

Scheme 2.

ture than the PA, hence meaning that the SA has a greater reactivity than the PA toward Bisphenol A epoxy resins modeled by phenyl glycidyl ether.

The fact that the SA has a greater reactivity toward epoxy group of phenyl glycidyl ether, can be explained by the mechanism suggested already by Shechter *et al.*<sup>15</sup> For a convenient understanding this is reproduced in Scheme 2. According to this mechanism, oxirane ring is opened by nucleophilic attack of carboxylate anion at the methylene carbon atom of the protonated oxirane ring to give the final ester product. The carboxylate anion and its counter oxonium ion are formed by dissociation of the acid and addition of proton to the oxirane ring, respectively, *via* complexation between the oxirane group and the -COOH group. It is conjecturable that the PA should be a stronger acid than the SA, because in the SA the electron-donating methyl group lies at  $\alpha$ -position to the -COOH group, whereas in the PA that lies at  $\beta$ -position, and hence the -COO<sup>-</sup> formed from the SA should be a stronger nucleophile than -COO<sup>-</sup> formed from the PA. Therefore, it may be assumed that the oxonium ion will be more easily formed by PA than by SA, but the protonated oxirane ring will be opened more easily by the more nucleophilic -COO<sup>-</sup> formed from SA than by the less nucleophilic -COO<sup>-</sup> formed from PA. The higher reactivity of the SA toward phenyl glycidyl ether than the PA, observed from the DSC measurements, indicates that oxirane ring opening reaction is the rate-determining step in the whole reaction path, as already reported earlier<sup>3-5</sup>.

A simple attempt was made to distinguish the acidity of PA and SA by measuring neutralization point upon titration of the acids with very dilute NaOH solution in methanol, but both acids revealed the same neutralization pH 9.2.

Investigations on relative reactivity of the carboxylate anions of PA and SA using their sodium salts are in progress.

In conclusion, the noncatalyzed curing of epoxy resins containing free hydroxyl groups with such an unsymmetric anhydride as MSA gives two different carboxylic acids in the initiation reaction and toward epoxy groups these carboxylic acids could have different reactivities which can readily be differentiated by DSC technique.

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9. 0.732 g 1,3-diphenoxy-2-propanol, 0.684 g 1,3-diphenoxypropane and 1.343 g methyl succinic anhydride were stirred for 48 h at determined temperatures under thorough exclusion of moisture. After evaporation of the solvent the residue was chromatographed.
10. Spectra Physics, pump: SP 8800, detector: UV-VIS (254 nm) SP 8490, column: ZORBAX Sil with 4.6 mm inside diameter and 25 cm length, eluent: *n*-hexane/acetic acid (25/1 v/v), flow rate: 2 ml/min.
11. Waters Delta Prep HPLC 30.000, detector: UV-VIS (254 nm), column: PrePAK-500/Silica with 57 mm inside diameter and 30 cm length, eluent: *n*-hexane/acetic acid (30/1 v/v), flow rate: 150 ml/sec.
12. Physical and <sup>1</sup>H-NMR data of PA: mp. 75°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  6.9-7.3 (m, 10H, 2 $\times$ phenyl), 4.25 (d, 4H, 2 $\times$ -O-CH<sub>2</sub>-), 5.50 (m, 1H, -OCH<sub>2</sub>-CH(OCO)-CH<sub>2</sub>O-), 2.93 (m, 1H, -CH(CH<sub>3</sub>)-CH<sub>2</sub>-COOH), 2.60 (2q, *J*=12.0, 2H, -CH<sub>2</sub>-COOH), 1.23 (d, 3H, -CH<sub>3</sub>).
13. Physical and <sup>1</sup>H-NMR data of SA: mp. 65°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$  6.9-7.3 (m, 10H, 2 $\times$ phenyl), 4.25 (d, 4H, 2 $\times$ -O-CH<sub>2</sub>-), 5.5 (m, 1H, -OCH<sub>2</sub>-CH(OCO)-CH<sub>2</sub>O-), 2.96 (m, 1H, -CH<sub>2</sub>(CH<sub>3</sub>)-COOH), 2.65 (2q, *J*=10.8, 2H, -OCO-CH<sub>2</sub>-CH(CH<sub>3</sub>)-), 1.26 (d, 3H, -CH<sub>3</sub>).
14. For DSC scans pressure-safe sample holders securing up to 10 atmospheres were used to avoid evaporation of the samples. The samples were prepared by mixing equivalent amounts of phenyl glycidyl ether with PA or SA. Scan rate: 0.5°C/min, scan range 50-200°C.
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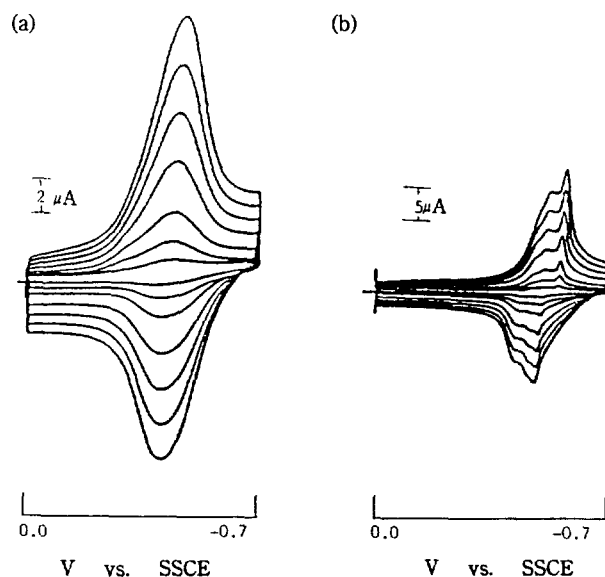
## Multiple Voltammetric Peaks of the First Redox Process of Self-assembled N-Docosyl-N'-Methyl Viologen(2+) Molecular Films at Electrode Surfaces

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Molecular self-assemblies of asymmetric viologens are of recent interest.<sup>1-4</sup> Bard was the first to describe the well-resolved two peaks of the first single-electron transfer process(2+/+) with Langmuir-Blodgett (LB) films of the N-hexadecyl-N'-methyl viologen (C<sub>16</sub>VC<sub>1</sub>) and N-docosyl-N'-methyl viologen (C<sub>22</sub>VC<sub>1</sub>) at indium-tin oxide (ITO) surfaces. At present, precise information is not available about the origin



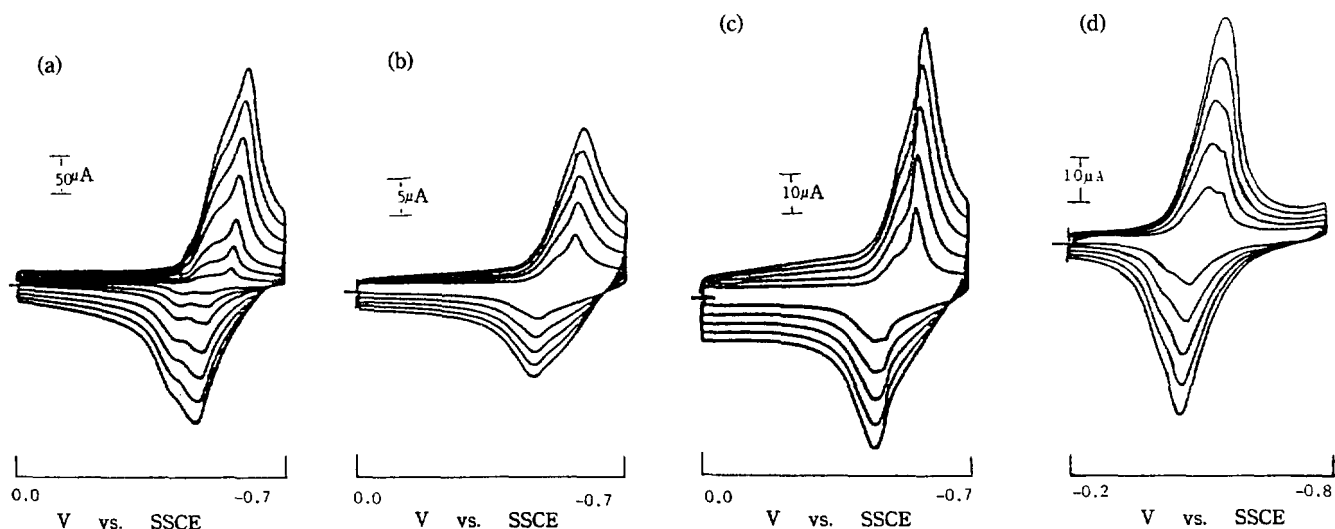
**Figure 1.** Cyclic voltammograms obtained at  $C_{22}VC_1/GC$  electrode immersed in an aqueous solution of 0.1 M NaCl with or without  $10 \mu M C_{22}V^{2+}C_1$  (a), and after transfer to the solution containing 0.1 M  $NaClO_4$  (b); Scan rates (mV/s): 500, 400, 300, 200, 100, 50, 20.

of the double voltammetric peaks, while the reproducibility of transfer of the films to the ITO substrate was poor so that films with high coverage were only obtained about 10% of the time. In this communication, we describe the multiple voltammetric peaks of the first redox process of viologens observed at  $C_{22}VC_1$  molecular films self-assembled irreversibly on electrode surfaces. The procedures are simple and easy with good reproducibility.

Conventional electrochemical instrumentation, cells and electrodes were employed.<sup>34</sup> ITO electrodes were cleaned with soap, base bath and distilled water. The other electrodes were polished with  $3 \mu m$  and  $0.05 \mu m$  alumina-water slurry successively, washed with copious amount of water,

and sonicated before each trial. Transfer of the electrodes with viologen assembly was made less than several minutes.

Figure 1(a) shows a cyclic voltammogram obtained at the glassy carbon electrode in the aqueous solution of  $10 \mu M C_{22}V^{2+}C_1$  and 0.1 M NaCl. The peak current ( $i_p$ ) versus scan rate ( $v$ ) yielded a linear line with zero intercept, as expected for surface-bound species.<sup>5</sup> The voltammetric signal observed with the self-assembled  $C_{22}VC_1$  molecular films at electrode surfaces changed little for at least one hour after transfer to the sample solution containing 0.1 M NaCl without the viologen. The coverage obtained from the integration of voltammogram was  $5(\bar{\Gamma}) \times 10^{-10}$  mole/cm<sup>2</sup>, which remained unchanged at the viologen concentration between 3–20  $\mu M$  and which is thus considered to correspond to a full monolayer. When the  $C_{22}VC_1/GC$  electrode was transferred to the solution containing 0.1 M  $NaClO_4$  with or without  $C_{22}VC_1$ , the cyclic voltammogram of multiple peaks was observed as shown in Figure 1(b). This may not be related to an ageing effect often observed with thick films at electrodes<sup>6</sup>, because (i) potential scan was limited to the first redox process in the present investigation of the viologen, (ii) multiply peaked voltammogram was observed at the first cycle immediately after transfer to the sample solution (<min), (iii) the singly peaked voltammogram was quickly recovered when the  $C_{22}VC_1/GC$  electrode was transferred to the sample solution of 0.1 M NaCl with or without  $C_{22}VC_1$ , (iv) multiple peaks with perchlorates appear in the more negative potential range than redox waves with chlorides and (v) similar multiple voltammetric peaks were observed with the self-assembled molecular films of  $C_{22}VC_1$  at the surfaces of ITO (Figure 2(a)), gold (Figure 2(b)), platinum (Figure 2(c)) and silver (Figure 2(d)) in the presence of perchlorate electrolyte. Thus the multiple voltammograms observed in this study are independent of the substrate employed. The voltammograms with ITO, gold, platinum and silver became singly peaked when the perchlorate was replaced with chloride electrolytes. In addition, the multiple peaks of the redox process were observed only when the surface coverage reached a full monolayer for each case investigated. Experiments in the presence



**Figure 2.** Cyclic voltammograms of self-assembled  $C_{22}VC_1$  at the surface of ITO (a), Pt (b), Au (c) and Ag (d) electrodes in an aqueous solution of 0.1 M  $NaClO_4$ ; Scan rates (mV/S): 500, 400, 300, 200, 100.

of sodium para-toluene sulfonate produced less well-developed multiple peaks.

The strongly multiple voltammetric peaks observed with the first redox process in the present studies appear to be caused by the perchlorate anion used. We notice that perchlorate electrolytes were employed in the electrochemical studies of the LB films of  $C_{22}VC_1$  and  $C_{22}VC_1$  at ITO surfaces.<sup>4</sup> Perchlorate ions are hydrophobic<sup>7</sup> and may cause positively charged  $C_{22}VC_1$  hydrophobic films to become highly compact at the full monolayer coverage, as was the case with the LB films, to produce thermodynamically distinguishable voltammetric peaks. The present procedures to obtain one-electron transfer multiple voltammetric peaks may be significant in that they can be easily applicable for spectroelectrochemical studies to investigate the unusual voltammograms observed at self-assembled viologens on electrode surfaces. Possible origin of multiply peaked voltammograms may be related to the effects of ion pairing or reorientation or both together with strong hydrophobic interactions. Spectroelectrochemical studies to probe the nature of multiple voltammetric peaks associated with the first electrochemical process of self-assembled viologen films are in progress in this laboratory.

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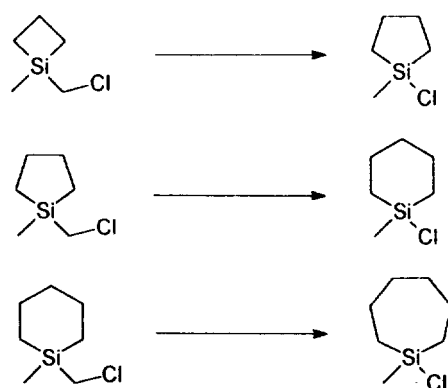
## Reaction Mechanism of the Ring Enlargement of Cyclic Si Ring Compounds with 1-(Chloromethyl) Substituents

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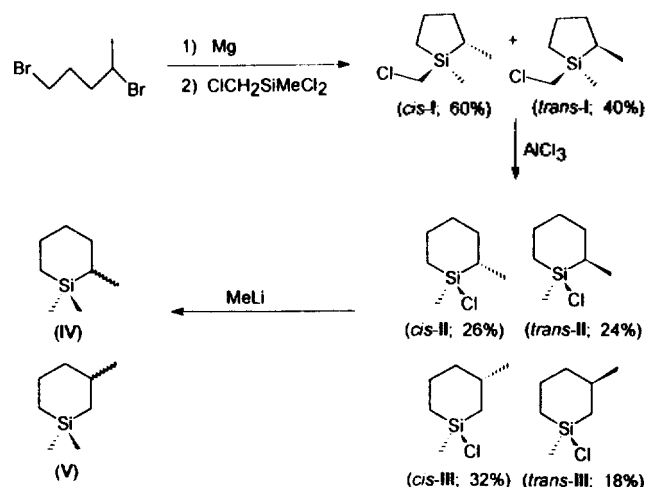
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Silicon chemists have had considerable interest in studying the reaction mechanism and synthetic utility of the rearrangement reactions of  $\alpha$ -chlorosilanes to chlorosilanes.<sup>1-3</sup> The rearrangement mechanism has been controversial for a long time. Various mechanisms have been proposed from analyses



Scheme 1.



Scheme 2.

of experimental data. Suggested mechanisms are (1) simultaneous double migration of Cl and R,<sup>4</sup> and (2) migration through  $\alpha$ -silyl cation,<sup>5</sup> or (3) stepwise migration involving an "inverse-ylide" pentacoordinated Si.<sup>6</sup> The ring enlarging rearrangement reactions are useful methods to provide new cyclic silanes<sup>2,3</sup> (see Scheme 1). 1-(Chloromethyl)-1,2-dimethylsilacyclopentane (**I**) can yield a new silacyclopentane through Me migration or two different chlorosilacyclohexane derivatives (**II** and **III**) by competitive migrations of the two different ring bonds (see Scheme 2). This particular system may allow the study of migratory aptitude of alkyl groups during the ring enlargement reaction.

**I** was synthesized as a *cis/trans* mixture<sup>7</sup> (ca. 60/40) from ring cyclization using the diGrignard reagent from 1,4-dibromopentane. Since **I** is formed as a mixture enriched in one isomer, we can identify the spectral properties of each signal of the *cis* and *trans*-isomers by using <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>1</sup>H-<sup>13</sup>C correlation, and gated proton decoupled spectra.<sup>8</sup>

At first, we attempted the rearrangement reaction under thermal conditions. *cis/trans*-**I** (60/40) was placed in a thick-walled tube, sealed and immersed in an oil bath at 200°C. After 1 week, no change was observed in proton NMR signals. Hence, a catalytic amount of AlCl<sub>3</sub> was added. Within 3 h,<sup>9</sup> the rearrangement is achieved cleanly at room temperature (without solvent). Four new peaks appear in the <sup>1</sup>H NMR spectrum at 0.37, 0.39, 0.41, and 0.44 ppm (all singlets)