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Simultaneous Construction of Polymer Backbone and Side Chains by Terpolymerization. Synthesis of Polyethers with Functional Side Chains from Dialdehydes, Alkylene Bis(trimethylsilyl) Ethers, and Trimethylsilyl Nucleophiles

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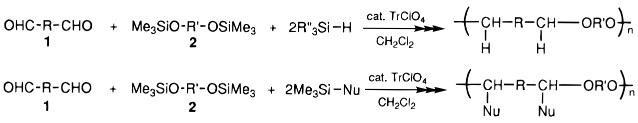
Polymers with functional groups in the side chains are usually synthesized by two alternative methods, the first one based on the polymer reaction with functional reagents, the second one on the polymerization of monomers with a functional group in the side chain. However, there is no synthetic method for these functional polymers that simultaneously constructs both polymer backbone and functional side chains from three monomers except for Suh's and Endo's works. Suh and Jung[1] have reported the synthesis of poly(thioacetal) containing the dicyanomethylidene groups in the side chains by the reaction of xylylene dichloride, carbon disulfide, and malononitrile in the presence of sodium hydroxide. Endo and Tomita[2] have prepared polyhydrocarbons containing malonic ester structures in the side chains by the reaction of diallenes, aromatic dihalides, and sodium diethyl malonate in the presence of Pd(0) catalyst. However, the structures of these polymers seem to be peculiar and do not contain general backbones such as polyether, polyester, polyamide, etc. and general functional groups such as ester, cyano, vinyl, etc., either. Furthermore, they have not proposed exactly the concept of simultaneous construction of polymer backbone and side chains.

We have recently reported the reductive polycondensation that yields polyethers from dialdehydes (**1**), alkylene bis(trimethylsilyl) ethers (**2**), and trialkylsilane.[3] The fact that nucleophilic hydrides were introduced to the polyether from trialkylsilanes suggests the possibility of introduction of a variety of functional groups into the polymer side chains by using silyl nucleophiles such as allylsilane,[4] silyl cyanide, and ketene silyl acetal, etc. instead of trialkylsilane. Therefore, the reaction of **1**, **2**, and the silyl nucleophile will produce simultaneously both the polyether backbone from **1** and **2** and the functional side chains from the silyl nucleophile (Scheme 1). Herein we wish to report the synthesis of polyethers with the allyl or cyano groups in the side chains by the simultaneous reactions of **1**, **2**, and allyltrimethylsilane (**3**) or cyanotrimethylsilane (**4**), respectively, in the presence of a catalytic amount of triphenylmethyl (trityl) perchlorate.

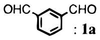
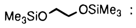
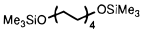
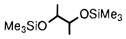
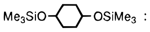
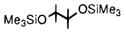
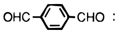
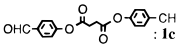
The reaction of **1**−**3** was carried out in the presence of 10 mol % trityl perchlorate in dichloromethane, similarly to the reductive polycondensation reported previously.[3] In the polymerization at ambient temperature, the polymer was precipitated during reaction, whereas the polymerization below 0 °C proceeded homogeneously even after 24 h. The results of the polymerization of a variety of **1**−**3** at −55 °C are summarized in Table 1.[5] The polymer molecular weights decreased in the order primary, secondary, and tertiary **2** except for 1,4-bis(trimethylsiloxy)cyclohexane (**2b**) in the reaction of isophthalaldehyde (**1a**), **2**, and **3**. The reactions of other aldehydes with ethylene bis(trimethylsilyl) ether (**2a**) or **2b** yielded also high molecular weight polymers. Of aldehydes, **1c** having weak electron-withdrawing groups gave better results, in analogy with the reductive polycondensation.[3]

Scheme 1



3: Nu = $CH_2CH{=}CH_2$
4: Nu = CN

Table 1. Terpolymerization of 1−3

1	**2**	yield, %[a]	$\overline{M}n$[b]	polymer content[c] **1 : 2 : 3**
 : **1a**	 : **2a**	0 (100)[d]	10400	28:24:48
1a		55	5200	25:25:50
1a		0 (100)[d]	2600	27:24:49
1a	 : **2b**	63	9500	25:25:50
1a		0 (100)[d]	1600	24:24:52
 : **1b**	**2a**	25	13400	27:19:54
1b	**2b**	80	8300	25:25:50
 : **1c**	**2a**	64	19500	26:22:52
1c	**2b**	98	22000	25:25:50

The polymerization was carried out with 10 mol% of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1}]_0=[\mathbf{2}]_0=0.50$ M, $[\mathbf{3}]_0=1.0$ M) at -55 °C for 48 h. [a] Polymer insoluble in MeOH. [b] Estimated by GPC based on polystyrene standards in DMF. [c] Estimated by ^{1}H NMR. [d] Polymer soluble in MeOH.

IR spectra of the polymers showed the characteristic absorption of a carbon−carbon double bond at 1641−1644 cm^{-1} and of an ether linkage at 1074−1104 cm^{-1}. An absorption of a carbonyl group around 1700 cm^{-1} was not observed. ^{1}H NMR spectra of the polymers showed the two signals of vinyl protons at δ 6.33−5.37 and 5.33−4.60 with the intensity ratio 1:2, the signal corresponding to the allyl methylene protons at δ 2.97−2.10, the signal assignable to the benzylmethine proton on a carbon atom of an ether linkage at δ 4.57−4.13, and the signals of the aromatic protons and the aliphatic protons of **2**, respectively. The intensity ratios of the signals derived from **1**−**3** were 1:1:2. Consequently, these spectra are compatible with the polymer structure as shown in Scheme 1, and the elemental analysis was also in good agreement with this structure.[6]

In the reaction of **1**, **2**, and **4**, the way of addition of reagents dramatically affected the polymer formation, in contrast to the reaction of **1**−**3**.[7] Thus, the addition of **4** into the mixture of **1**, **2**, and trityl perchlorate yielded the polymer, whereas the addition of **1** into the mixture of **2**, **4**, and the catalyst did not afford the polymer at all. Accordingly, the reactions were carried out with the former way of addition (Table 2).[8] The polymerization proceeded homogeneously even at room temperature, contrary to the polymerization using **3**, and the molecular weight of the polymer obtained at ambient temperature was higher than that below 0 °C. Secondary **2** resulted in low molecular weight polymers, and further short carbon-chain primary **2** also gave similar results. When hexyl or octyl disilyl ethers were used, the polymers with the molecular weights being higher than 10 000 were obtained.

In the IR spectra of the polymers obtained, absorptions of a cyano group at 2260−2248 cm^{-1} and of an ether linkage at 1086−1071 cm^{-1} were observed, respectively. The ^{1}H NMR spectra showed the signal assignable to the benzylmethine proton on a carbon between the cyano group and the ether linkage at δ 5.30−5.27, which appeared at a field lower than that

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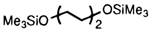
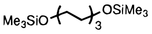
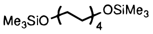
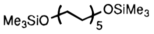
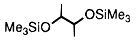
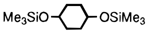
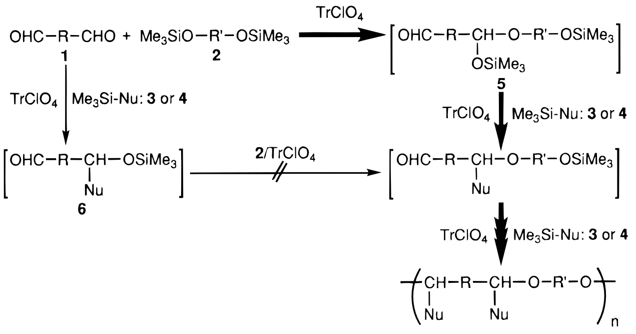
Table 2. Terpolymerization of 1a, 2, and 4

2	temp, °C	yield, %[a]	$\overline{M}n$[b]	polymer content[c] **1a** : **2** : **4**
	25	0 (100)[d]	1800	*e*
	25	6	3100	25:25:50
	25	40	12000	25:25:50
	-23	11	7800	25:25:50
	0	38	12000	25:25:50
	25	38	13000	25:25:50
	25	6	7000	25:25:50
	25	0 (100)[d]	1500	*e*
	25	0 (80)[d]	2200	*e*

The polymerization was carried out with 10 mol% of $TrClO_4$ in CH_2Cl_2 ($[\mathbf{1a}]_0=[\mathbf{2}]_0=0.33$ M, $[\mathbf{4}]_0=0.66$ M) for 24 h. [a] Polymer insoluble in MeOH. [b] Estimated by GPC based on polystyrene standards in DMF. [c] Estimated by ^1H NMR. [d] Polymer soluble in MeOH. [e] Not determined.

Scheme 2



in the allyl-substituted polyether described above, and the signals of the aromatic protons of **1** and the aliphatic protons of **2**. Baed on the signal intensities of aromatic protons, aliphatic protons, and the cyano group-substituted methine protons, the molar ratios of **1**:**2**:**4** were 1:1:2.[9] The spectra of the polymers are consistent with the structure in Scheme 1.

The polymerization process is considered in the following way, as shown in Scheme 2, according to the proposed mechanism in organic chemistry.[4a] The aldehyde **1** reacts with the silyl ether **2** to give a hemiacetal-type compound **5**, which is subjected to the attack of the silyl nucleophile **3** or **4** accompanied by the elimination of hexamethyldisiloxane to form both the carbon–oxygen and the carbon–nucleophile bonds. In both steps, the trityl cation activates the formyl group and the hemiacetal moiety, respectively. The observed difference in the effect of the manner of monomer addition on the polymer formation is accounted for by the respective reactivities of **2**–**4** toward **1**. On the basis of the model reactions with monofunctional compounds,[10] the reactivities were found to decrease in the order **4** > **2** > **3**. Accordingly, in the polymerization of **1**–**3**, the polymers were obtained by any addition method, because **2** reacts with **1** faster than **3**, even in the presence of many **3**, to give the polymerization intermediate **5**. In the polymerization of **1**, **2**, and **4**, however, **1** would react with **4** faster than **2** when **1** was added to the mixture of **2** and **4** to form a cynohydrine-type compound **6**,[11] which no longer reacts with **2** and does not yield polymer.

In order to demonstrate the function of the polyether having the allyl groups in the side chains, the cross-linking of the polymer obtained from **1a**, **2b**, and **3** was carried out. The polymer was heated at 80 °C in bulk for 48 h to give a cross-linked polymer in 33% yield. Addition of 4 mol % azobis(isobutyronitrile) (AIBN) as a radical initiator and heating in benzene at 60 °C for 40 h resulted in the production of the cross-linked polymer in 50% yield. Furthermore, when the polymer was treated with ethanedithiol equimolar to the allyl groups in the polymer and 4 mol % AIBN in benzene at 60 °C, the cross-linked polymer was obtained in 95% yield even in 1 h. Since the absorption of a carbon–carbon double bond of the polymer at 1641 cm^{-1} became weak in the IR spectrum of the cross-linked polymer, the radical addition of the thiol groups in ethanedithiol to the allyl groups in the polymer would take place to yield the cross-linked polymer.

In summary, we are confident that examples of these terpolymerizations of **1**, **2**, and **3** or **4** will render considerable impulse to the conventional synthetic method for polymers with functional side chains. This system is unusual in that it simultaneously constructs both polymer backbone and functional side chains from three monomers. Furthermore, a broad variety of functional groups would be introduced to polyethers as side chains by using many well-known silyl nucleophiles in this system. Experiments along these lines are in progress.

References and Notes

(1) Suh, D. H.; Won, J. C.; Kim, D. K.; Jung, J. C. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 83.
(2) Miyaki, N.; Tomita, I.; Endo, T. *Polym. Prepr. Jpn.* **1993**, *42*, 493, 1962.
(3) (a) Yokozawa, T.; Nakamura, F. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 167. (b) Yokozawa, T.; Nakamura, F. *Macromolecules* **1995**, *28*, 4668.
(4) For the preparation of homoallyl ethers by the acid-catalyzed reactions of carbonyl compounds, alkoxytrimethylsilanes, and allyltrimethylsilane, see: (a) Mukaiyama, T.; Ohshima, M.; Miyoshi, N. *Chem. Lett.* **1987**, 1121. (b) Mekhalfia, A.; Marko, I. E. *Tetrahedron Lett.* **1991**, *32*, 4779.
(5) A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (34 mg, 0.1 mmol) and purged with argon. After the addition of dry dichloromethane (0.5 mL), the flask was cooled to −55 °C, and a solution of **1** (1.0 mmol) and **2** (1.0 mmol) in dichloromethane (1.0 mL) was added slowly via a syringe. After 5 min of stirring, a solution of **3** (0.23 g, 2.0 mmol) in dichloromethane (0.5 mL) was added, and the reaction mixture was stirred for 48 h at −55 °C. The polymerization was terminated with ammoniacal methanol at −55 °C, and the solution was poured into a large amount of methanol (40 mL). The precipitated white polymer was collected and dried in vacuo.
(6) Calculated for the polymer obtained from **1a**, **2b**, and **3** ($C_{20}H_{26}O_2$): C, 80.50; H, 8.78. Found: C, 80.00; H, 8.51.
(7) Similar molecular weight polymers were obtained in the reaction of **1**–**3**, whether **3** was added to the mixture of **1**, **2**, and the catalyst or **1** was added to the mixture of **2**, **3**, and the catalyst.
(8) A round-bottomed flask equipped with a three-way stopcock was charged with trityl perchlorate (34 mg, 0.1 mmol) and purged with argon. After the addition of dry dichloromethane (1.0 mL) and after the trityl perchlorate dissolved, a solution of **1** (1.0 mmol) and **2** (1.0 mmol) in dichloromethane (1.0 mL) was added at ambient temperature via a syringe. After 5 min of stirring, a solution of **4** (0.20 g, 2.0 mmol) in dichloromethane (1.0 mL) was added, and the reaction mixture was stirred for 24 h at that temperature. The polymerization was terminated with ammoniacal methanol, and the solution was poured into a large amount of methanol (60 mL). The precipitated orange polymer was collected and dried in vacuo.
(9) When the signal intensities of the aromatic carbons, the aliphatic carbons, and the cyano carbons (δ 117.1) were measured with the ^{13}C NMR NNE mode, the molar ratio of **1**:**2**:**4** in the polymer also indicated 1:1:2.
(10) The reactions of benzaldehyde and **3** or **4** were carried out with or without methoxytrimethylsilane in the presence of trityl perchlorate, and the conversions of these compounds were measured with time by GC.
(11) The cyanohydrine-type compound obtained from benzaldehyde and **4** was ascertained to react with neither methoxytrimethylsilane nor benzaldehyde.

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