

## NOTES

## Simultaneous Construction of Polymer Backbone and Arbitrary Amounts of Allyl Side Chains by Three-Component Polycondensation of Dialdehyde, Trialkylsilane, and Allylsilane

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There are two general approaches to the preparation of functional polymers.<sup>1</sup> In one approach the required functional group is attached to a readily available polymer by an appropriate reaction. The second approach is to synthesize an appropriate monomer with the desired functional group and then polymerize or copolymerize the monomer. The second approach is generally achieved by polymerization of vinyl monomers, and polycondensation has been rarely applied for this purpose except for some examples.<sup>2–4</sup>

In recent papers<sup>5</sup> we described a novel approach to synthesis of functional polymers by polycondensation, which simultaneously constructs both polymer backbone and functional side chains<sup>6</sup> such as the allyl groups and cyano groups from dialdehydes, diol disilyl ethers, and silyl nucleophiles (Scheme 1). This approach awoke our further interest in whether the diol disilyl ethers in the above polycondensation could be replaced with trialkylsilanes, because the silyl ether groups are formed *in situ* by the reaction of the formyl group with trialkylsilanes.<sup>7</sup> In addition, the amount of functional side chains could be arbitrarily controlled by changing the feed ratios of trialkylsilanes to the silyl nucleophiles, if the reactivity of trialkylsilanes toward the formyl group was not so different from that of the silyl nucleophiles. This paper reports the three-component polycondensation of dialdehyde (**1**), triethylsilane (**2**), and allyltrimethylsilane (**3**) in the presence of a catalytic amount of triphenyl

(trityl) perchlorate at various feed ratios, yielding polyethers with arbitrary amounts of the allyl side chains according to the feed ratios of **2** to **3** in one step (Scheme 1).

### EXPERIMENTAL

#### *Model Reaction*

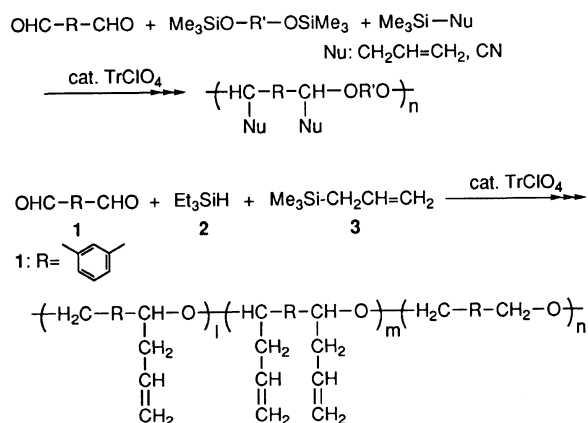
A round bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (0.034 g, 0.1 mmol) and purged with argon. After the addition of dry CH<sub>2</sub>Cl<sub>2</sub> (1 mL), the flask was cooled to –78°C, and a solution of benzaldehyde (0.212 g, 2.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL) was added. After 5 min, a solution of **3** (0.137 g, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) and solution of **2** (0.116 g, 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) were successively added, and the mixture was stirred at –78°C for 2 h. The reaction mixture was quenched with aqueous NaHCO<sub>3</sub> and extracted with ether. The ether layer was washed with water and dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude product was purified with column chromatography on silica gel and a preparative HPLC to yield **4**<sup>7b</sup> (31% yield), **5** (23% yield), and **6** (27% yield).

$\alpha$ -Allylbenzyl ether **5**: IR (neat) 1641, 1082 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.44–7.21 (m, 10H), 5.89–5.69 (m, 1H), 5.26–4.98 (m, 2H), 4.50–4.23 (m, 3H), 2.71–2.36 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  141.9, 138.6, 134.9, 116.9, 81.3, 76.5, 42.7.

$\alpha,\alpha'$ -Diallylbenzyl ether **6**: IR (neat) 1641, 1083 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.38–7.15 (m, 10H), 5.88–5.57 (m, 2H), 5.06–4.87 (m, 4H), 4.43 and 4.10 (2t, *J* = 6.2 Hz, 2H), 2.65–2.26 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  142.4, 142.1, 135.0, 134.8, 128.3, 128.1, 127.6, 127.2, 126.8, 117.1, 116.8, 79.4, 78.3, 42.9, 41.7.

#### *Three-Component Polycondensation of 1, 2, and 3*

A round bottomed-flask equipped with a three-way stopcock was charged with trityl perchlorate (0.017 g, 0.05 mmol) and purged with argon. After the addition of dry CH<sub>2</sub>Cl<sub>2</sub> (0.4 mL), the flask was cooled to –20°C, and a solution of **1** (0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) was added slowly *via* a syringe. After 5 min of stirring, a solution of **2** and **3** (total 1.0 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.3 mL) was added, and the reaction mixture was stirred for 1 h at –20°C. The polymerization was terminated with



Scheme 1.

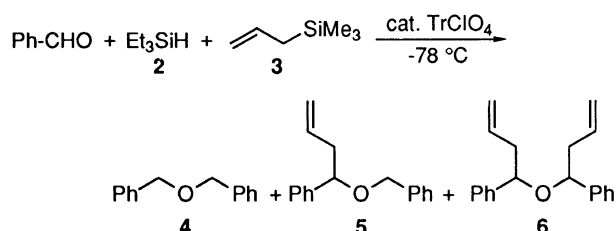
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ammoniacal methanol at  $-20^{\circ}\text{C}$ , and the solution was poured into excess of hexane (20 mL). After centrifugation, the polymer was collected and dried *in vacuo*: IR (neat)  $1641, 1101\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.60–7.00 (m), 5.96–5.60 (br), 5.28–4.85 (br), 4.85–4.20 (br), 2.65–2.26 (br).

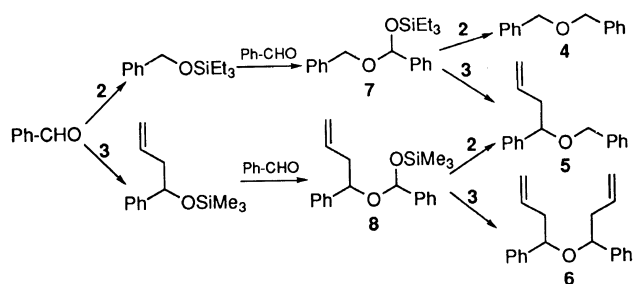
## RESULTS AND DISCUSSION

### Model Reaction

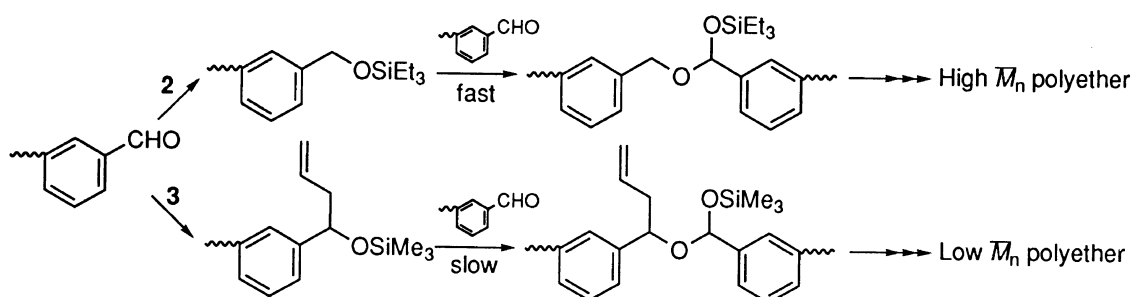
To estimate the relative reactivities of **2** and **3** toward the formyl group, a model reaction was carried out using a monofunctional aldehyde. Benzaldehyde was reacted with **2** and **3** in the presence of 5 mol% of trityl perchlorate in  $\text{CH}_2\text{Cl}_2$  at  $-78^{\circ}\text{C}$  for 2 h to yield benzyl ether (**4**),  $\alpha$ -allylbenzyl ether (**5**), and  $\alpha, \alpha'$ -diallylbenzyl ether (**6**) in 31, 23, and 27% yield, respectively.



The reaction mechanism is considered that shown in Scheme 2 based on the proposed mechanism of etherification<sup>8</sup> and allylation<sup>9</sup> of aldehydes in organic chemistry. Triethylsilane **2** reacts with 2 equiv of benzaldehyde to give hemiacetal-type intermediate **7** via benzyl silyl ether. Similarly **3** reacts with 2 equiv of the aldehyde to give allylated hemiacetal-type intermediate **8**. Intermediate **7** undergoes substitution reaction with **2** to yield **4**, and **8** undergoes similar reaction with **3** to yield **6**. Monoallylated ether **5** is formed by the reaction of **7** with **3** or of **8** with **2**. The production of **4** in slightly preference to **6** implies that the reactivity of triethylsilane **2** toward the formyl group is slightly higher than that



Scheme 2.



Scheme 3.

of allylsilane **3**. The production of the reduced and allylated ethers in the model reaction shows that the desired three-component polycondensation of **1**, **2**, and **3** takes place.

### Three-Component Polycondensation

Three-component polycondensations of isophthalaldehyde (**1**), **2**, and **3** were carried out with 10 mol% of trityl perchlorate at  $-20^{\circ}\text{C}$  for 1 h at various feed ratios of **2** to **3**. The two-component polycondensations of **1** with **2** or with **3** were carried out under the same conditions as control experiments (Table I). The IR spectra of the polymers showed characteristic absorptions of a carbon-carbon double bond at  $1641\text{ cm}^{-1}$  and of an ether linkage at  $1101\text{ cm}^{-1}$ . The  $^1\text{H NMR}$  spectra of the polymers were in fair agreement with those of **4**, **5**, and **6** obtained in the model reaction. These spectra of the polymers are consistent with the structures of the polyethers with the allyl side chains. The ratios of signal areas for the vinyl protons of the allyl groups were used to calculate the content of the allyl groups in the polymers.

The allyl groups could be introduced at 8 to 50 mol% according to the feed ratios of **3** in **2** and **3** from 10 to 80 mol%, indicating that the content of the allyl groups in the polymer was arbitrarily controlled up to 50 mol%. However, the molecular weights of the polymers dramatically decreased when the feed ratios were 20–80 mol%. The two-component polycondensation of **1** with **3** gave a polymer with the lowest molecular weight in Table I.

The decrease in polymer molecular weight for the polycondensation of **1**, **2**, and **3** at feed ratios of **3** being more than 20 mol% may be due to the production

Table I. Three-component polycondensation of **1**, **2**, and **3**<sup>a</sup>

Feed molar ratio	Yield <sup>b</sup>	$\bar{M}_n$ <sup>c</sup>	Allyl content <sup>d</sup>
<b>2</b> : <b>3</b>	%		mol%
10 : 0	56 <sup>e</sup>	10200	0
9 : 1	56 <sup>e</sup>	15500	8
8 : 2	59	2800	17
7 : 3	62	2400	25
5 : 5	45	2600	33
2 : 8	10	4000	50
0 : 10	11	1300	100

<sup>a</sup> Polymerization was carried out with 10 mol% of  $\text{TrClO}_4$  in  $\text{CH}_2\text{Cl}_2$  ( $[\text{1}]_0 = 0.5\text{ M}$ ,  $[\text{2} + \text{3}]_0 = 1.0\text{ M}$ ) at  $-20^{\circ}\text{C}$  for 1 h. <sup>b</sup> Polymer insoluble in hexane. <sup>c</sup> Estimated by GPC with solvent DMF (based on polystyrene standards). <sup>d</sup> Estimated by  $^1\text{H NMR}$ . <sup>e</sup> Polymer insoluble in diethyl ether.

of a secondary silyl ether by the reaction of the formyl group with **3** resulting in slow propagation and probable undesired reduction of the formyl group with **2** (Scheme 3). In practice, low molecular weight polyethers are obtained in the three-component polycondensation of **1**, **3**, and secondary diol disilyl ethers, contrary to primary diol disilyl ethers.<sup>5</sup> When the feed ratio of **3** is less than 10 mol%, the formyl group is considered to predominantly react with **2** to yield a primary silyl ether, which leads to the hemiacetal-type intermediate, followed by the reaction of **2** or **3** to yield the high molecular weight polyether with the allyl side chains. The slightly higher reactivity of **2** toward the formyl group than **3** was also shown in the model reaction.

## REFERENCES

- (a) N. K. Mathur and R. E. Williams, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C15**, 117 (1976). (b) G. Manecke and P. Reuter, *Pure Appl. Chem.*, **51**, 2313 (1979). (c) W. H. Daly, *Makromol. Chem., Suppl.*, **2**, 3 (1979). (d) G. Manecke and W. Storck, *Angew. Chem. Int. Ed. Engl.*, **17**, 657 (1978). (e) W. Heitz, *Adv. Polym. Sci.*, **23**, 1 (1977). (f) Y. Chauvin, D. Commereuc, and F. Dawans, *Prog. Polym. Sci.*, **5**, 95 (1977). (g) P. Hodge, *Chem. Br.*, **14**, 237 (1978). (h) D. C. Neckers, *Chem. Technol.*, 108 (1978). (i) O. Vogel, *Pure Appl. Chem.*, **51**, 2409 (1979).
- For example of chemoselective polyamidation: (a) Y. Iwakura, S. Izawa, F. Hayano, and K. Kurita, *Makromol. Chem.*, **104**, 66 (1967). (b) K. Sanui and N. Ogata, *J. Polym. Sci., Polym. Chem. Ed.*, **7**, 889 (1969). (c) M. Ueda, A. Kameyama, and K. Hashimoto, *Macromolecules*, **21**, 19 (1988). (d) M. Ueda, T. Morozumi, M. Kakuta, and R. Sato, *Polym. J.*, **22**, 733 (1990).
- For example of chemoselective polyesterification: (a) C. Wang and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 413 (1994). (b) C. Wang and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 1255 (1994). (c) C. Wang and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 2027 (1995). (d) C. Wang and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **33**, 2157 (1995). (e) C. Wang and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 493 (1996). (f) C. Wang, T. Takayama, and S. Nakamura, *J. Polym. Sci., Polym. Chem. Ed.*, **34**, 755 (1996).
- For example of chemoselective polyimidation: K. Iwakura, K. Kurita, and F. Hayano, *J. Polym. Sci., Polym. Chem. Ed.*, **7**, 609 (1969).
- (a) T. Yokozawa and K. Takenoya, *Macromolecules*, **29**, 497 (1996). (b) T. Yokozawa and K. Takenoya, *Reactive and Functional Polym.*, **30**, 251 (1996).
- For other examples of simultaneous construction of polymer backbone and side chains by terpolymerization, see: (a) D. H. Suh, J. C. Won, D. K. Kim, and J. C. Jung, *J. Polym. Sci., Polym. Lett. Ed.*, **26**, 83 (1988). (b) N. Miyaki, I. Tomita, and T. Endo, *Polym. Prep., Jpn.*, **42**, 493, 1962 (1993).
- (a) T. Yokozawa and F. Nakamura, *Makromol. Chem., Rapid Commun.*, **14**, 167 (1993). (b) T. Yokozawa and F. Nakamura, *Macromolecules*, **28**, 4668 (1995).
- J. Kato, N. Iwasawa, and T. Mukaiyama, *Chem. Lett.*, 743 (1985).
- T. Mukaiyama, M. Ohshima, and N. Miyoshi, *Chem. Lett.*, 1121 (1987).