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POLYESTERIFICATION OF POLYHYDROXY-POLYBASIC ACID: PART IV— POLYMOLECULARITY*

An attempt has been made to characterize the polymolecularity of three self-esters of the dibasic acid, 9,10-dihydroxyhexadecane-1,16-dicarboxylic acid, having low, medium and high degrees of polymerization by subjecting them to fractionation. The integral, differential weight and number distribution curves for the various fractions of the esters show that the fractions are distinct and that the ester molecules exhibit varying degrees of homogeneity in their chain length.

IT WAS OBSERVED DURING THE COURSE OF A STUDY of the physico-chemical properties of 9,10-dihydroxyhexadecane-1,16-dicarboxylic acid that a polyester of the acid can be fractionated by adding a precipitant to a solution of the polyester¹. The fractions separated have different molecular sizes and acid values and hence different solubilities. In the present study, an attempt has been made to characterize the polymolecularity of a few polyesters of 9,10-dihydroxyhexadecane-1,16-dicarboxylic acid consisting of molecules which are more or less alike in chemical composition and mode of linkages, but have heterogeneous molecular weights.

The method of precipitation followed was the same as developed by Mark² for cellulose and Kraemer and Lansing³ and Signer and Gross⁴ for polystyrenes. It consists in dissolving the entire sample in a chemically inert solvent and then precipitating the successive fractions by the addition of a suitable precipitant. Precipitation may also be accomplished by stepwise changes in temperature.

Three polyesters with different degrees of polymerization (DP), referred to as A, B and C, were prepared by isothermal heating of 9,10-dihydroxyhexadecane-1,16-dicarboxylic acid in a test tube as described previously⁵ by suitable adjustment of temperature and duration of heating.

The fractionation of each polyester A, B and C was carried out as follows: An accurately weighed sample of the polyester was dissolved in dry acetone in a

stoppered conical flask and placed in a thermostat ($30^{\circ} \pm 1^{\circ}\text{C}$). Water from a burette was added to the solution and after the appearance of first turbidity (a black paper screen background was employed to detect the formation of precipitate), the precipitate was allowed to settle. The precipitate, after removing the supernatant liquid, was redissolved by warming and allowed to settle. It was separated by decantation, redissolved in acetone and the solvent evaporated for the recovery of the precipitate. To the decanted solution, a further amount of water was added from the burette and a second fraction was similarly collected and treated. The process of fractionation was continued till no further precipitate could be separated from the supernatant liquid. During precipitations, care was taken to see that the volume of the solutions did not increase excessively as the separation of the precipitate from large volumes of the solutions towards later stages always proved to be laborious and time-consuming.

The degree of polymerization (DP) of each of the fractions separating out was determined by the usual end-group method. The weight of each of the fractions separating out was determined and from it the cumulative percentage of the material remaining in the solutions at each stage was calculated. Since a small amount of the precipitate is always lost in the course of successive fractionations, it is not possible to recover the exact amount of the starting material from the solution and hence the cumulative percentages of the material remaining in solution have been calculated on the basis of the actual total amount recovered rather than on the amount of the starting material.

The degrees of polymerization of the various fractions have been plotted against the weights of polyesters remaining in solution at different stages. It is clear from the curves in Fig. 1 that the fractions obtained are sufficiently distinct, indicating efficient fractionation. The curve for polyester A shows an inflexion around DP 1.175 (Fig. 1). The steep portion near this point signifies a high concentration of molecules in this region (Fig. 2). Curve B has got two inflexion points near about DP 1.3 and 1.425. Curve C has also two points of inflexion at about DP 1.20 and 1.325. The maxima and minima corresponding to these inflexion points for different polyesters are evident from the differential weight distri-

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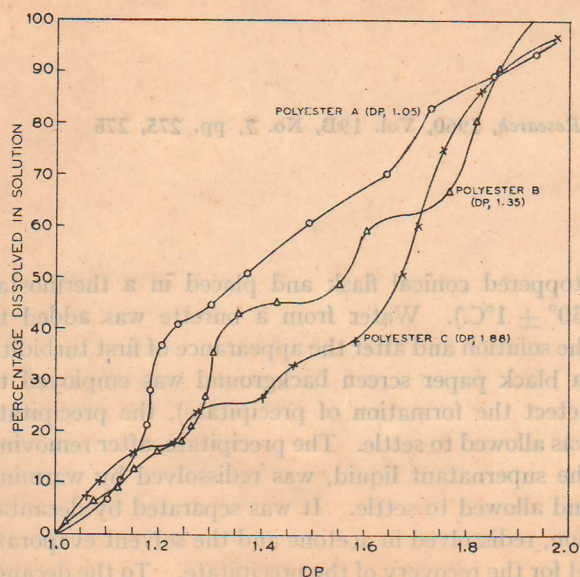


FIG. 1— DEGREE OF POLYMERIZATION (DP) VERSUS WEIGHT OF POLYESTER REMAINING IN SOLUTION

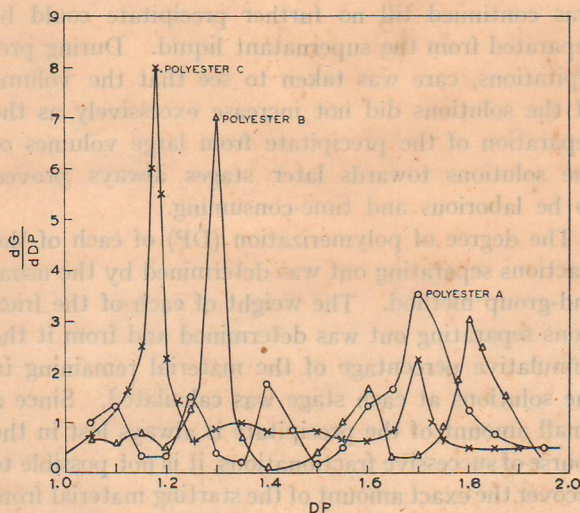


FIG. 2— RATE OF GROWTH OF MOLECULES $\left(\frac{dG}{dDP}\right)$ VERSUS DEGREE OF POLYMERIZATION (DP)

bution and differential number distribution curves presented in Figs. 2 and 3. In the integral weight distribution curves, all these points of inflexion are located before the point representing half-way in the range of total polymerization, indicating a more non-homogeneous character of the polymer molecule during this stage. In the latter half of the curve, the molecules conform to a more uniform composition.

In the differential weight distribution curves of the three polyesters (Fig. 2), the values represented along the ordinates have been obtained by graphic differentiation of the values presented in the integral weight distribution curves (Fig. 1) for each polymer.

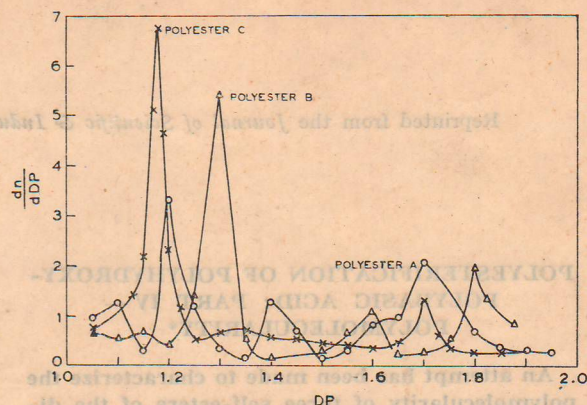


FIG. 3— DIFFERENTIAL NUMBER DISTRIBUTION CURVES

This is accomplished by dividing the change in the weight per cent (dG) by the change in the degree of polymerization (dDP). The curves for polyesters A and B are not so sharp and each has its own prominent peaks. The curve for polyester C is relatively smooth and sharp and the peaks are less prominent. Polyesters A and B have maxima and minima near about the region where the inflexion points are located, which probably means that these polymers are less homogeneous in chain length. But it has been found generally that such uniformity in chain length is always less pronounced in the case of synthetic polymers than for certain natural cellulose derivatives. In the differential number distribution curves shown in Fig. 3 the degree of polymerization has been plotted against the quotient of the functions of the weight distribution curves and the corresponding molecular weights or any values equivalent to the length of the polymer chain, e.g. the intrinsic viscosity of the function. The curves are almost similar to those in Fig. 2. Though homogeneity of chain length is an important physical property of polymers, an average value is usually taken to represent the different chain lengths and the non-homogeneity of chain length is ignored.

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