Notes

Determination of End Unsaturation in Polyetherpolyols by the Wijs Procedure

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Polyetherpolyols are widely used as raw materials for the production of polyurethane resin. Both allyl and *cis*-propenyl end groups are present as byproducts in polyetherpolyols synthesized by the base-catalyzed addition of propyleneoxide to initiator compounds, such as polyfunctional alcohols.¹ That is, during the course of the addition reaction, a small portion of propyleneoxide acts as an allyl initiator to produce mono-ol of lower molecular weight. Thus, to some extent, the allyl end groups produced in this reaction are thermally rearranged into *cis*-propenyl end groups in the reactor.

Because such unsaturated mono-ols in polyetherpolyols prevent cross-linkage of the polyurethane, the physical property of the resin is seriously affected by the amount of these byproducts. For determining these unsaturations, mercuric acetate titration has so far been widely used for industrial purposes^{2,3}, however, a new method that is less toxic to the environment is required. Since the concentration of olefinic unsaturation in polyetherpolyols is considerably low compared with other unsaturated industrial materials, such as drying oils and fatty compounds, a titration technique using highly reactive iodine-monochloride (the Wijs procedure)⁴⁻⁷ was examined.

Experimental

Samples

All of the samples analyzed in this work were chosen from experimentally synthesized polyetherpolyols at the Research Center of Asahi Glass Co., Ltd. or industrially produced polyetherpolyols by Asahi Olin Co., Ltd. Propyleneglycol, glycerin and allyl alcohol were used as initiator compounds. Propyleneoxide (PO) was added in the presence of a KOH catalyst. Some of the samples were subsequently treated with ethyleneoxide (EO) for end-capping to obtain primary polyols.

Reagents and solutions

Analytical-grade reagents and deionized-distilled water were used throughout the experiments.

The Wijs reagent.⁸ After 9.0 g of iodine was dissolved in 900 ml of warmed glacial acetic acid, iodine trichloride (ICl₃) dissolved in 60 ml of glacial acetic acid was added. They were then mixed, cooled and made up to a 1 l solution. The Wijs solution was kept in a cool, dark place in a tightly capped bottle.

Sodium thiosulfate standard solution (0.1 N). After 26 g of sodium thiosulfate (Na₂S₂O₃·5H₂O) was dissolved in water and diluted to 1 l, 0.1 g of sodium carbonate (Na₂CO₃) was added. The solution was standardized against a potassium iodate (KIO₃) primary standard as follows: about 40 mg of the KIO₃ was weighed into a glass-stoppered 300 ml flask and dissolved in 30 ml of water. Then, 2 g of KI was added; as soon as this was dissolved, 5 ml of a 2 M HCl solution was also added. Liberated iodine was titrated immediately with the Na₂S₂O₃ solution, using a starch indicator near to the end point. The normality of the Na₂S₂O₃ solution was calculated as follows:

$$\text{Normality} = W / (35.67 \times V)$$

where *W* is the amount of KIO₃ used in mg and *V* the volume of Na₂S₂O₃ solution in ml required for titration of the KIO₃.

Potassium iodide solution. Two grams of potassium iodide (KI) was dissolved in 100 ml of water.

Starch indicator solution. After making a homogeneous paste of 10 g of soluble starch, it was added to 200 ml of boiling water, stirred rapidly, and cooled. About 10 mg of thymol was added as a preservative.

Apparatus

All titrations were carried out using ordinary laboratory equipment.

Procedure

A quantity of the sample specimen (ca. 5–20 g) was weighed into a glass-stoppered 500 ml flask and dissolved in chloroform. If the unsaturation value falls about 0.07, for example, the specimen size of 10 g with 30 ml of chloroform is recommended.

Table 1 Unsaturation obtained by two methods

Polyetherpolyols analyzed			Unsaturation (meq/g)	
Initiator	Molecular weight	EO Capping, wt%	Wijs procedure	Mercuric acetate procedure
Propyleneglycol	4000	23	0.037	0.036
Propyleneglycol	4000	23	0.057	0.057
Glycerin	5000	0	0.074	0.073
Glycerin	5000	0	0.067	0.068
Glycerin	6000	5	0.135	0.135
Glycerin	6500	0	0.067	0.065
Glycerin	7000	15	0.091	0.088
Allyl alcohol	1700	0	0.520	0.519

The Wijs reagent (20 ml) was added and the flask was stoppered, shaken and allowed to stand in a dark place for 1 h. The flask was occasionally stirred.

A potassium iodide solution (100 ml) was added into the flask. The flask was stoppered, swirled and the released iodine was titrated with a $\text{Na}_2\text{S}_2\text{O}_3$ solution by adding from the 50 ml buret, with continuous agitation using a starch indicator solution. The titration was completed in the usual manner when both the water-phase and the chloroform-phase become entirely colorless.

Blank determinations were conducted simultaneously by following the same procedure as described, except that no sample was added.

The total unsaturation value (meq/g) was calculated as follows:

$$\text{Unsaturation value} = (B - V) \times F / 2S$$

where B is the volume of $\text{Na}_2\text{S}_2\text{O}_3$ solution in ml required for titration of the blank and V is that of $\text{Na}_2\text{S}_2\text{O}_3$ solution in ml required for titration of the sample, F is the normality of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, and S is the amount of sample used in g.

The reason why the numerator of the equation is divided by two is as follows. In the mercuric acetate procedure, one acetic acid molecule is released from one $\text{C}=\text{C}$ double bond.

Thus, the unsaturation is expressed with units of "milliequivalent per gram". On the other hand, in the Wijs procedure, one $\text{C}=\text{C}$ double bond reacts with one ICl molecule, which means a di-equivalent reaction:

Conventional method

Conventional mercuric acetate titration was also conducted according to ASTM.² The results obtained by both titration methods were compared.

Results and Discussion

Unsaturation by the Wijs procedure and the conventional mercuric acetate procedure are in good agreement (see Table 1). It is noted that if the samples contain antioxidants, such as BHT (2,6-di-*t*-butyl-4-methylphenol), the unsaturation obtained by the Wijs procedure becomes slightly higher. For example, the addition of 1000 ppm of BHT to polyetherpolyols increases by about 0.01 meq/g the unsaturation measure. Therefore, a correction is necessary if the sample contains such additives. It is also noted that since the reaction between BHT and ICl is relatively slow, the correction value is a variable according to the experimental condition.

Thus, the Wijs procedure gives quite satisfactory results, and the reagents used in the procedure are practically stable. This technique is less toxic to the environment. It is concluded that the Wijs procedure can be an alternative technique to the conventional mercuric acetate procedure.

References

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