27
	1,3-Butadiene			2.39 ^a	-1.05 ^a
	Isoprene			3.33 ^a	-1.22 ^a

^a Ref. 23.

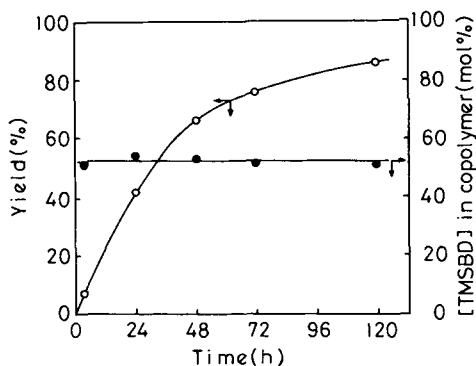


Fig. 5. Copolymerization of TMSBD with AN in dioxane at 60°C. $[TMSBD] = [AN] = 5.0$ mmol; $[AIBN] = 1.0$ mol %; dioxane, 5 mL.

gether with the Q and e values of TMSBD calculated using the Q and e values of AN (0.60 and 1.20, respectively²³). The Q value of TMSBD estimated on the results of the copolymerization with AN is considerably smaller than that obtained from the results of the copolymerization with ST. The evaluation of Q values of diene monomers using the monomer reactivity ratios obtained from the copolymerization with AN tends to afford considerably low Q values for the diene monomers.²⁵ This could be related to the formation of a charge-transfer complex between a diene monomer and AN, as observed for the copolymerization system composed of TMSBD and AN. Therefore, the Q and e values calculated on the monomer reactivity ratios for the copolymerization with ST will be rather valid.

Figure 6 also demonstrates the decreases in the rate of copolymerization and the molecular weight of the copolymers with increasing concentration of TMSBD in monomers in a similar manner as the copolymerization with ST. Such reduction in the rate of copolymerization with respect to the feed composition of TMSBD was also fitted with eq. (1).

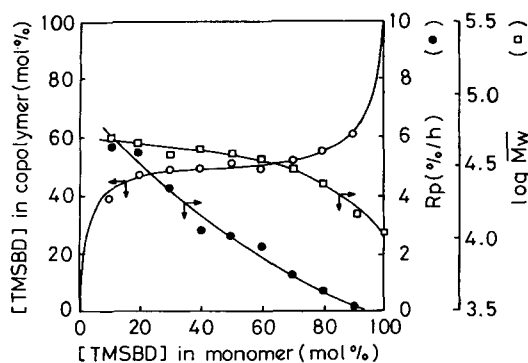
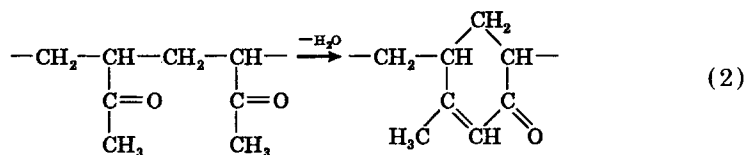


Fig. 6. Copolymerization of TMSBD with AN in dioxane at 60°C. $[TMSBD] + [AN] = 10.0$ mmol; $[AIBN] = 1.0$ mol %; dioxane, 5 mL. R_p , the rate of copolymerization expressed in %/h.

Desilylation of Polymer and Copolymers

In general, silyl ethers can be readily cleaved in the presence of acids, bases and fluorides as catalysts.⁶ However, considerable amounts of hydrochloric acid and a prolonged heating were required to accomplish a complete desilylation of the copolymers of TMSST.¹¹ On the other hand, the silyl groups in the polymer and copolymers produced here should be the silyl enol ether groups which will be more easily desilylated to give carbonyl groups.

The results on the desilylations of the homopolymer and the copolymers are presented in Table III. As expected, completely desilylated products were obtained even in the reactions at room temperature. Tetrabutylammonium fluoride was also active as catalyst in addition to hydrochloric acid. Figure 7(a) shows the IR spectrum of the desilylated product of the homopolymer, indicating a complete disappearance of the absorptions at 840 and 1250 cm^{-1} for silyl groups and those at 1660 cm^{-1} for carbon-carbon double bonds. The spectrum exhibits a small peak at 1650 cm^{-1} in addition to a strong peak at 1720 cm^{-1} which is characteristic of carbonyl groups. The former absorption has been suggested to also appear in IR spectra of poly(methyl vinyl ketone) (PMVK) heated at a considerably high temperature and to be assigned to the unsaturated carbonyl groups formed through an intramolecular dehydration represented by eq. (2)^{26,27}



The IR spectrum shown in Figure 7(b) indicates that PMVK appears to undergo a similar intramolecular dehydration under the conditions used for the desilylation with hydrochloric acid. The starting polymer contains ca. 18% 3,4-structures, which should be converted to the same monomer units as those of PMVK through the desilylation, and hence some unsaturated carbonyl groups, shown in eq. (2), could be involved in the desilylated product of the polymer.

Figure 8 shows $^1\text{H-NMR}$ spectrum of the desilylated product of the polymer. The spectrum exhibits two main absorptions in the range of 1.1 to 3.1 ppm and two small absorptions at 1.5 and 2.2 ppm. The main absorptions at a lower and higher field can be assigned to methylene protons at α - and β -positions of carbonyl groups, respectively. The peak at the lower field also involves an absorption due to α -methine protons resulting from 3,4-structures of the starting polymer. The ratio of these areas for the main peaks was ca. 1.7, indicating that the starting polymer contains some 3,4-structures. The ratio gave a proportion of 80% 1,4-structures and 20% 3,4-structures for the starting polymer, which is in fairly good agreement with that determined from olefinic protons in its NMR spectrum described above.

The characteristic peak at 2.2 ppm can be assigned to methyl protons adjacent to carbonyl groups derived from 3,4-structure of the starting polymer. In addition, the small peak at 1.5 ppm could be due to protons of methyl groups attached to olefinic double bonds in the structure shown by eq. (2), though

TABLE III
 Desilylation of the Polymer and Copolymers of TMSBD^a

Run no.	Copolymer ^b	TMSBD (mol %)	Catalyst ^c		Product W/W ⁰ ^d	W'/W' ⁰ ^e
				(g)		
DB1	HB	100.0	HCl	0.3	0.504 ^f	0.493
DB2	BS	56.9	HCl	0.2	0.671 ^g	0.688
DB3	BS	11.4	TBAF	0.06	0.923	0.924
DB4	BM	6.6	TBAF	0.06	0.946 ^h	0.954
DB5 ⁱ	BA	52.3	HCl	0.2	0.615 ^j	0.621
DB6 ^k	BA	51.6	AA	3.0	0.619	0.624

^a Polymer or copolymer, 100–400 mg; acetone, 20 mL; temperature, room temperature; time, 24 h.

^b HB, homopolymer; BS, copolymer with ST; BM, copolymer with MMA; BA, copolymer with AN.

^c HCl, concentrated hydrochloric acid; TBAF, tetrabutylammonium fluoride; AA, acetic acid.

^d The ratio of the weight of the product, W, to that of the starting polymer, W⁰.

^e The ratio of the molecular weight per the repeating unit of the product, W', to that of the starting polymer, W⁰.

^f ANAL.: C, 68.46%; H, 8.72%.

^g ANAL.: C, 81.50%; H, 8.01%.

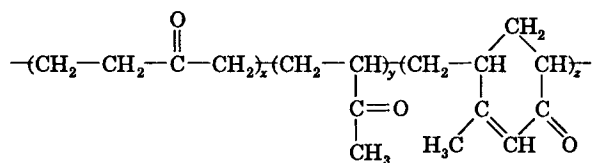
^h ANAL.: C, 57.25%; H, 8.21%.

ⁱ Time, 48 h.

^j ANAL.: C, 67.68%; H, 7.22%; N, 10.07%.

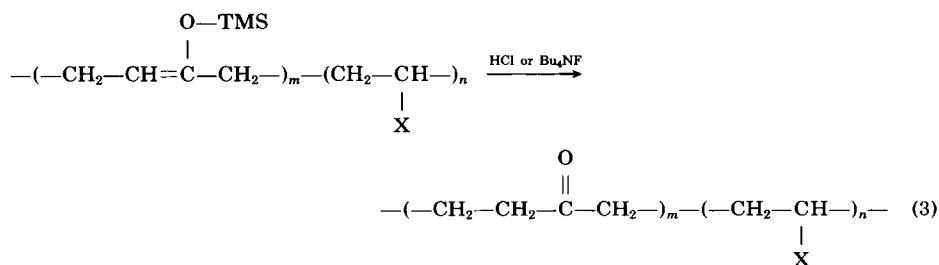
^k Temperature, 50°C; time, 168 h.

concomittant olefinic protons were not clearly observed owing to a minor contribution. Thus, the desilylated product of the polymer is composed of the following units:



where x and $y + z$ are 0.8 and 0.2, respectively, and z could be small.

The copolymers synthesized here are also desilylated in the presence of hydrochloric acid or tetrabutylammonium fluoride as catalyst to form the expected products having carbonyl groups, as evidenced by the absorption at 1720 cm^{-1} in their IR spectra in Figure 9 [eq. (3)]:



where TMS = $\text{Si}(\text{CH}_3)_3$, X = C_6H_5 , COOCH_3 , CN.

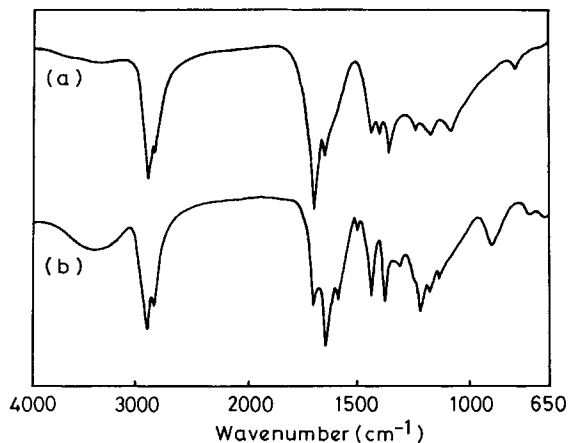
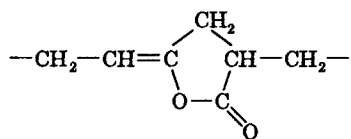


Fig. 7. IR spectra of the products of poly(TMSBD) and poly(methyl vinyl ketone) obtained in the reactions under the conditions shown in run DB1 in Table III: (a) the product of poly(TMSBD), (b) the product of poly(methyl vinyl ketone).

The desilylation is also accomplished even by a weak acid such as acetic acid as the catalyst, though the reaction is slow. As can be seen in Figure 9(c), the IR spectrum of the product through the desilylation of the copolymer with AN using hydrochloric acid exhibits an additional, small peak at 1780 cm^{-1} . Such absorption was also observed in the IR spectra of the products formed in the desilylation of the copolymer of TMSST with AN under similar conditions and it was assigned to γ -lactone rings.¹¹ Therefore, the desilylated product obtained using hydrochloric acid as catalyst could contain a small amount of the γ -lactone structures as follows:



On the other hand, the desilylation with acetic acid as catalyst is not accompanied by the lactonization, as demonstrated by the IR spectrum in Figure 9(d).

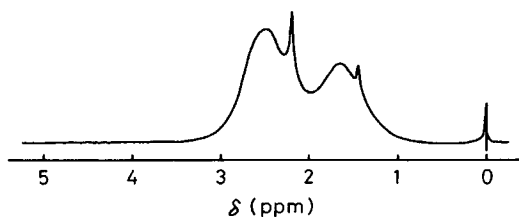


Fig. 8. ^1H -NMR spectrum of the product of poly(TMSBD) in the desilylation (run DB1 in Table III).

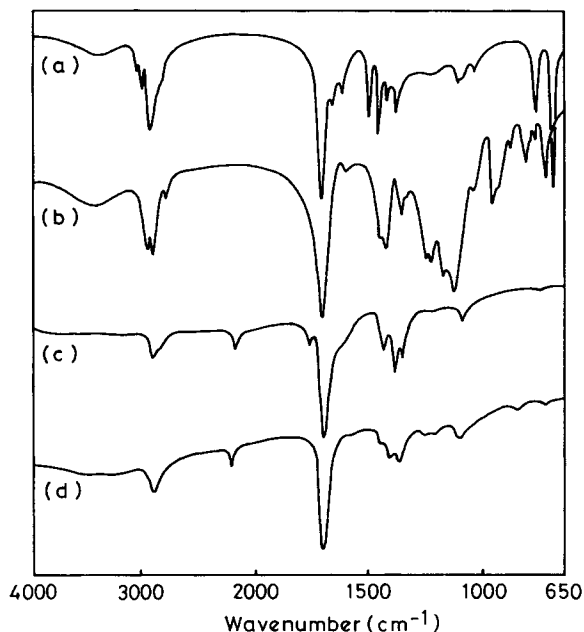


Fig. 9. IR spectra of the products obtained in the desilylations shown in Table III: (a) the product of the copolymer with ST (obtained in run DB2), (b) the product of the copolymer with MMA (obtained in run DB4), (c) the product of the copolymer with AN (obtained in run DB5); (d) the product of the copolymer with AN (obtained in run DB6).

As can be seen in Table III, the ratios of the weight of the desilylated products, W , to that of the starting polymers, W° , are in fairly good agreement with the ratios, W'/W'° , estimated based on eq. (3). Furthermore, the analytical data of some desilylated products, shown in footnotes f, g, h, and j in Table III, are also close to those calculated on the formula represented by eq. (3).

Thus, TMSBD readily copolymerizes with various comonomers to give copolymers which are easily desilylated and hence it will be a useful monomer for the preparations of the polymers containing carbonyl groups mainly in the chains.

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

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Received August 22, 1989

Accepted February 13, 1990