Figure 1.

to observe a variable (e.g., dielectric loss) which is sensitive to changes in the amorphous phase only, instead of the specific volume which reflects the behavior of the entire sample.

Conclusions. Each of the six polymers treated by Saito and Nakajima undergoes a glass transition with relaxation times whose temperature dependence is given by the WLF equation. For the case of the three crystallizable polymers an additional transition occurs at a nearby temperature. This additional transition reduces the amount of the sample that undergoes the glass transition. This second transition, at least for the case of PVDC, can also be observed by dilatometry. In the case of noncrystallizable PVAc, high-speed dilatometry yields a value of T_g which is too high.

We should like to thank our colleague, Dr. D. O. Schissler, for bringing the paper of Saito and Nakajima to our attention.

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T. F. SCHATZKI

Shell Development Company
Emeryville, California

* This thermodynamic temperature is precisely the glass transition temperature of WLF within an additive constant, the value of which must be the same for all systems.

Poly-3-(2,5-Diacetoxyphenyl)Propylene Oxide

There are a number of polymers described in the scientific and patent literature which are known as electron exchange polymers, redox polymers, or sometimes as nondiffusible reducing agents. Examples of these are polyvinyl hydroquinone,[1-3] copolymers of vinyl hydroquinone,[4,5] polyvinyl gentisal,[4] polyacrylyl ascorbic acid,[4] and some acylated polyvinyl hydroquinones.[6] We have prepared and studied briefly a new hydroquinone-type monomer whose structure is given below:
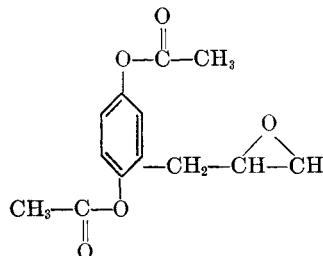
Monomer Preparation

Allyl hydroquinone (m.p. = 90–91°C.) was dissolved in a slight excess of acetic anhydride and a catalytic amount of concentrated sulfuric acid was added. After the reaction mixture had cooled it was poured onto crushed ice. The crystalline diacetate, after recrystallization, had a melting point of 47–48°C. Results of analysis[7] were as follows: Calcd. C, 66.6; H, 6.0. Found: C, 66.4; H, 5.8.

Allyl hydroquinone diacetate (29 g., 0.124 mole) and 24.6 g. (0.2 mole) of perbenzoic acid were dissolved in 200 ml. of chloroform. The reaction was maintained at 0°C. for 24 hr. and then extracted three times with cold, aqueous, dilute sodium carbonate solution. After washing with water, drying over anhydrous magnesium sulfate, and removal of the chloroform by distillation, the residue was fractionated through a short distillation column. A small forerun of solid distillate (2 g., boiling range 100–110°C./0.6 mm.) was obtained, followed by 18 g. of product (b.p. 161°C./0.6 mm.). The epoxide of allyl hydroquinone diacetate is a crystalline, almost colorless solid, m.p. = 32°C. Analysis[7] for C and H gave: Calc'd: C, 62.4; H, 5.6. Found: C, 62.3; H, 5.5. The molecular weight, measured by the freezing point depression of benzene, was determined as 266 as against a theoretical value of 250. The infrared spectrum of the pure epoxide is presented in Figure 1.

Polymerization

In some preliminary polymerization experiments it was found that typical epoxide polymerization catalysts such as anhydrous ferric chloride, boron trifluoride etherate and zinc chloride–aluminum isopropoxide yield oily and semisolid polymers when the pure monomer is treated with these catalysts at 80°C.

In a controlled polymerization, a small reaction vessel, equipped with a stirrer and protected from atmosphere moisture, was charged with 5 g. of pure epoxide, 0.038 g. of freshly prepared aluminum isopropoxide and 0.038 g. of Matheson ACS zinc chloride. The polymerization was carried out at 80°C. with continuous stirring for 6 days. The resulting orange-colored solid was dissolved in 5 ml. of
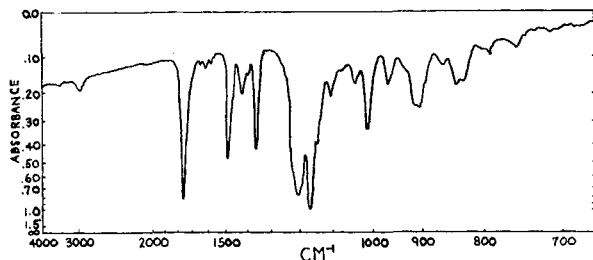
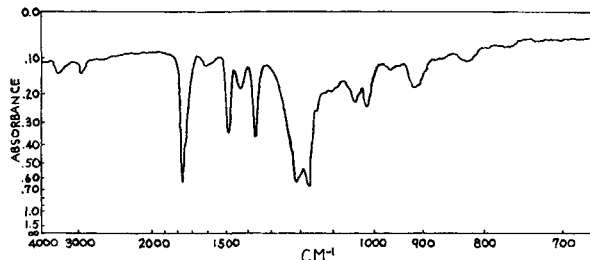Fig. 1. Infrared spectrum of 3-(2,5-diacetoxyphenyl)-propylene oxide.

Fig. 2. Infrared spectrum of poly-3-(2,5-diacetoxyphenyl)-propylene oxide.

Fig. 3. Infrared spectrum of poly-3-(2,5-dihydroxyphenyl)-propylene oxide.

acetone and precipitated into ether. The solid precipitate was filtered off, washed with ether, and dried. Yield was 2.2 g. (fraction 1). The ether filtrate, after evaporation almost to dryness, and on the addition of fresh ether, yielded an additional 0.33 g. of solid polymer (fraction 2). Finally, evaporation of the ether gave 2.44 g. of an orange-colored gum (fraction 3). The softening points, molecular weights as determined by freezing point depression of benzene, and the intrinsic viscosities in benzene at 30°C. of these fractions are given in Table I.

·TABLE I
Properties of Poly 3-(2,5 Diacetoxyphenyl)Propylene Oxide Fractions

Fraction	Yield, %[a]	Softening range, °C.	Mol. Wt.	$\overline{DP}$	$[\eta]$ benzene, 30°C.
1	44.0	48–52	1438	5.75	0.025
2	6.6	42–45	958	3.83	0.021
3	48.8	gum	406	1.62	—

[a] In an identical run, carried out for only 3 days at 80°C., the total yield of solid polymer (fractions 1 and 2) amounted to 2.0 g.

The polymers are of low molecular weight, similar in this respect to some of the polymers obtained from phenyl glycidyl ether[8] and styrene oxide.[9] The infrared spectrum of the fraction 1 polymer cast from acetone onto silver chloride is presented in Figure 2. The spectrum is very similar to that of the monomer. The appearance of a small band at 3500 cm.$^{-1}$ may be associated with the initiation reaction. A change in absorption characteristics at 1240 cm.$^{-1}$ and a disappearance of absorption bands at 830–840 cm.$^{-1}$ result from utilization of the epoxy ring during polymerization. In the 1120 cm.$^{-1}$ region of the spectrum of Figure 2, there is some evidence for the presence of aliphatic ether groups.

The polymeric diacetoxyphenyl propylene oxide is readily soluble in many organic solvents, i.e., benzene, acetone, and dioxane. It dissolves in dilute aqueous alkali on continued stirring by hydrolysis of the acetate groups to yield the free hydroquinone polymer. If the aqueous alkaline solution so prepared is exposed to air, it undergoes many color changes associated with the various oxidation states of the polymer. A sample of the polyhydroquinone polymer was prepared from fraction 1 by treating 0.5 g. of the diacetate with 3 ml. of dioxane and 1 ml. of 1N hydrochloric acid at 100°C. for 10 min. The polymer was precipitated into water, reprecipitated from acetone into ether, and dried. The infrared
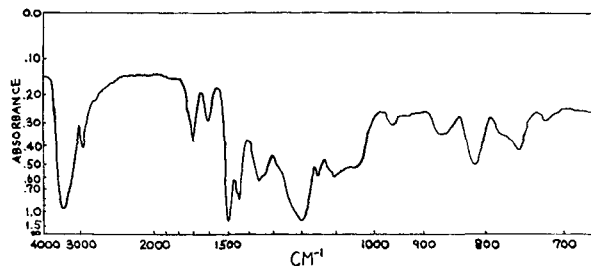
spectrum of the hydroquinone polymer, cast from acetone onto silver chloride, is given in Figure 3. The spectrum looks appropriate for this material except for some absorption at 1700 cm.$^{-1}$ whose origin we do not understand. We do know, however, that identical spectra are obtained for this polymer whether $FeCl_3$, BF_3, or the $ZnCl_2$–aluminum isopropoxide catalyst is employed in the polymerization.

In a few attempts to alkylate polyvinyl alcohol with diacetoxy-phenyl propylene oxide in pyridine at 80°C., the epoxide polymerized independently of the polyalcohol. Presumably, however, with the proper choice of conditions, this epoxide could be used for the modification of certain polymers.

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HOWARD C. HAAS
NORMAN W. SCHULER

Chemical Research Laboratories
Polaroid Corporation
Cambridge, Massachusetts