throughout the transition range, but do not show any shifts or anomalies that would accompany changes in the coordination state of either protein. Instead, we tentatively interpret the abrupt disappearance of quenching as signaling a transition in the interfacial docking geometry *within* the protein complex,[18] the alternate possibility being freezing of one or both proteins into a set of non-redox-active conformational substates.[15] This interpretation is congruent with data suggesting that intracomplex ET near ambient temperatures involves a conformational conversion from inactive to active forms (conformational "gating").[19]

Remarkably, the transition temperature is independent of the solvent composition (Figures 1B and 2B), occurring in the same temperature range for solutions that glass below T_{mid} (60% EGOH) as for those solutions that crystallize at a temperature comparable to (45% EGOH) or greater than (15% and 30% EGOH) T_{mid}.[20] Clearly, the abrupt change in kinetics is an intrinsic molecular phenomenon that, unlike the CO rebinding to myoglobin,[18] is not "slaved" to the solvent.[21] However, the intracomplex quenching rate constant does vary with the solvent composition in the high-temperature region (Figure 1B), which may reflect a more subtle change in the mode of docking for the [ZnCcP, Fe^{3+}Cc] complex. To elucidate the structural basis for this fluctional process, we are extending these studies to include nonhomologous complexes as well as complexes in which the intracomplex interface is modified by site-directed mutagenesis.[22]

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(19) (a) Unpublished observations. (b) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237-6243.
(20) (a) Published glassing points for EGOH cryosolvents are as follows: 15%, ~266 K; 30%, 256 K; 45% ~238 K; 60%, 204 K (ref 20b). However, the addition of buffer and protein to these solvents lowers the freezing transition by 5-10 deg. (b) Douzou, P. *Cryobiochemistry: An Introduction*; Academic Press: New York, 1977.
(21) In addition to the large change in k_t during the transition range, one detects a small discontinuity in k_t at the freezing point ($T \sim 256$ K) for the 15% solvent (Figure 1B).
(22) Interestingly, we have seen that the midpoint of the transition in a given solvent changes with the cytochrome.

New Germanium-Containing Polymers via Alternating Copolymerization of a Germylene with *p*-Benzoquinone Derivatives

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Much attention has been paid to polymers having silicon in the main chain due to their scientific and application importance.[1] Few studies on polymers containing atoms of other IVB elements, however, have been reported in spite of their unique properties.[2-5]

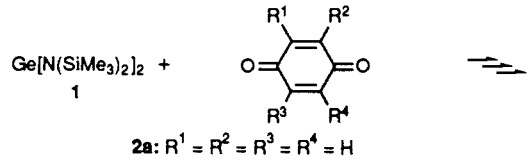
Table I. Copolymerization of Germylene **1** with *p*-Benzoquinone Derivatives **2**[a]

entry	oxidant monomer **2**	copolymer **3** yield,[b] %	M_w[c]	M_w/M_n[c]
1[d]	**2a**	quant	1.4×10^5	2.32
2	**2a**	85	1.3×10^5	2.36
3[e]	**2a**	94	1.4×10^5[f]	2.63
4	**2b**	94	5.8×10^4	2.51
5	**2c**	quant	2.9×10^4	1.98
6	**2d**	89	8.6×10^4	2.72
7	**2e**	96	3.6×10^5	2.15
8[e]	**2e**	93	2.0×10^5[g]	2.69

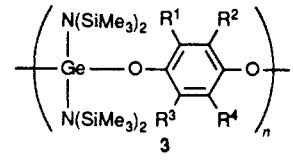
[a] Copolymerization was carried out by using 2.0 mmol each of **1** and **2** in 10 mL of toluene at -78 °C for 1 h under argon. [b] Isolated yield. [c] Determined by gel permeation chromatography (GPC): eluent, $CHCl_3$; flow rate, 1.0 mL/min; column, TSK-GEL G5000H, polystyrene standard. [d] Copolymerization was carried out at 0 °C for 1 h. [e] THF was used as solvent. [f] $M_n = 4.0 \times 10^4$ (determined by vapor pressure osmometry (VPO) in benzene at 40 °C). [g] $M_n = 7.9 \times 10^4$ (determined by VPO in benzene at 40 °C).

Organogermane polymers were photoactive and showed bleaching behavior,[2] strong thermochromic properties,[3] and semiconductivity.[4] Tin-containing polymers of alkoxy or ester type showed biological activity such as fungicidal properties.[5] Synthesis of these polymers utilizes the sodium coupling of a IVB metal dihalide[2,3] or polycondensation between a IVB metal dihydroxide or dihalide and a bifunctional organic compound such as a diol or dicarboxylic acid.[4,5]

The present communication describes a novel synthesis of germanium-containing polymers **3** by copolymerization of a divalent germanium compound (germylene), bis[bis(trimethylsilyl)amido]germanium (**1**),[6] with various *p*-benzoquinone derivatives **2**. The resulting copolymer **3** has alternating germanium(IV) and *p*-hydroquinone units in the main chain. All copolymers **3** are of relatively high molecular weight and soluble in organic solvents. During the copolymerization, germylene **1** (reductant monomer) is oxidized and *p*-benzoquinone derivative **2** (oxidant monomer) is reduced.[7] Thus, we propose the term "oxidation-reduction copolymerization" for the reaction.



2a: $R^1 = R^2 = R^3 = R^4 = H$
b: $R^1 = R^4 = {}^t$Bu, $R^2 = R^3 = H$
c: $R^1 = R^4 = Cl$, $R^2 = R^3 = H$
d: $R^1 = R^4 = Ph$, $R^2 = R^3 = H$
e: $R^1 = R^2 = H$, $R^3 + R^4 = CH{=}CHCH{=}CH$



3

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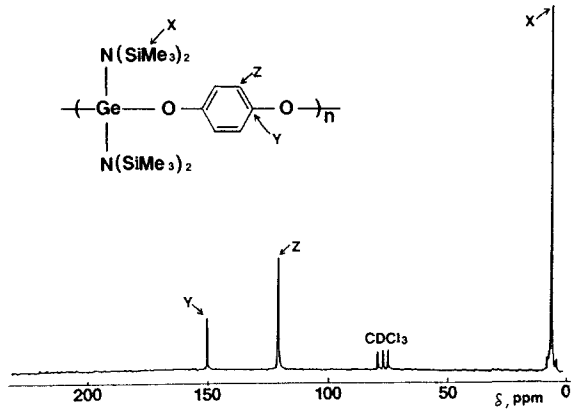
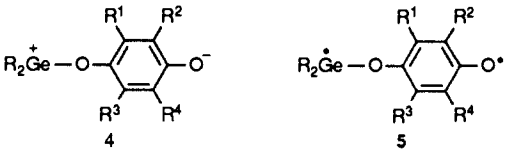


Figure 1. ^{13}C NMR spectrum of copolymer **3a** (entry 1) in $CDCl_3$.

The copolymerization took place smoothly at −78 °C in toluene without any added catalyst, to give the corresponding copolymer **3** in good yields (Table I). Under these conditions, the polymerization was completed within 1 h. The reaction proceeded readily even when sterically hindered *p*-benzoquinone derivatives (e.g., **2b** and **2d**) were used as oxidant monomers. These results indicate the high nucleophilicity of germylene **1** toward compounds having a carbon–oxygen double bond (similar reactivity is shown toward carbon–carbon double bonds in α,β-unsaturated carbonyl compounds[8]).

The resulting copolymers **3**[9] are white fine powders soluble in *n*-hexane, benzene, and chloroform and insoluble in acetone and acetonitrile. The copolymers have moderately high molecular weights ($M_w > 2.9 \times 10^4$); a copolymer of especially high molecular weight ($M_w = 3.6 \times 10^5$)[10] was obtained with 1,4-naphthoquinone as oxidant monomer (entry 7). Copolymer structures have been determined by ^1H and ^{13}C NMR as well as elemental analysis. The ^1H NMR spectrum of the copolymer obtained from **1** and **2a** in toluene (entry 1) exhibited signals at δ 0.25 ppm ascribable to the methyl protons of the trimethylsilyl group and at δ 6.92 ppm due to the aromatic protons of the *p*-hydroquinone unit, supporting structure **3a**. The ^{13}C NMR spectrum of copolymer **3a** shows three peaks at δ 5.5, 120.9, and 150.1 ppm, assignable to carbon atoms denoted as X, Z, and Y, respectively, in Figure 1. The elemental analysis of the copolymer also supported structure **3a**.[11]

The following reaction mechanism may be proposed for the oxidation–reduction copolymerization. The first step probably involves the formation of zwitterion **4** or diradical **5**.[12] Two molecules of **4** or **5** give a dimeric zwitterion or a dimeric diradical. Successive reactions between these intermediates lead to the alternating copolymer **3**.



(8) For example, the formation of a cyclic germanium(IV) enolate by the reaction of germylene **1** and α,β-unsaturated carbonyl compounds has been reported. Kobayashi, S.; Iwata, S.; Shoda, S. *Chem. Express* **1989**, *4*, 41.

(9) The resulting copolymers **3** are quite stable to the moisture. For example, no decrease of the molecular weight was observed by means of GPC after stirring an aqueous THF solution of **3b** for 24 h at room temperature. The product polymers are thermally stable and melt without decomposition. The glass transition and melt transition temperatures (T_g and T_m, respectively) were measured under air by means of differential scanning calorimetry (DSC), e.g., for copolymer **3a** (entry 3), $T_g = 75.6$ °C and $T_m = 234.7$ °C, and for copolymer **3e** (entry 8), $T_g = 46.1$ °C and $T_m = 234.9$ °C.

(10) Copolymer **3e** gave a film by casting from chloroform.

(11) Elemental analysis found for copolymer **3a** $(C_{18}H_{40}GeN_2O_2Si_4)_n$: C, 43.58; H, 8.24; N, 5.53. Calcd: C, 43.11; H, 8.04; N, 5.39.

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In conclusion, we have successfully synthesized new germanium(IV)-containing polymers **3** by a novel facile copolymerization of substituted germylene and *p*-benzoquinone derivatives. Further studies including physical properties of the resulting copolymers and the mechanism of the present copolymerization are now in progress.

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Synthesis of Avermectin B_{1a} Aglycon

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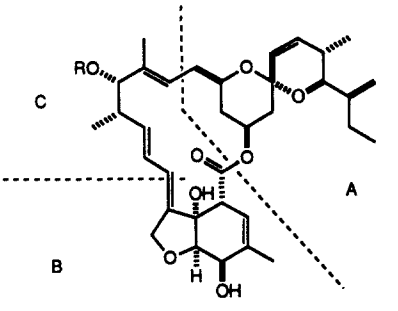
The emergence of avermectins as potent antiparasitic agents[1] with economic significance in animal health care[2] has elicited strong interest in their chemical properties and synthesis.[3] We previously reported routes to the spiroketal (A)[4] and oxahydrindene (B)[5] segments of avermectin B_{1a} (**1**) in anticipation that these would be linked to a third subunit (C) before closure to the macrolide. We now describe the concluding phase of this effort, culminating in a total synthesis of avermectin B_{1a} aglycon (**2**).[6]



1, R = L-Oleandrosyl-L-oleandrosyl

2, R = H

The linear segment C of **2** was elaborated from ethyl levulinate, which was converted in straightforward fashion to ketal **3**.[7] This ester was reduced to allylic alcohol **4**, and the latter was subjected to the catalytic version of the Sharpless epoxidation[8] to produce **5**. Opening of the epoxide with lithium dimethylcuprate proceeded with the expected regiospecificity[9] to yield **6**, and the primary alcohol was then selectively protected[10] as its pivalate **7**. The ketal

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(6) For an account of the pioneering accomplishments of Hanessian in this area, which resulted in a synthesis of (+)-avermectin B_{1a} from a spiroketal segment obtained synthetically and an oxahydrindene subunit derived from degradation of **1**, see: Hanessian, S.; Ugolini, A.; Hodges, P. J.; Beaulieu, P.; Dubé, D.; Andrē, C. *Pure Appl. Chem.* **1987**, *59*, 299. Hanessian, S.; Ugolini, A.; Dubé, D.; Hodges, P. J.; Andrē, C. *J. Am. Chem. Soc.* **1986**, *108*, 2776. Subsequently the oxahydrindene was prepared by synthesis from (−)-quinic acid (Dubé, D. Ph.D. Thesis, University of Montreal, 1988).

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