

Correlation between Adsorbabilities and the Functional Groups of Glycidyl Homo Polymer*

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Synopsis

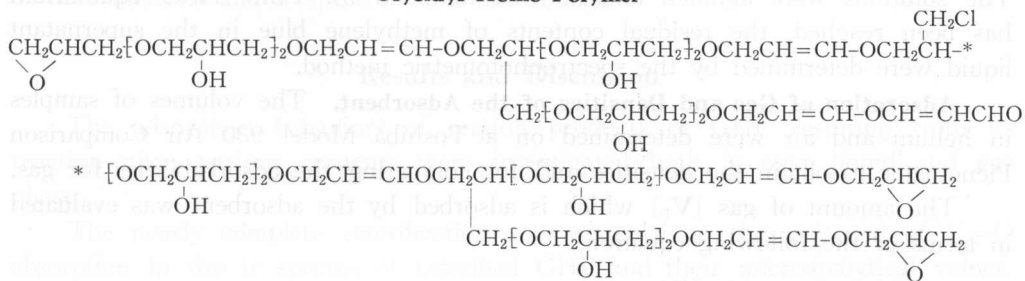
Glycidyl homo polymer obtained from the reaction of epichlorohydrin with sodium hydroxide in bulk was converted to acetylated-, butyrate-, oxydated-, cleaved-GHP etc. in order to compare the adsorbabilities of the derived polymers for methylene blue in liquid phase and air. The adsorbabilities for methylene blue: Purified-, 0.181; cleaved-, 0.178; oxydated-, 0.177; butyrate-, 0.137; acetyrate-GHP, 0.121 etc. (cf. GHP, 0.192). The difference of volume ($V_{He} - V_{Air}$)/ V_{He} : cleaved-, 9.2; butyrate-, 3.1; acetyrate-, 1.5; oxydated-GHP, 0.0 (cf. GHP, 4.9).

It was noted that the adsorbability of a molecule is not in proportion to the surface area and under the influence of functional groups included according to the experimental results.

Introduction

Epichlorohydrin react with 100 mole-% sodium hydroxide at 80°C in bulk to give the crosslinked polymer, glycidyl homo polymer I (GHP), in the yield about 60%¹⁾. This material has interesting adsorbabilities and various functional groups, -OH, $\begin{matrix} \diagup \\ \text{O} \\ \diagdown \end{matrix}$ -CO, -Cl, and -CHO in the molecule.

Glycidyl Homo Polymer



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In this paper the chemical transformations of functional groups in a GHP molecule and several interesting aspects of the correlation between the adsorbabilities and the functional groups of GHP are described and discussed. Presumably, by comparison with the adsorbabilities of the derived polymers our attention is drawn to the influence of the functional groups on them. For this purpose we

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1) M. Ito and K. Abe: *Memoirs Kitami Inst. Tech.* **1**, No. 3, 19-27 (1965).

synthesized several derivatives available, acetylated-GHP, butyrate-GHP, oxydated-GHP, cleaved-GHP etc. The adsorbabilities of these compounds for methylene blue in liquid phase and air were determined. Their surface areas and densities were also detected in regard to the adsorbabilities. The data is shown in Table 1.

Table 1. Adsorbabilities of Derivatives of GHP

Product	Adsorbability for Methylene blue mg M.B./g. GHP	Surface area m ² /g	Density ρ He	Difference of Volume ($V_{He} - V_{Air}$)/ V_{He}
Purified	0.181	1.68	1.30	5.0
Cleaved	0.178	0.92	1.32	9.2
Oxydated	0.177	1.04	1.30	0.0
Acetylated	0.121	1.00	1.28	1.5
Butyrate	0.137	1.86	1.24	3.1
GHP	0.192	0.96	1.23	4.9
Silica gel (Wako, Q-50)	—	—	—	179
Alumina (basic, Woelm)	—	—	—	53.7

Experimental Section

Infrared (ir) spectra were recorded on a Shimadzu Model IR-27 infrared spectrophotometer as potassium bromide discs.

Adsorption of Methylene Blue in Liquid Phase. The samples (1.0 g) were added to each flask containing 20 ml of aqueous solution of 0.2 mg methylene blue. The solutions were agitated and allowed to stand for 1 hr. After equilibrium has been reached, the residual contents of methylene blue in the supernatant liquid were determined by the spectrophotometric method.

Adsorption of Gas and Densities of the Adsorbent. The volumes of samples in helium and air were determined on a Toshiba Model 930 Air Comparison Picnometer to obtain the densities and for comparing the adsorbabilities for gas.

The amount of gas (V_D) which is adsorbed by the adsorbent was evaluated in terms of the following equation,

$$V_D = (V_{He} - V_{Air})/V_{He}$$

Measurement of the Surface Area. The values of the surface area were measured on a Sibata Model SA 200 Self-recording Surface Area Apparatus and calculated on the basis of the adsorption isotherm of nitrogen at -196°C .

Acetylation of GHP. A mixture of GHP (6.0 g) and acetic anhydride (38 ml) were allowed to react under refluxing for 9 hrs. The mixture was diluted with some water and filtered. The residue was washed with water until neutralization and with acetone, followed by drying in vacuo; yield 87%.

The ir spectrum showed characteristic absorption at 1240 (s, acetate) and 1730 cm^{-1} (s, carbonyl), and OH absorption disappeared.

Anal. Calcd for $[C_{99}H_{155}O_{52}Cl]_n$: C, 53.8; H, 7.0; Cl, 1.6. Found: C, 53.9; H, 7.1; Cl, 1.8.

Butyration of the GHP. A mixture of GHP (1.2 g), butyric anhydride (12 ml) and pyridine (12 ml) were refluxed for 9 hrs. The mixture was treated in the same manner as mentioned above; yield 83.8%.

The ir spectrum showed characteristic absorption at 1735 cm^{-1} (s, carbonyl). Anal. Calcd for $[C_{123}H_{203}O_{52}Cl]_n$: C, 58.0; H, 8.0; Cl, 1.4. Found: C, 57.2; H, 7.5; Cl, 1.7.

Oxydation of GHP. GHP (6.0 g) was allowed to stand in an aqueous solution including periodic acid (5.0 g) for 3 days. The mixture was filtered and washed with water until neutralization, and with acetone, followed by drying in vacuo; yield 96%.

Anal. Calcd for $[C_{75}H_{120}O_{40}Cl]_n$: C, 52.1; H, 7.3; Cl, 2.1. Found: C, 51.3; H, 7.1; Cl, 4.0.

Cleavage Reaction of the Oxirane Ring in GHP. GHP (6.0 g) was refluxed with a solution of HCl-dioxane (20:60 ml) for 20 mins. The mixture was filtered and washed with water until neutralization, and with acetone, followed by drying in vacuo; yield 93%.

The ir spectrum showed characteristic absorption at 1630 cm^{-1} (s, C=C) and at $13\ \mu$ (w, C-Cl).

Anal. Calcd for $[C_{75}H_{132}O_{40}Cl_4]_n$: C, 49.5; H, 7.3; Cl, 8.0. Found: C, 48.8; H, 6.9; Cl, 1.3.

Purification of GHP with Sodium Bisulfite. GHP (6.0 g) was shaken overnight with a 40 ml saturated solution of sodium bisulfite, but no reaction occurred and weighting percentage was zero. But this material was bleached. The values of microanalysis and ir spectrum did not change.

Results and Discussion

The adsorption behaviors of reaction products of GHP resulting from its reaction upon various reagents were investigated both in over liquid and gas phase.

The nearly complete esterification was assigned to the presence of C=O absorption in the ir spectra of esterified GHP and their microanalytical values. Neither acetylated-GHP nor butyrated-GHP showed increases in their adsorbability. In contrast, butyrated-GHP has a larger surface area than acetylated-GHP and slightly larger adsorbability for methylene blue, but butyrated-GHP showed greater adsorbability twice as large as acetyrated-GHP in gas adsorption.

Periodic acid oxidation of GHP gave yield 96%. In the ir spectrum, the cleavage of oxirane rings were assigned to the disappearance of absorption at $8\ \mu$ and the decrease of absorption at $11\ \mu$, and characteristic frequencies of carbonyl groups and alkenes showed multiple absorption, but the spectrum all over was similar to those of GHP. The oxydated product did not show any adsorption for gas, but approximately the same adsorption as GHP in liquid phase.

The product treated with HCl-dioxane, which doesn't appear to have no oxirane ring according to its ir spectrum, showed nearly the same adsorbability for methylene blue as the oxydated product, but showed the largest adsorbability for gas among the GHP and its derivatives. The ir spectrum showed the striking absorption of alkene at 1630 cm^{-1} , assuming double-bond migration which are easily induced by acid.

These indicate that adsorption for gas is independent of the presence of oxirane ring and carbonyl group, and dependent on the presence of double bonds.

In comparing their adsorbabilities with those of inorganic adsorbent used usually, GHP and its derivatives had nearly the same values for methylene blue in liquid phase, but very small values in gas phase. However, in organic polymeric adsorbents, it should be noted that the adsorbability of a molecule is not in proportion to the surface area and under the influence of functional groups included according to the above experimental results.

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