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Novel Poly(silyl enol ether)s via Radical Ring-Opening Polymerization and Their Conversion to Polyketones

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Silyl enol ethers are among the most versatile synthetic intermediates in organic syntheses.[1] Although a wide variety of functional groups can be prepared from silyl enol ethers, poly(silyl enol ether)s, which would be versatile reactive polymers, have not been synthesized. On the basis of the reactions of silyl enol ethers, a wide variety of functional polymers can be derived from poly(silyl enol ether)s. Further, hydrolysis of poly(silyl enol ether)s can afford the corresponding polyketones, which are expected to be not only reactive polymers as precursors of functional polymers but also photodegradable polymers.[2] To prepare polymers with reactive moieties in the main chain, chemoselective radical polymerization is generally appropriate. The silyl enol ether group is generally unstable under cationic and anionic polymerization conditions;[3] however, the controlled introduction of the silyl enol ether group in the main chain is difficult by the usual radical polymerization methods. Recently, we have reported radical ring-opening polymerization of unsaturated cyclic monomers such as vinylcyclopropanes, by which carbon–carbon double bonds can be introduced into the polymer main chain at controlled positions.[4] In this communication, we report the successful synthesis of poly(silyl enol ether)s *via* radical ring-opening polymerization of trimethylsiloxy-substituted vinylcyclopropanes, their hydrolysis, and a preliminary polymer reaction.

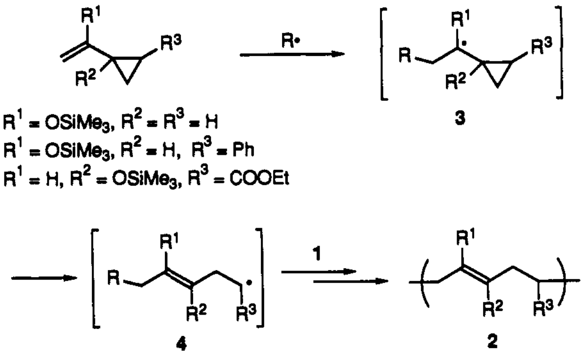
Radical polymerizations[5] of trimethylsiloxy-substituted vinylcyclopropanes **1a**,[6] **1b**,[8] and **1c**[10] were carried out under various conditions to afford the corresponding polymers **2a**,[13] **2b**,[14] and **2c**.[15] The results are summarized in Table 1. ^{1}H-NMR, ^{13}C-NMR, and IR spectra indicated that the desired poly(silyl enol ether)s were produced, and no other unit was observed in the polymers. All of the poly(silyl enol ether)s were very soluble in common organic solvents. In the case of **1a** and **1c**, yield and $\bar{M}_n$ decreased as the polymerization temperature was raised because of chain-transfer reactions. On the contrary, in the case of **1b**, yield and $\bar{M}_n$ increased as the polymerization temperature was raised because the highly stabilized terminal benzyl radical may exhibit rather low reactivity. Similar polymerization behavior has been reported in the polymerization of vinylcyclopropanes having no siloxy group.[16,17]

Table 1. Radical Polymerization of **1**[a]

monomer	initiator	temp (°C)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[b] of **2**	yield[c] (%)	$\bar{M}_n$ ($\bar{M}_w/\bar{M}_n$)[b] of **5**
1a	AIBN[f]	60	5000 (1.81)	33	*d*
1a	BPO[g]	80	2050 (1.49)	26	*d*
1a	DTBP[h]	120		*e*	*d*
1b	AIBN[f]	60	1930 (1.35)	9	1830 (1.27)
1b	BPO[g]	80		0	
1b	DTBP[h]	120	5140 (2.16)	60	5820 (1.84)
1c	AIBN[f]	60	10400 (1.97)	69	9720 (1.82)
1c	BPO[g]	80	5850 (1.64)	23	7550 (1.45)
1c	DTBP[h]	120	3520 (3.71)	43	5460 (3.33)

[a] Polymerizations were carried out in bulk for 48 h using 5 mol % of initiator. [b] Estimated by GPC (THF, based on PSt standards). [c] *n*-Hexane-insoluble part after hydrolysis. [d] Insoluble in organic solvents. [e] Only cross-linked gel. [f] 2,2′-Azobis(isobutyronitrile). [g] Benzoyl peroxide. [h] Di-*tert*-butyl peroxide.

Scheme 1



1a; $R^1 = OSiMe_3$, $R^2 = R^3 = H$
1b; $R^1 = OSiMe_3$, $R^2 = H$, $R^3 = Ph$
1c; $R^1 = H$, $R^2 = OSiMe_3$, $R^3 = COOEt$

The selective formation of poly(silyl enol ether)s can be explained by the attack of a terminal radical to the olefinic group of monomer followed by the quantitative ring-opening to reproduce the terminal radical. Since the ring-opening reaction of cyclopropylmethyl radical **3** to 3-butenyl radical **4** is very rapid,[18] radical intermediate **3** did not react with **1** at all (Scheme 1). Further, the direction of the ring-opening was completely controlled by the radical stabilizing group, *i.e.*, by the phenyl group in the case of **2b** and the ethoxycarbonyl group in the case of **2c**. Although attack of the radical species to the olefinic group in the polymer was usually observed in radical ring-opening polymerization,[17] no such side reaction was observed in the case of **2**, since trisubstituted olefins are far less reactive toward radicals than the vinyl groups in the monomers.[19]

Silyl enol ethers can be easily hydrolyzed to form the corresponding ketones.[1] Thus, hydrolyses of **2** by aqueous HCl

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(1) Brownbridge, P. *Synthesis* **1983**, *1*, 85.

(2) Hocking, P. J. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1992**, *C32*, 35.

(3) Hirao, A.; Kato, K.; Nakahama, S. *Macromolecules* **1992**, *25*, 535.

(4) Bailey, W. J.; Chen, P. Y.; Chen, S.-C.; Chiao, W.-B.; Endo, T.; Gapud, B.; Kurugant, V.; Lin, V.-N.; Nl, Z.; Pan, C.-Y.; Shaffer, S. E.; Sidney, L.; Wu, S.-R.; Yamamoto, N.; Yamazaki, N.; Yonezawa, K. *Makromol. Chem., Makromol. Symp.* **1986**, *6*, 81.

(5) A mixture of **1** and radical initiator was heated in a sealed tube for 48 h at the temperature mentioned. The polymers were separated out from the reaction mixture by preparative HPLC eluted by freshly distilled THF.

(6) **1a** was synthesized from cyclopropyl methyl ketone by treatment with lithium diisopropylamide (LDA) followed by chlorotrimethylsilane.[7]

(7) Monti, S. A.; Cowherd, F. G.; McAninch, T. W. *J. Org. Chem.* **1975**, *40*, 858.

(8) **1b** was synthesized from 1-acetyl-2-phenylcyclopropane, which was prepared by cyclopropanation of chalcone using dimethyloxosulfonium methylide,[9] by treatment with LDA followed by chlorotrimethylsilane.[7]

(9) Corey, E. J.; Chaykovsky, M. *J. Am. Chem. Soc.* **1965**, *87*, 1353.

(10) **1c** was prepared from 2-(trimethylsiloxy)butadiene[11] by selective cyclopropanation of the more electron-rich carbon–carbon double bond with ethyl diazoacetate catalyzed by cupric acetylacetate.[12]

(11) Jung, M. E.; McCombs, C. A.; Takeda, Y.; Pan, Y.-G. *J. Am. Chem. Soc.* **1981**, *103*, 6677.

(12) Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 512.

(13) ^{1}H-NMR (90 MHz, $CDCl_3$): δ 4.75–4.38 (br, 1H), 2.23–1.85 (br, 4H), 1.70–1.30 (br, 1H), 0.22 (s, 9H) ppm. ^{13}C-NMR (22.5 MHz, $CDCl_3$): δ 150.7, 150.5, 107.8, 107.0, 36.5, 27.4, 25.0, 0.65, 0.39 ppm. IR (film): 2957, 2861, 1671, 1454, 1362, 1254, 1142, 1053 cm^{-1}.

(14) ^{1}H-NMR (90 MHz, $CDCl_3$): δ 7.40–6.55 (br, 5H), 4.35–3.80 (br, 1H), 2.90–1.55 (br, 4H), 0.15 and 0.00 (s, 9H) ppm. ^{13}C-NMR (22.5 MHz, $CDCl_3$): δ 150.2, 148.7, 145.2, 127.9, 127.7, 125.7, 108.1, 107.5, 43.0, 38.3, 31.6, 0.76, 0.18 ppm. IR (film): 2957, 1667, 1603, 1493, 1453, 1362, 1252, 1150, 1009, 910 cm^{-1}.

(15) ^{1}H-NMR (90 MHz, $CDCl_3$): δ 4.60–4.30 (br, 1H), 4.12 (q ($J = 7.0$ Hz), 2H), 3.00–1.50 (br, 5H), 1.24 (t ($J = 7.0$ Hz), 3H), 0.20 (s, 9H) ppm. ^{13}C-NMR (22.5 MHz, $CDCl_3$): δ 175.0, 149.4, 106.1, 60.0, 43.3, 38.8, 28.0, 14.2, 0.59 ppm. IR (film): 2959, 2905, 1734, 1672, 1442, 1375, 1254, 1159, 1040 cm^{-1}.

(16) Cho, I.; Lee, J.-K. *Makromol. Chem., Rapid Commun.* **1984**, *5*, 263.

(17) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818.

(18) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(19) Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 5748.

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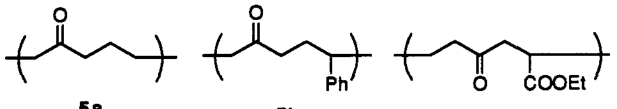
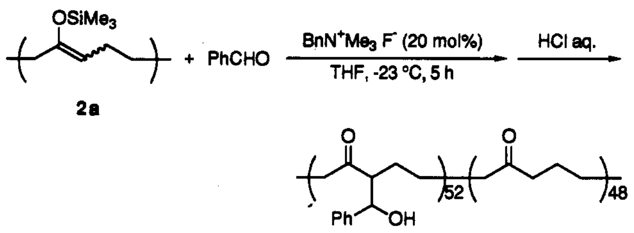
Chart 1



5a **5b** **5c**

were carried out to obtain the polyketones **5** quantitatively[20] (Chart 1). $\bar{M}_n$ of **5b** and **5c** corresponded to those of **2b** and **2c**,[21] and no signals that could not be assigned to the structures of **5a**, **5b**, and **5c** were observed in their NMR and IR spectra,[23] indicating that no side reaction such as aldol reaction occurred during the acid-catalyzed hydrolysis.

Scheme 2



A preliminary polymer reaction of **2a** with benzaldehyde catalyzed by quarternary ammonium fluoride was carried out in THF at −23 °C for 5 h.[24] After acidic hydrolysis, the desired polyketone in which 52% of the aldol group was introduced was obtained[25] (Scheme 2).

In summary, we have demonstrated the novel synthesis of poly(silyl enol ether)s *via* radical ring-opening polymerization and their typical polymer reactions. It is noteworthy that radical ring-opening polymerization of trimethylsiloxy-substituted vinylcyclopropane is a novel method to prepare silyl enol ethers.

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(20) A solution of **2** in dichloromethane was vigorously stirred with 30% aqueous HCl solution at room temperature for 10 min. The organic layer was washed with water and dried with magnesium sulfate before evaporation. The residual polymer was purified by precipitation with dichloromethane–ether.

(21) $\bar{M}_n$ of **5a** could not be estimated because of its insolubility.[22]

(22) Hiraguri, Y.; Endo, T. *J. Am. Chem. Soc.* **1987**, *109*, 3779.

(23) **5a**: ^{1}H-NMR (90 MHz, CDCl$_3$) δ 2.80–2.20 (br, 4H), 1.80–1.10 (br, 4H) ppm; ^{13}C-NMR (22.5 MHz, CDCl$_3$) δ 210.2, 42.4, 23.2 ppm; IR (film) 2936, 2866, 1701, 1460, 1415, 1379, 1246, 1076 cm^{-1}. **5b**: ^{1}H-NMR (90 MHz, CDCl$_3$) δ 7.40–6.60 (br, 5H), 3.15–2.65 (br, 1H), 2.65–2.18 (br, 2H), 2.18–1.22 (br, 4H) ppm; ^{13}C-NMR (22.5 MHz, CDCl$_3$) δ 208.7, 143.3, 128.5, 127.4, 126.5, 49.8, 41.2, 40.3, 29.5 ppm; IR (film) 2934, 1713, 1493, 1453, 1410, 1372, 1252, 1192, 1098, 912 cm^{-1}. **5c**: ^{1}H-NMR (90 MHz, CDCl$_3$) δ 4.12 (q (J = 6.9 Hz), 2H), 3.05–2.21 (br, 5H), 2.08–1.53 (br, 1H), 1.26 (t, (J = 6.9 Hz), 3H) ppm; ^{13}C-NMR (22.5 MHz, CDCl$_3$) δ 207.1, 174.4, 60.5, 44.2, 39.7, 39.2, 25.2, 14.0 ppm; IR (film) 2982, 2907, 1734, 1450, 1375, 1182, 1098, 1032 cm^{-1}.

(24) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K.; Noyori, R. *J. Org. Chem.* **1983**, *48*, 932.

(25) ^{1}H-NMR (90 MHz, CDCl$_3$): δ 7.6–6.8 (br, phenyl), 4.9–4.4 (br, benzyl), 3.7–1.8 (br, OH and α-position of ketone) 1.8–0.4 (β-position of ketone) ppm. IR (film): 3455, 2938, 2874, 1705, 1454, 1372, 1028, 766, 735, 702 cm^{-1}.