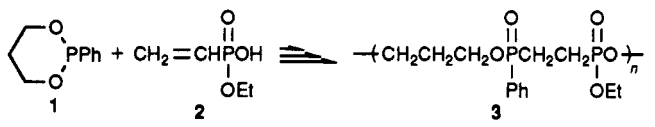
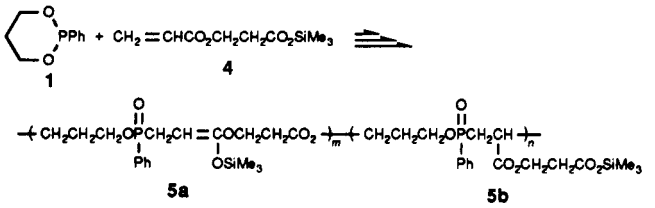
Communications to the Editor

Group-Transfer Alternating Copolymerization of 2-Phenyl-1,3,2-dioxaphosphorinane with Trimethylsilyl 3-(Acryloyloxy)propionate

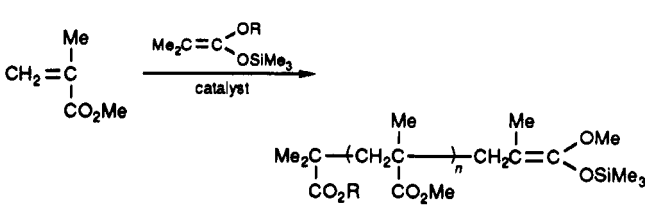
In our series of the studies on alternating copolymerizations via zwitterion intermediates, several monomers having an acidic hydrogen, e.g., acrylic acid, acrylamide, ethylenesulfonamide, and α-keto acids, have been employed in conjunction with cyclic phosphorus(III) compounds. The copolymerizations using these monomers proceeded by a hydrogen-transfer process.[1] Recently, we have reported an alternating copolymerization of 2-phenyl-1,3,2-dioxaphosphorinane (**1**) with vinylphosphonic acid monoethyl ester (**2**) to produce 1:1 alternating copolymer **3** by a hydrogen-transfer process.[2]



The present paper describes an alternating copolymerization of **1** with trimethylsilyl 3-(acryloyloxy)propionate (**4**), which proceeds via a trimethylsilyl group-transfer

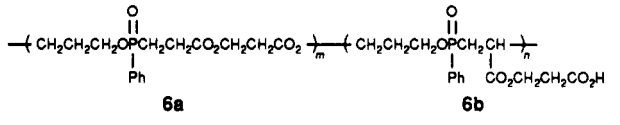


process (*group-transfer copolymerization*). This is the first example of the alternating copolymerization involving a group-transfer process. When an equimolar mixture of **1** and **4** in a solvent was heated without catalyst, the copolymerization occurred to afford alternating copolymer **5**, which consists of two units: **5a** derived by group transfer of $SiMe_3$ and **5b** produced via an ordinary reaction mode. It should be noted that the unit structure is different depending upon whether or not the group transfer is involved. The present copolymerization can be compared to regular group-transfer polymerization (GTP), in which methyl methacrylate (MMA) is polymerized by a ketene silyl acetal initiator in the presence of catalyst involving a trimethylsilyl group transfer during each propagation step.[3]



The following is a typical procedure (entry 4): An equimolar mixture of **1** (0.091 g, 0.5 mmol) and **4** (0.108 g, 0.5 mmol) containing 0.01 mmol of *p*-methoxyphenol as a radical inhibitor in CD_3CN (0.3 mL) was heated under argon at 150 °C for 22 h. Figure 1a shows the ^1H NMR spectrum of the copolymerization mixture in CD_3CN before workup, in which the two monomers are almost completely reacted. Two peaks at δ −0.03 and 0.13 due to the different trimethylsilyl groups were observed. This result indicates that two kinds of polymer units exist. The assignments of other peaks are shown in Figure 1a. The peaks in the ^{13}C NMR spectrum are assigned as follows (Figure 1b): peak j at around δ 0.0 due to $Si(CH_3)_3$, a doublet peak i at δ 25.6 (J_{cp} = 24.27 Hz) due to $PCH_2CHC{=}O$, peak h at δ 27–31 due to CCH_2C, a doublet peak g at δ 30.7 (J_{cp} = 41.8 Hz) due to $PCH_2CH{=}C$, a doublet peak f at δ 35.2 (J_{ccp} = 23.8 Hz) due to $PCH_2CHC{=}O$, peak e at δ 59–63 due to OCH_2, a doublet peak d at δ 68.8 (J_{ccp} = 1.5 Hz) due to $PCCH{=}COSi$, peak c at δ 129–133 due to aromatic carbons, a peak b at δ 142.0 due to $CH{=}COSi$, and peak a at δ 171–173 due to carbonyl carbons. These observations show that the copolymer consists of two units, **5a** and **5b**, where the former was formed by the trimethylsilyl group-transfer process and the latter was afforded without the group-transfer process. The unit ratio of **5a** to **5b** was calculated as 51:49 based on the integral ratio of the ^1H NMR peaks due to trimethylsilyl groups.

Then, the reaction mixture was poured into a large amount of diethyl ether–*n*-hexane (2:5) to precipitate the copolymer, which was isolated by decantation and dried in vacuo to give 0.121 g (61% yield) of the isolated copolymer **6**. During the workup and isolation procedures, hydrolysis of copolymer **5** took place; labile trimethylsilyl groups were cleaved off. Figure 2a shows the ^1H NMR spectrum ($CDCl_3$) of **6**. The peaks at δ −0.03 and 0.13 due to a trimethylsilyl group and at δ 3.57 due to a $CH{=}C$ of unit **5a** in Figure 1a completely disappeared, whereas the peak at δ 7.19 due to an OH group appeared, and the peak at δ 2.57 due to $CH_2C{=}O$ increased compared with that in Figure 1a. These results show that units **5a** and **5b** were converted into units **6a** and **6b**, respectively, by hydrolysis with moisture. By comparison of the integral value



of peaks a and c in the ^1H NMR spectrum (Figure 2a), the content of monomers **1** and **4** in **6** was calculated to be 50%. In the ^{13}C NMR spectrum of the isolated copolymer (Figure 2b), the peaks j, g, d, and b, observed in Figure 1b, due to the ketene silyl acetal group and the silyl ester group disappeared completely and a new peak e at δ 33.4 due to $PCH_2CH_2C{=}O$ in the unit **6a** appeared. These data also support the occurrence of the hydrolysis of the ketene silylacetal and silyl ester groups and two unit structures of the alternating copolymer, **6a** and **6b**, respectively.

The ^{31}P NMR spectrum of the isolated copolymer in $CDCl_3$ showed a singlet peak at δ +43.3 (relative to H_3PO_4 external standard). The peak is reasonably assigned to the phosphinate unit of the copolymer **6**.

The copolymerization of **1** with **4** was performed under various conditions (Table I). The copolymerization took

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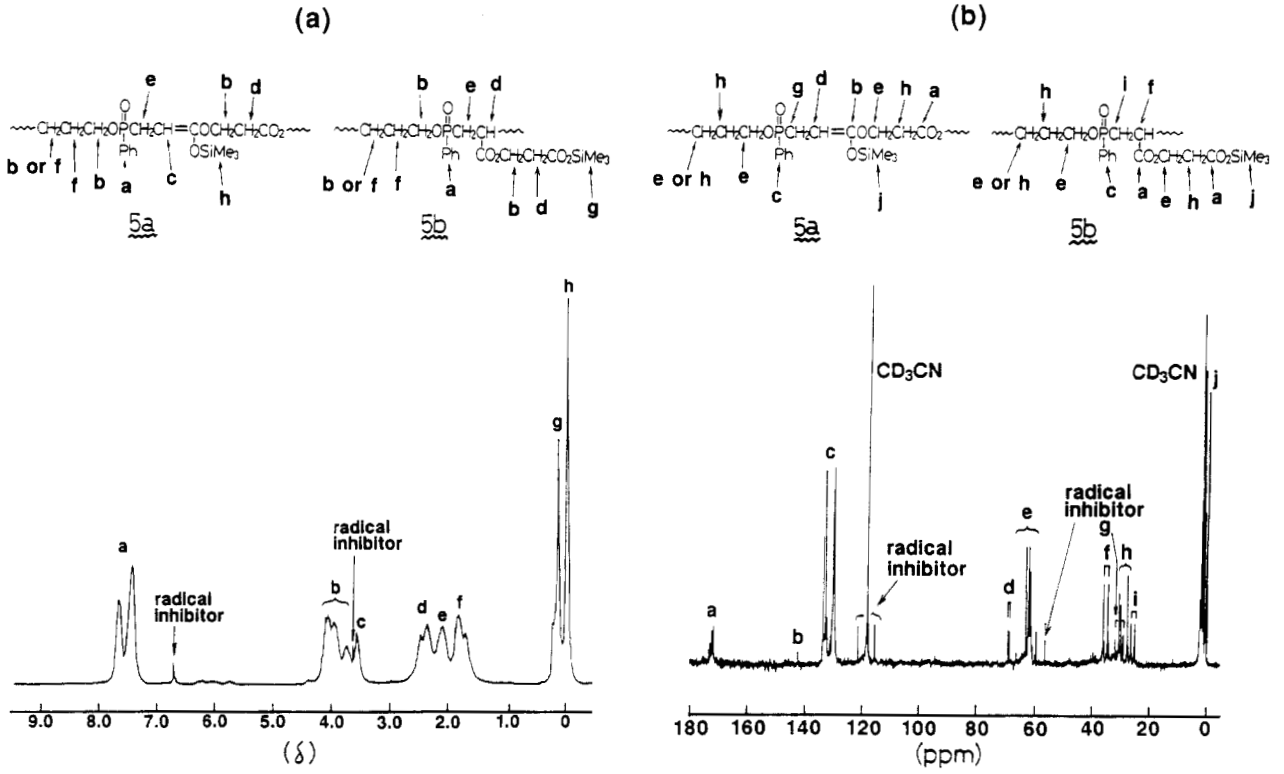


Figure 1. ^1H (250-MHz) (a) and ^{13}C (62.8-MHz) (b) NMR spectra of the copolymerization system of **1** with **4** in CD_3CN after heating 150 °C for 22 h.

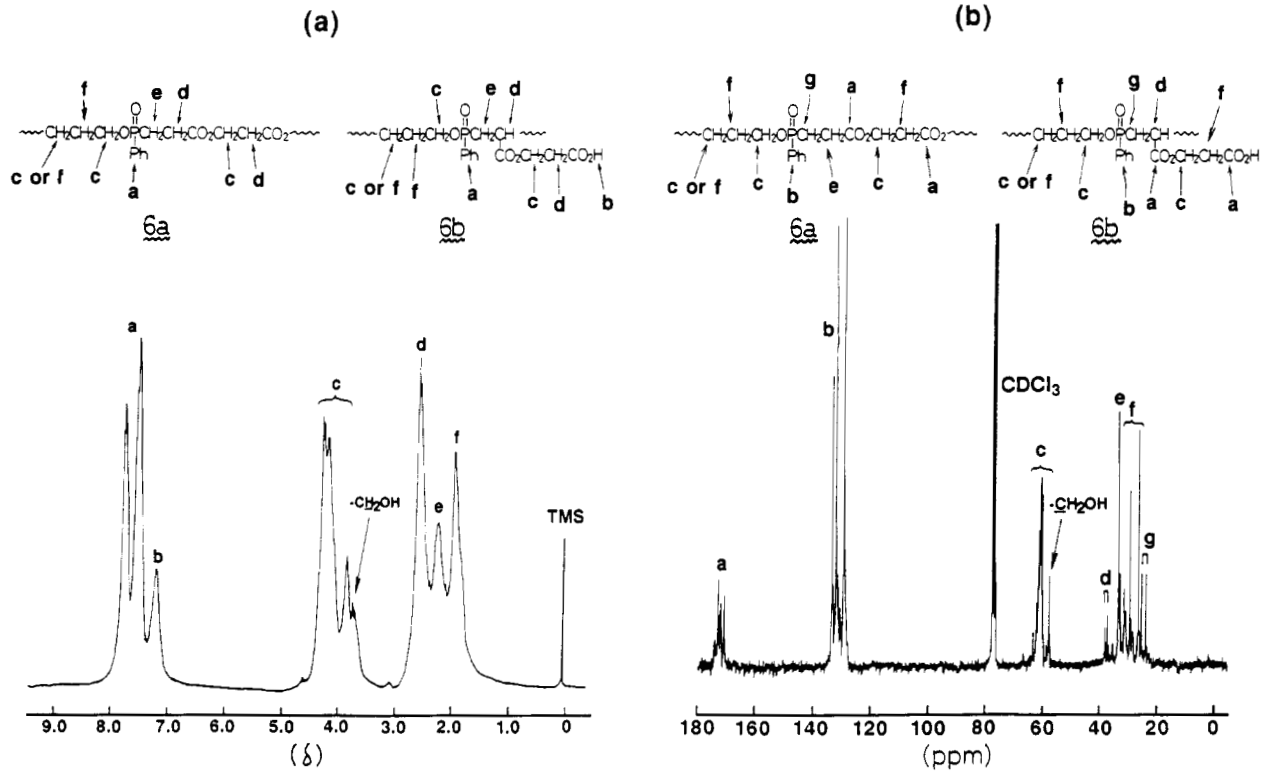


Figure 2. ^1H (250-MHz) (a) and ^{13}C (62.8-MHz) (b) NMR spectra of copolymer **6** in $CDCl_3$.

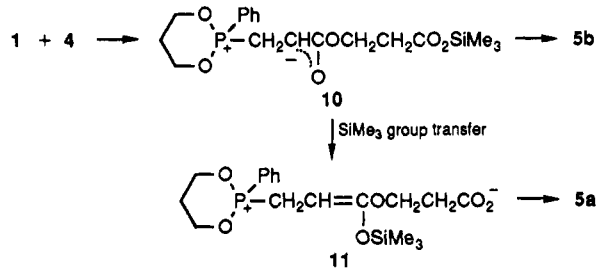
place even at 35 °C (entry 7). Although the monomer conversions were always quantitative, isolated copolymer yields were not quantitative. This indicates that the relatively lower molecular weight polymer was lost during a reprecipitation procedure. The molecular weight of the copolymer produced in polar solvents such as *N*,*N*-dimethylformamide (DMF) or hexamethylphosphoric triamide (HMPA) was higher compared to that formed in less polar solvents such as benzene or chloroform. The highest molecular weight, 3000, was observed in a DMF–HMPA (1:1) mixed solvent (entry 9). In all cases, however, the molecular weight of the copolymers was not so high. This is probably due to the lower reactivity of the anionic site of the zwitterion species. In the copolymerizations of a cyclic phosphonite with acrylic acid and with methyl acrylate, an alternating copolymer of low molecular weight was also produced, in which the structure of the anionic sites in the zwitterions of the copolymerizations is similar

Table I
Group-Transfer Alternating Copolymerization of 1 with 4[a]

entry	solv	temp, °C	time, h	yield,[b] %	mol wt[c]	m:n[d]
1	C_6H_6	120	49	49[e]	1200	19:81
2	$CDCl_3$	120	63	63[e]	1000	24:76
3	CD_3CN	120	17	69	1100	30:70
4	CD_3CN	150	22	61	1100	51:49
5	DMF	120	17	74	2200	43:57
6	HMPA	120	17	89	1800	40:60
7	DMF-HMPA[f]	35	19	57	1400	30:70
8	DMF-HMPA[f]	60	19	61	1700	33:67
9	DMF-HMPA[f]	120	17	93	3000	53:47

[a] Each monomer (0.5 mmol) in 0.3 mL of solvent. [b] Diethyl ether–*n*-hexane (2:5 in volume) insoluble part. [c] Determined by gel permeation chromatography using a Gelpack GL-A130 column with chloroform eluent at a flow rate of 1.0 mL/min at 40 °C. The calibration curves were obtained by using polystyrene standards. [d] Determined by ^1H NMR. [e] *n*-Hexane insoluble part. [f] Mixture of 1:1 in volume.

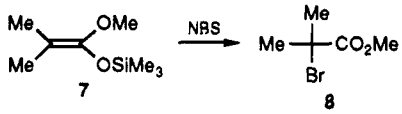
Scheme I



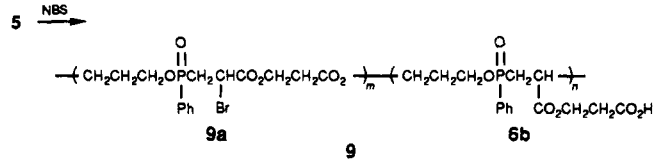
to those of the present copolymerization.[4,5]

The extent of the group transfer was higher in polar solvents as well as in DMF–HMPA mixed solvent (entries 5, 6, and 9) than in less polar solvents (entries 1–3). The extent was highest, 53%, in a DMF–HMPA mixed solvent at 120 °C (entry 9). It also depends on the reaction temperature. In a DMF–HMPA mixed solvent it increased with increasing temperature (entries 7–9). The same tendency was observed in CD_3CN (entries 3 and 4).

Bromination of the silyl enol ether groups using *N*-bromosuccinimide (NBS) has been reported.[6] Therefore, methyl trimethylsilyl dimethylketene acetal **7** was used as a model compound for unit **5a**, and its bromination by NBS was carried out. It has been found that α-bromo ester **8** was produced in a good yield (79%). In order to



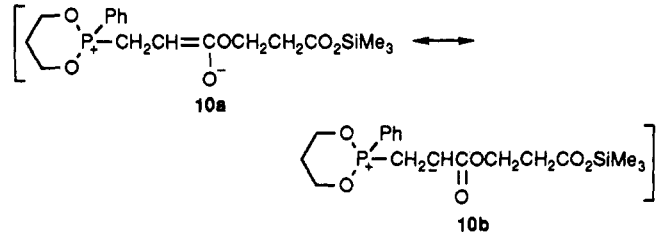
confirm the copolymer structure **5**, it was brominated with NBS. To a solution of NBS (0.39 g, 2.2 mmol) in 1.0 mL of CH_3CN was added at room temperature a reaction mixture from the copolymerization of 2 mmol of each monomer in 1.0 mL of CH_3CN at 150 °C for 22 h (**5a**/**5b** = 51/49). After stirring for 1.5 h, the mixture was poured into a large amount of diethyl ether to precipitate the product. The copolymer was isolated by decantation and dried in vacuo to give 0.616 g (89% yield). In the ^1H NMR spectrum of the copolymer, the peaks due to the ketene silyl acetal group in the unit **5a** disappeared, whereas a new peak due to CHBr at δ 3.44 appeared. The ^{13}C NMR spectrum also showed the disappearence of the peaks due to the ketene silyl acetal group and the appearance of the peak due to CHBr at δ 53.4. The disappearance of the peaks due to the trimethylsilyl group in the unit **5b** was also observed in both ^1H and ^{13}C NMR spectra. These spectroscopic data indicate that the bromination of the ketene silyl acetal group as well as the hydrolysis of the trimethylsilyl ester group took place to produce the copolymer **9**, which has two kinds of the units **9a** and **6b**. The result of the elemental analysis supports the



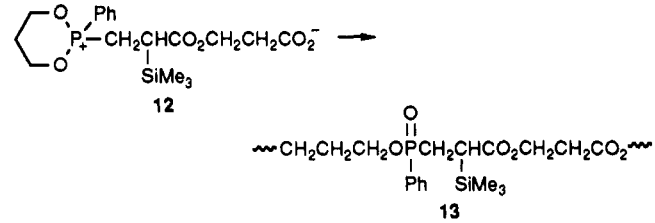
copolymer structure of **9**. Anal. Calcd for $(C_{15}H_{18}O_6PBr)_{0.51}(C_{15}H_{19}O_6P)_{0.49}\cdot 0.5H_2O$: C, 47.96; H, 5.20; Br, 10.87. Found: C, 47.20; H, 4.95; Br, 11.82.

On the basis of the above data, the zwitterion mechanism is proposed to explain the course of the present alternating copolymerization (Scheme I). The first step is the formation of a zwitterion **10** by the Michael-type addition of **1** to **4**. Then, a part of **10** is converted into a zwitterion **11** by trimethylsilyl group transfer to the enolate anion site in **10**. The next step is the reaction between two molecules of **10** and/or **11**, in which the phosphonium ring of **10** and/or **11** is opened by a nucleophilic attack of the anion of another molecule **10** and/or **11** according to an Arbuzov-type reaction. The propagation proceeds via the successive attack of **10** and/or **11** onto dimeric zwitterions, leading to alternating units **5a** or **5b**, respectively.

In the copolymerization, the enolate anion in **10** is of an ambident nature, having an anion site at oxygen (**10a**) and at carbon (**10b**). Therefore, there are two possibilities

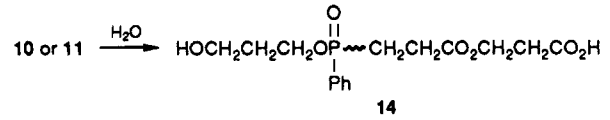


for the structure of the zwitterion derived from **10** via the trimethylsilyl group-transfer process: the ketene silyl acetal structure **11** and the ester structure **12**, which leads to the alternating unit **13**. However, no detection of a



$CSiMe_3$ group in the product copolymer excludes the possibility of unit structure **13**; the group-transfer process took place exclusively through **10a** to give the zwitterion **11** in a regiospecific manner.

As to the terminal groups on the isolated copolymer, alcohol and carboxylic acid structures are probably present, the former due to hydrolysis of the phosphonium ring and the latter coming from proton abstraction by the carboxylate or enolate anion group during the isolation process as given by **14**. The shoulder signal at δ 3.72 in the ^1H NMR and a small signal at δ 57.7 in the ^{13}C NMR spectra (Figure 2) support the terminal methylene group $HOCH_2^-$. In addition, the strong absorption at 3200–3400 cm^{-1} in



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the IR spectrum of the copolymer supports the presence of the terminal OH groups.

In conclusion, the present study provides the first example of copolymerization involving a group-transfer process, which belongs to a new class of reaction in polymerization chemistry.

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References and Notes

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