Recently Glasgow, Streiff and Rossini[3] have published a method for determining both the freezing point of a sample of a compound and the freezing point of the same compound with zero per cent. impurity from the same time-temperature cooling curve. We have applied this method to the determination of the freezing points of our phthalic anhydride samples.

Temperatures were measured with a Bureau of Standards calibrated platinum resistance thermometer used in conjunction with a White Double Potentiometer. The resistance of the thermometer was checked at the ice-point before and after the work on phthalic anhydride.

The highest freezing point of any sample obtained was 130.97° with several samples freezing at 130.95°. Our average value for the freezing point of phthalic anhydride with zero impurity is 130.95 ± 0.03°. This value is the average of those found for nine different samples of phthalic anhydride.

Our value for the freezing point of pure phthalic anhydride is in much better agreement with the value given by Monroe (130.84°) than with that given by Burriel-Marti (131.60°).

Monroe has also published data for the system phthalic anhydride–phthalic acid. Our value for the freezing point (129.80°), and composition (1.65 mole per cent. phthalic acid), of the eutectic is in fair agreement with the values published by Monroe (129.74° and 1.75 mole per cent. phthalic acid).

(3) A. R. Glasgow, Jr., A. J. Streiff and F. D. Rossini, J. Research Nat. Bur. Standards, 35, 355 (1945).

CALIFORNIA RESEARCH CORPORATION
RICHMOND, CALIFORNIA   RECEIVED JUNE 7, 1946

The Variation of Composition of 40:60 Isoprene–Styrene Copolymers with Conversion[1]

BY ELIZABETH DYER AND DOROTHY LEVIS MUNROE[2]

There is little published work dealing with the emulsion copolymerization of isoprene and styrene.[3,4] In ascertaining the effect of varying conditions on the emulsion copolymerization of a 40:60 mixture of isoprene and styrene, an approximately equimolecular mixture, it was observed that the initially formed copolymer contained about 80% of styrene. As the reaction was continued to maximum conversion, the styrene content decreased to approximately 60%. These results show that at this monomer ratio
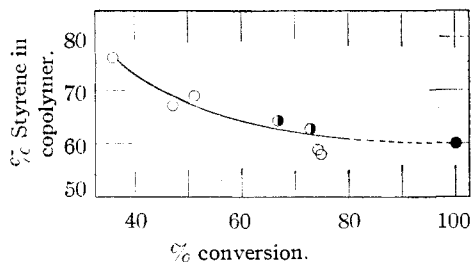

Fig. 1.—Variation of styrene content with degree of conversion: O, run 20; ◑, run 21; ●, theoretical point.

(1) From the Master's Thesis of Dorothy Levis Munroe, University of Delaware, 1946.

(2) Armstrong Cork Company Research Fellow.

(3) Copolymers of styrene and isoprene were described by Fryling at the Atlantic City Meeting of the American Chemical Society, which was held after the completion of this thesis.

(4) Soday, U. S. 2,317,857. April 27, 1943.

styrene enters the copolymer faster than does isoprene. This behavior is similar to that of styrene when copolymerized with acrylonitrile and with vinylidene chloride.[5] The evidence also indicates that the copolymer is not homogeneous with respect to composition.

Procedure.—The most satisfactory polymerization recipe in parts by weight was: isoprene, 40; styrene, 60; water, 200; potassium persulfate, 0.30; sodium oleate, 20; dodecyl mercaptan, 0.25. The experiments were carried out with 10 g. of monomers in 50-ml. test-tubes[6] which had been cleaned with concentrated nitric acid and which were seated on a rotating shaft and turned end over end in an insulated water-bath at 40°.

After agitation for the specified time, the latex was steam distilled to remove unchanged monomers and the polymer was coagulated with 0.6 M hydrochloric acid. The tough, rubbery coagulum was cut into small pieces to facilitate removal of acid, then dissolved in benzene containing phenyl-β-naphthylamine in an amount equal to 2% by weight of the polymer. The benzene solution was dried with calcium chloride, and the polymer further purified by several reprecipitations from benzene and methanol. The removal of most of the solvent prior to analysis was done by the frozen benzene technique.[7] The samples were finally dried to constant weight at 56° and a pressure of about 2 mm.

The conversion was measured by drying a known portion of the acid coagulum to constant weight at 80°.

The composition of the polymer samples in terms of percentage of styrene was determined from their iodine numbers according to the method of Kemp and Peters[8] in which % styrene = $100 - (100 \times \text{iodine value}/372.6)$. Results from two runs are shown in Fig. 1. The data of Run 20 were obtained from samples taken after reaction periods of three, eight, thirteen, twenty-one, and twenty-four hours, respectively, while those of Run 21 were from ten and sixteen hour samples.

(5) Lewis, Mayo and Hulse, THIS JOURNAL, 67, 1704 (1945).

(6) Fryling, Ind. Eng. Chem., Anal. Ed., 16, 2 (1944).

(7) Lewis and Mayo, Ind. Eng. Chem., Anal. Ed., 17, 135 (1945).

(8) Kemp and Peters, Ind. Eng. Chem., Anal. Ed., 15, 455 (1943).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE   RECEIVED AUGUST 17, 1946

Ionization Constants of Some Weak Acids in Aqueous Tertiary Butyl Alcohol

BY WILLIAM H. FLETCHER[1]

The objective of the work reported in this paper was to obtain reasonably accurate information regarding the ionization constants of certain mercaptans and alkyl substituted phenols. A review of the literature failed to show any recorded work on the ionization constants of aliphatic mercaptans, although thiophenol and a number of its derivatives have been investigated by Schwarzenbach and Egli,[2] using cells with liquid junctions in 49 and 95% (by vol.) ethanol.

(1) Present address: University of Minnesota, Minneapolis, Minn.

(2) Schwarzenbach and Egli, Helv. Chim. Acta, 22, 360 (1939). 17, 1176 (1934).