

Table 1. The Structures of Peaks in the Chromatograms

Chromatogram	Peaks	Commercial name	Chemical name	Structure
Figure 2	A	Zoalene	2-Methyl-3,5-dinitrobenzamide	
	B	Thiamphenicol	D-threo-2,2-dichloro-N-[β-hydroxy-α-(hydroxymethyl)-p-(methylsulfonyl)phenethyl]acetamide	
Figure 3	A	Nicarbazin	N,N'-Bis(4-nitrophenyl)urea, and 4,6-dimethyl-2-(1H)-pyrimidinone (1 : 1)	
	B	Carbadox	2-(2-Quinoxalinylmethylene)hydrazinecarboxylic acid methyl ester N ¹ , N ⁴ -dioxide	

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Reactivity Study by DSC on the Noncatalyzed Model Curing Reaction of Epoxy Resin with an Unsymmetric Acid Anhydride

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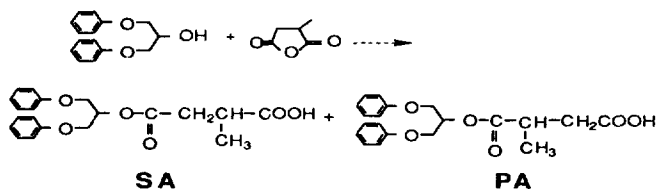
Received September 1, 1993

Epoxy resins are certainly an important class of commercial polymers¹ having various applications due to their excellent physical properties revealed when cured. To cure them

are used various compounds known as curing agents² such as amines, phenols, acids and acid anhydrides. The last generally include phthalic, maleic, succinic, tetrahydro- and hexahydrophthalic and methyl succinic anhydride(MSA) as well as many others. In acid anhydride curing of technical epoxy resins, which are derived mostly from Bisphenol A and epichlorohydrin and hence contain free, secondary hydroxyl groups, it is known³⁻⁸ that the curing reaction is started by the reaction of such a secondary hydroxyl group with the anhydride, to generate a monoester with a free carboxylic acid group, and this acid reacts then with an epoxy group to form another hydroxyl group which, in turn, reacts with another anhydride.

If a symmetric anhydride is reacted with a hydroxyl group, the ester acid formed by the initiation should have the same structure. If MSA is used as an unsymmetric anhydride, the ester acid with two different structures should be formed, of which one is a primary acid and the other is a secondary acid. These two acids could have different reactivity in the next-step reaction with epoxy group.

To make a study on the different reactivity of the two ester acids to be formed in the noncatalyzed initiation reaction of acid anhydride curing of epoxy resins containing hydroxyl groups on their main chains, 3-[(1,3-diphenoxy)-2-propyloxyacarbonyl]-butanoic acid(PA) and 2-[(1,3-diphenoxy)-2-propyloxyacetyl]-propanoic acid(SA) were prepared by reaction⁹ of MSA with 1,3-diphenoxy-2-propanol at 80°C, 100°C and 140°C in 1,3-diphenoxy-propane, as shown in Scheme 1. PA is a primary acid and SA is a secondary acid, both con-



Scheme 1.

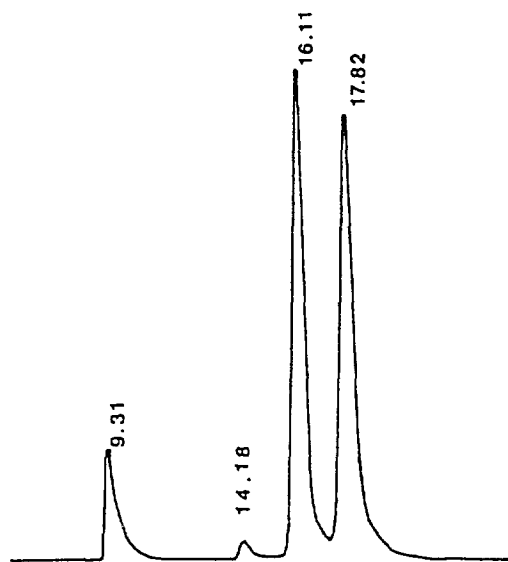


Figure 1. HPLC chromatogram of reaction product of MSA with 1,3-diphenoxy-2-propanol. Retention time(RT) in min. RT=9.31; 1,3-diphenoxypropane, 14.18; 1,3-diphenoxy-2-propanol, 16.11; SA and 17.82; PA.

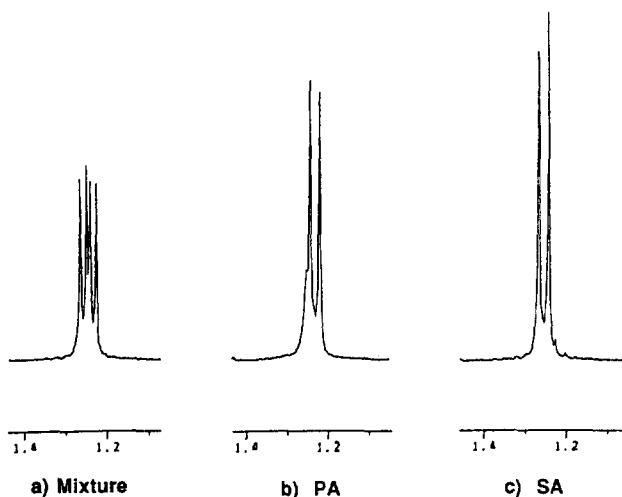


Figure 2. ^1H -NMR absorption of methyl protons (CDCl_3).

taining an ester group. The 1,3-diphenoxy-propane is used as the solvent to keep the reaction conditions similar to epoxy curing environment. The different reactivity between PA and SA toward an epoxy group, which was modeled by phenyl glycidyl ether, was measured by differential scanning calorimetry(DSC).

Preparation of PA and SA was carried out in the absence of any catalysts. Formation of them was confirmed by an analytical HPLC¹⁰ whose chromatogram is shown in Figure 1. After isolation to high purity by preparative HPLC¹¹ PA¹² and SA¹³ were identified by ^1H -NMR spectroscopy, parts of whose spectra are reproduced in Figure 2. It shows clearly that methyl protons of PA appear at upper magnetic field than those of SA, because the former are positioned farther to the electron-withdrawing $-\text{COOH}$ group than the latter. The identification^{12,13} helped assign the peaks of analytical

Table 1. PA/SA Ratio at Different Temperatures

Reaction temperature($^{\circ}\text{C}$)	PA/SA ratio
85	1/1.40
100	1/1.32
140	1/0.99

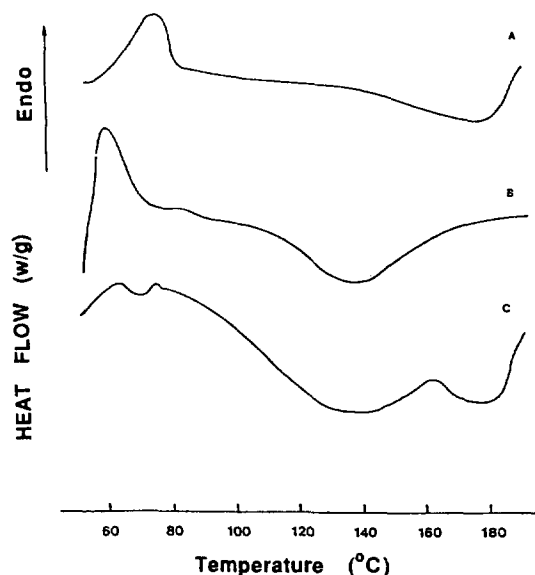
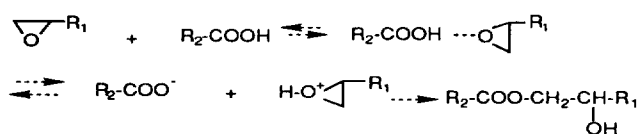


Figure 3. DSC thermograms obtained from the reactions of phenyl glycidyl ether with PA(curve A), SA(curve B) and their mixture(curve C).

HPLC chromatogram as illustrated in Figure 1.

Effect of temperature on product ratio PA/SA was investigated by peak area ratios obtained from the analytical HPLC chromatograms and this result is summarized in Table 1. It shows that SA is the dominant product at 85°C , while at 140°C the ratio is 1 : 1. This fact indicates that at lower temperature formation of SA is dominant and at higher temperature that of PA increases. This tendency means again that the methyl group of MSA plays a role in determining the product ratio, because the SA is formed by nucleophilic attack of the fairly bulky secondary alcohol of 1,3-diphenoxy-2-propanol at MSA's $\text{C}=\text{O}$ of 5-position, while the PA is formed by its attack at MSA's $\text{C}=\text{O}$ of 2-position. However, the $\text{C}=\text{O}$ of 2-position must be higher in electron density and sterically more hindered than the $\text{C}=\text{O}$ of 5-position due to the presence of the methyl group at 3-position. This conjecture might be able to explain the experimental result that the attack at $\text{C}=\text{O}$ of 5-position is preferred to that at $\text{C}=\text{O}$ of 2-position. With increase in reaction temperature the reactivity difference becomes insignificant.

DSC scan¹⁴ enabled us to study the reactivity difference between PA and SA toward the phenyl glycidyl ether, because ring-opening reaction of epoxy group is exothermic and DSC measures the heat flow very accurately. The DSC thermograms obtained are reproduced in Figure 3. It shows clearly that the PA has its exotherm peak (ca. 177°C) at higher temperature than the SA (ca. 137°C). This indicates that the SA reacts with phenyl glycidyl ether at lower tempera-



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.*¹⁵. 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 α -position to the -COOH group, whereas in the PA that lies at β -position, and hence the -COO⁻ formed from the SA should be a stronger nucleophile than -COO⁻ 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⁻ formed from SA than by the less nucleophilic -COO⁻ 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 earlier³⁻⁵.

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.

Acknowledgement. Financial support from the Korea Science and Engineering Foundation is gratefully appreciated.

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- 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.
- 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.
- 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.
- Physical and ¹H-NMR data of PA: mp. 75°C; ¹H-NMR (CDCl₃) δ 6.9-7.3 (m, 10H, 2 $\times$ phenyl), 4.25 (d, 4H, 2 $\times$ -O-CH₂-), 5.50 (m, 1H, -OCH₂-CH(OCO-)-CH₂O-), 2.93 (m, 1H, -CH(CH₃)-CH₂-COOH), 2.60 (2q, *J*=12.0, 2H, -CH₂-COOH), 1.23 (d, 3H, -CH₃).
- Physical and ¹H-NMR data of SA: mp. 65°C; ¹H-NMR (CDCl₃) δ 6.9-7.3 (m, 10H, 2 $\times$ phenyl), 4.25 (d, 4H, 2 $\times$ -O-CH₂-), 5.5 (m, 1H, -OCH₂-CH(OCO-)-CH₂O-), 2.96 (m, 1H, -CH₂(CH₃)-COOH), 2.65 (2q, *J*=10.8, 2H, -OCO-CH₂-CH(CH₃)-), 1.26 (d, 3H, -CH₃).
- 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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Received September 23, 1993

Molecular self-assemblies of asymmetric viologens are of recent interest.¹⁻⁴ 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 (C₁₆VC₁) and N-docosyl-N'-methyl viologen (C₂₂VC₁) at indium-tin oxide (ITO) surfaces. At present, precise information is not available about the origin