

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

## Simultaneous Polymerization and Degradation in Polymer Systems: Styrene in Toluene Solution

BY ROBERT MESROBIAN AND ARTHUR TOBOLSKY

The polymerization of styrene in toluene solution in the presence and absence of catalysts has been studied in some detail.<sup>1</sup> It is also well known that when a toluene solution of high molecular weight polystyrene is heated in the presence of small amounts of air, a decrease in the viscosity of the solution occurs, indicating the existence of a degradation process. Furthermore, polystyrene vacuum distilled at high temperatures is degraded almost completely to monostyrene. It is the purpose of this paper to show that both polymerization and degradation occur under the same conditions of temperature, concentration and catalytic conditions, and in fact must occur simultaneously in all styrene solutions. It will be shown that catalysts of polymerization are also in general catalysts for degradation, and that in many cases steady states, or possibly equilibrium states, are reached for which the rates of polymerization and degradation become equal.

To demonstrate the simultaneous occurrence of polymerization and degradation, monostyrene and various polystyrene solutions of the same weight concentration were maintained at elevated temperatures under the same conditions of temperature and catalytic environment. The viscosities of these solutions were measured at suitable intervals during the course of the experiments.

To prepare the styrene solutions, commercial monostyrene was used. Commercial polystyrene was used in some instances, while in other cases polystyrene of varying degrees of polymerization was prepared in the laboratory. Since the commercial monostyrene was stabilized with hydroquinone, before use it was washed several times with sodium hydroxide, dried, and vacuum distilled three times to remove the inhibitor.

In the first experiment, seven 8.82-cc. portions of this purified styrene were placed in test-tubes 18 mm.  $\times$  150 mm. and 0.01 g. of benzoyl peroxide was added in each test-tube. The tubes were then sealed off and placed in an air oven at 100°, and heated for definite lengths of time. One test-tube was removed after five minutes, and successively the remaining test-tubes were removed after twenty minutes, forty-five minutes, one hour, three hours, five hours and nine hours of heating at 100°. In this way products ranging from very fluid liquids to very viscous liquids to soft plastics and to hard plastics were obtained. The contents of the various test-tubes were each dissolved in sufficient toluene to make up a solution of concentration equivalent to 16 g. per 100 cc. of toluene. From each of these solutions 8 cc. were sealed in air in special reversible viscosimeters (described below and shown in Fig. 1).<sup>2</sup> The

time of flow for these viscosimeters had previously been calibrated with pure toluene and amounted to about 25 seconds. The relative viscosities of the solutions (compared to toluene) varied from nearly unity in the case of the styrene polymerized for five minutes to about one hundred in the case of the styrene polymerized for nine hours.

The sealed viscosimeters were then placed on an asbestos board five inches beneath a G. E. no. 1 Sunlamp mounted with a standard reflector. The steady state temperature that was attained at the level of the viscosimeter bulbs was 100°. Under the combined influence of light, heat and possibly the oxygen sealed into the viscosimeters the viscosity of the styrene solutions began to change. This change was followed by periodically measuring the time of flow of the solutions through the capillary of the reversible viscosimeter which during the measurement was kept in a constant temperature water-bath at 25°.

The results of this experiment are shown in Fig. 2 where the natural logarithms of relative viscosity for the seven solutions are shown plotted against time of heating under the Sunlamp. It is evident that after about 350 hours a steady state is reached and the viscosity of all the solutions stops changing. Furthermore, the relative viscosities of all the solutions approach the same value. The viscosimeters were opened after 425 hours and benzoyl peroxide catalyst was added and also, incidentally, new air was admitted to the viscosimeters. When replaced under the light there was no appreciable change in time of flow after another seventy-five hours. It is also notable that one of the solutions (the one hour polymerized styrene) did not change its viscosity within the limits of experimental error during the entire course of heating under the Sunlamp.

The results of the above experiment indicate clearly that the degradation and polymerization process are intimately related, and that a steady state, or possibly a true equilibrium state, is reached for which the rates of polymerization and degradation become equal.

about 0.4 mm. and the length of the tube slightly over 8 cm. Inasmuch as only comparative values of the relative viscosities of various solutions were of interest, no attempt was made to take into account kinetic energy corrections or to correct for the possibility of non-linear flow. In all cases relative viscosity was defined as the time of flow for the solution at 25° between the two marks shown in Fig. 1 divided by the time of flow of pure toluene at 25°.

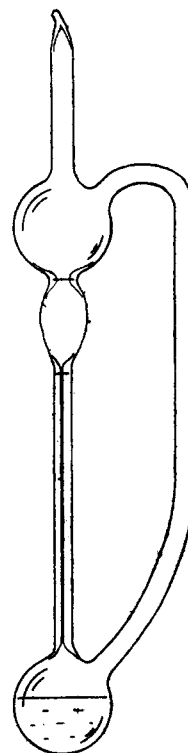


Fig. 1.—Reversible viscosimeter.

(1) (a) G. V. Schulz, A. Dinglinger, and E. Husemann, *Z. physik. Chem.*, **B39**, 246 (1938); (b) H. Suess, K. Pilch and H. Rudorfer, *ibid.*, **A179**, 361 (1937); (c) H. Suess and A. Springer, *ibid.*, **A181**, 81 (1937); (d) J. W. Breitenbach and A. Maschin, *ibid.*, **A187**, 175 (1940).

(2) The reversible viscosimeters used in these studies were first employed in this Laboratory by Dr. M. Magat, the original design coming from the Russian literature. The bore of the capillary is

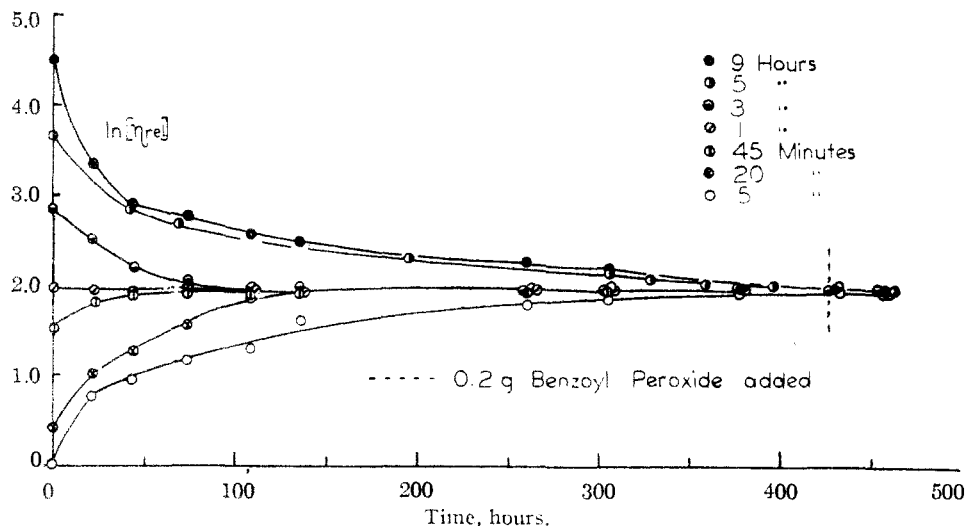


Fig. 2.—Polymerization degree vs. time: styrene (concn. 16 g./100 cc. of toluene), 100°, light catalysis.

It is generally believed that the degradation reaction in vinyl polymers is an oxidative scission reaction in which free oxygen combines chemically with the hydrocarbon causing oxidative cleavage. The results of Fig. 2 can perhaps be regarded as evidence that the degradation is a true depolymerization in which light and oxygen have purely catalytic roles.<sup>3</sup> Any slight amount of oxygen found incorporated in the polymer might possibly be explained as due to side reactions such as termination of free radical chains. If the degradation products could not be repolymerized, and if the process were an oxidative cleavage that would occur any place along the chain, it would be expected that the viscosity of all the solutions would continue to fall to a relative viscosity of unity because in all cases the polymerizable monomer must eventually disappear.

In order to ascertain whether a true equilibrium or a photo-chemical steady state was attained at the conclusion of the experiments, two of the viscosimeters were removed from the light and placed in an oven at 100°. One of these viscosimeters was transferred from the light to the oven unopened and a small amount of catalyst was introduced into the other viscosimeter before placing in the oven. After heating for several days at 100° the viscosities were again measured. No appreciable change in viscosity was observed as a result of removing the solutions from the light.

The evidence cited above is insufficient. There are reasons to believe that the steady states attained under certain conditions may possibly depend upon environmental factors such as amount of oxygen in the sealed tubes or upon

(3) It should be pointed out that although the polystyrene was prepared at 100°, the same temperature at which it was exposed to light in toluene solution, true thermal equilibrium might possibly involve depolymerization of the high molecular weight polystyrene because of the effect of solution in lowering the equilibrium average molecular weight.

light intensity. The only truly conclusive criterion for thermal equilibrium would be to demonstrate that at a given temperature the same equilibrium state is attained irrespective of catalytic conditions. Attempts are therefore in progress to attain steady states for polymerization-degradation under the action of heat and air alone, and also to study the effect of various amounts and methods of benzoyl peroxide addition. The theory for thermodynamic equilibrium in polymer systems and a simple case of the kinetics of simultaneous polymerization-depolymerization have already been published.<sup>4,5</sup>

The following experimental results have also already been noted:

(1) When monostyrene and high molecular weight polystyrene solutions of the same weight concentrations are heated in air at 100° without catalyst, the viscosity of the monostyrene solution increases and the viscosity of the polystyrene solution decreases appreciably at first and then very slowly. The very slow change of the viscosity of the polystyrene solution precludes the attainment of any possible equilibrium state within reasonable times. However, it appears that the monostyrene solution approaches a steady state viscosity, the course of polymerization not being very different from the polymerization of monomer solution in light at the same temperature.

(2) If benzoyl peroxide is added to the monostyrene and high molecular weight polystyrene solutions and these are then heated at 100°, the viscosity of the monostyrene solution rises rapidly initially and soon changes only very slowly. The viscosity of the polystyrene solution falls rapidly and very markedly and then also stops changing. If further addition of catalyst is made the viscosities of both solutions gradually approach each

(4) (a) A. V. Tobolsky, *J. Chem. Phys.*, **12**, 402 (1944); (b) P. J. Flory, *ibid.*, **12**, 425 (1944).

(5) A. V. Tobolsky and P. J. Blatz, *J. Phys. Chem.*, in press.

other, and once this occurs further catalyst addition does not change the viscosity of either solution. Rapid degradation can be achieved by addition of large amounts of catalyst, whereas the most effective and rapid way of increasing the over-all solution viscosity of monomeric solutions is by successive additions of *very* small amounts of catalyst.

It must be noted that in all cases the viscosity of the entire solution is measured including possible unreacted monomer.

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### Summary

The existence of simultaneous polymerization and degradation in toluene solutions of styrene and polystyrene has been demonstrated. Steady states resulting from the competition of these reactions have been observed.

PRINCETON, N. J.

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## The Acylation of Pectin

By J. F. CARSON, JR., AND W. D. MACLAY

This paper describes the preparation of a series of esters of citrus pectin. These derivatives were prepared for a further study of the physical chemistry of pectin and as possibly useful materials for determinations of molecular weight and molecular size distributions. Because of the incomplete solubility of the esters in organic solvents, no viscosity or osmotic pressure measurements are reported. The method used, namely, esterification with an acid anhydride or acid chloride in the presence of excess pyridine, has not heretofore been applied successfully to pectin.

Schneider and co-workers,<sup>2</sup> who attempted the direct acetylation of purified citrus pectin, described their products as poorly soluble and degraded. Their reactions were carried out by swelling pectin in acetic acid, followed by esterification at 20–40° with acetic anhydride in the presence of various catalysts such as sulfuric acid, perchloric acid, zinc chloride and pyridine in 1% concentration. These investigators prepared the diformate and diacetate of pectin by the reaction of formic acid and acetic anhydride, respectively, on the previously prepared pectin dinitrate. These esters were soluble in acetone, but always contained residual nitrogen and were actually mixed nitrate-formate and nitrate-acetate esters.

The technique used for the esterification of pectin consists in preparing a pectin-water paste, partially dehydrating the pectin with acetone, and gradually replacing the water and acetone with pyridine to yield the pectin in a highly swollen gelatinous state. As an alternative method, freshly precipitated pectin can be swollen directly in pyridine. In this form, pectin is readily esterified by lower fatty acid anhydrides in excess pyridine. Of all esterification procedures, the pyridine-acid anhydride method is considered

to be the mildest and least degrading on polysaccharides, as studies with cellulose<sup>3a</sup> and starch<sup>3b</sup> have shown. The extent of degradation occurring in the acylation of pectin by this procedure was not determined. It has been established, however, that pyridine itself under the same conditions of temperature as used in the esterification reactions has no appreciable degrading action, as shown by viscosity measurements and methoxyl analyses on pectin recovered from its pyridine gel.

Pectin diacetate, dipropionate, and dibutyrate were obtained by the reaction of citrus pectin with the corresponding acid anhydride in pyridine at 45°. Esterification was usually 90–95% complete in three to five hours and, by esterifying a second time at room temperature, esters were obtained with acyl contents very close to the theoretical values calculated for a diester of a partially methylated polygalacturonide.<sup>4</sup> Repeated esterification in pyridine failed to increase the acyl content beyond the diester stage. The reaction proceeds apparently without loss of methyl ester groups. Pectin diacetate prepared in this way is insoluble in water and has a low solubility in organic solvents. It is partially soluble in chloroform, tetrachloroethane, pyridine, and acetic acid, but is insoluble in ethanol, acetone, ether, and benzene. The dipropionate and dibutyrate

(3) (a) Staudinger and Daumiller, *Ann.*, **529**, 219 (1937); (b) Staudinger and Husemann, *ibid.*, **527**, 195 (1937); Mullen and Pacsu, *Ind. Eng. Chem.*, **34**, 1209 (1942).

(4) Analyses for methoxyl and uronic anhydride indicate that 90% of the molecule can be accounted for as polygalacturonide. The 10% of non-galacturonide material probably consists largely of araban and galactan as shown by Beaven, Hirst and Jones, *J. Chem. Soc.*, 1867 (1939). Although the presence of an araban diester would increase the acyl analyses only slightly, the presence of appreciable quantities of galactan triester should yield an acyl content significantly higher than the actual values found. Because of uncertainty as to the relative quantities of araban, galactan, and non-carbohydrate materials in the non-galacturonide fraction, the actual percentages of acyl found were compared with the theoretical values for a diester of a pure polygalacturonide as explained in Table I, footnote (a).

(1) Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Schneider and co-workers, *Ber.*, **69**, 309, 2530 (1936); **71**, 1353 (1938).