718. *The Kinetics of Formation of Some Polyesters.*

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The kinetics of the condensation polymerisation of adipic acid with diethylene glycol, catalysed by toluene-*p*-sulphonic acid, are of simple second order after an initial period in which they are more complex. The early stages in the reaction at 140° occur at a greater rate than the later steps but the situation is more confused at lower temperatures. The molecular-weight distributions in the polymers are examined and discussed.

Condensation polymerisation between dibasic acids, $[CH_2]_n(CO_2H)_2$, and dihydric alcohols, $[CH_2]_n(OH)_2$, leads to linear polyesters of considerable molecular weight. The kinetics of the acid-catalysed esterifications such as those of the reaction between adipic acid and diethylene glycol have been described by Flory [1] who was able to explain the later stages of the reaction leading to a wide range of high polymers of molecular weight from a few hundred up to 10,000. On the other hand, he was unable to account for the initial stages of the reaction leading to polymers of molecular weight below about 500. The present investigation was designed to study these early stages of reaction.

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[1] Flory, *J. Amer. Chem. Soc.*, 1940, **62**, 1057.

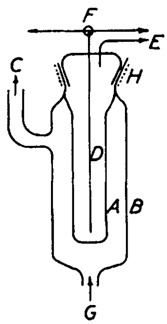
EXPERIMENTAL

Materials.—Purified adipic acid, recrystallised from water, had m. p. 154·0—154·5°. Diethylene glycol was fractionally distilled at low pressure, b. p. 133°/14 mm. Both compounds were stored in a vacuum desiccator. The catalyst, crystalline toluene-*p*-sulphonic acid tetrahydrate, was not purified.

Apparatus and Method.—The reaction, which was studied in the melt, is

$$HO_2C\cdot[CH_2]_4\cdot CO_2H + HO\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot OH \longrightarrow HO_2C\cdot[CH_2]_4\cdot CO\cdot O\cdot[CH_2]_2\cdot O\cdot[CH_2]_2\cdot OH + H_2O$$

FIG. 1. *Apparatus.*



The extent of this reaction was found at different times by three techniques: (*a*) measuring the water liberated, (*b*) determining the bulk viscosity of the melt, and (*c*) titrating the residual acid end groups. The second method was calibrated by the third. The same apparatus, used in all the polymerisations (Fig. 1) and similar to that employed by Flory,[2] consisted of a reaction finger, *A*, kept at a constant temperature in the vapour jacket, *B*, which was connected to a condenser, *C*. Purified, oxygen-free nitrogen was bubbled into the finger through a capillary, *D*. The nitrogen stirred the polymer and carried water into the trap *E*. The top of the trap was heated electrically so that the water was completely removed. The water liberated was determined by weighing the trap at different times. The nitrogen supply was cut off from time to time at the two-way tap, *F*, and the capillary then connected to a suction pump so that polymer could be drawn up the capillary, *D*. After the suction had been turned off and the capillary opened to the atmosphere, the time of fall of the meniscus of the fluid polymer was measured between two marks on the capillary. The nitrogen flow was then resumed. The time of fall was related to the bulk viscosity of the polymer, η, by a previous calibration of the capillary with liquids of standard bulk viscosity. The reaction was stopped at any desired time by rapid cooling of the contents of the finger. The residual acid end groups of the final polymer were then determined by titration in acetone or acetone–ethanol with aqueous alkali and α-naphtholphthalein as indicator. This gave M_n or z_n, the number-average molecular weight and chain length respectively. For polymers of high molecular weight we have shown that the molecular-weight distribution is that of the most probable distribution.[3] Thus $M_n = M_w/2$ and $z_n = z_w/2$ where w refers to the weight average. Determination of M_n and the bulk viscosity of the final polymers therefore permitted us, following Flory,[1] to establish the relationships: (1) $\log \eta = -1{\cdot}92 + 0{\cdot}120 z_w^{\frac{1}{2}}$ at 140°; (2) $\log \eta = -1{\cdot}21 + 0{\cdot}099 z_w^{\frac{1}{2}}$ at 109°. Flory gave $\log \eta = -1{\cdot}04 + 0{\cdot}099 z_w^{\frac{1}{2}}$ at 109°. The relationships were used to find the extent ofpolymerisation at any time in a polymerisation from the bulk viscosity, η.

Kinetics.—In Fig. 2 we plot time against x_n, the degree of polymerisation given by $z_n = zx_n + 1$, where z is the number of chain atoms per polymer segment. Except at low degrees of polymerisation the observations fit Flory's equation $C_0C_{\text{cat}}kt = x_n + 1$, where C_0 is the initial concentration of reactants, C_{cat} is the concentration of catalyst, and k is a true third-order rate constant. At 140° the value of $C_{\text{cat}}k$ was 0·95 mole^{-1} l.sec.$^{-1}$ over the linear part of the plot in Fig. 2. By following the rate of evolution of water over the earliest part of the reaction (Fig. 3) we again observed that Flory's equation was true but the constant $C_{\text{cat}}k$ was 1·50 mole^{-1} l. sec.$^{-1}$. The reaction proceeds more rapidly at low degrees of conversion. Such an observation implies that the molecular-weight distribution at low degrees of conversion should be different from the most probable distribution. Studies of the amounts of adipic acid in the polymers and of the molecular-weight distribution confirm this.

Concentration of Adipic Acid in the Polymers.—Adipic acid was determined by a modification of the method described by Kröller.[4] Two solutions were made up in ethanol; (*a*) contained 0·50 g. of polymer in 5·0 ml., and (*b*) contained 0·01 g. of adipic acid in the same volume of solvent. To each were added 5 ml. of a 5·0% ethanolic solution of mercuric acetate containing five drops of N-acetic acid. A crystalline precipitate was rapidly formed in (*b*) but (*a*) remained clear. Further experiments demonstrated that 0·0003 g. of adipic acid when added to 0·5 g. of

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[2] Flory, *J. Amer. Chem. Soc.*, 1939, **61**, 3334.

[3] Pope, Weakley, and Williams, *J.*, 1959, 3442.

[4] Kröller, *Deut. Lebensm. Rundschau*, 1947, **43**, 1.

the same polymer as in solution (*a*) could be detected by the test. A simple calculation from the known molecular weight of the polymer showed that if the rate of polymerisation had remained constant throughout the whole extent of the polymerisation, *i.e.*, if the polymer had the most probable distribution, solution (*a*) should have contained 0·0985 g. of uncombined adipic acid. The above experiment demonstrated that there was less than 0·3% of this amount present, a result confirming the view that the early stages of the reaction were more rapid than the subsequent stages. The analysis was repeated on several polymers with the same result.

FIG. 2. *Change of degree of polymerisation, x_n, with time at* (*A*) 140°, (*B*) 124·5°, (*C*) 109°.

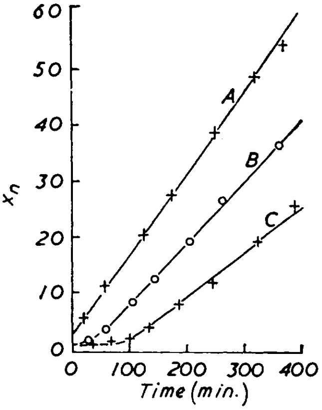


FIG. 3. *Evolution of water during polymerisation. Three separate experiments are illustrated in order to demonstrate reproducibility. The broken line is the theoretical maximum.*

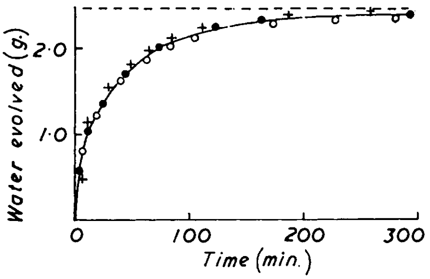


FIG. 4. *Molecular-weight distributions in polyesters of four different average molecular weights*: *A*, 375; *B*, 570; *C*, 870; *D*, 1760.

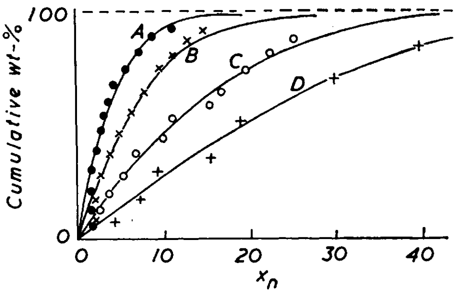
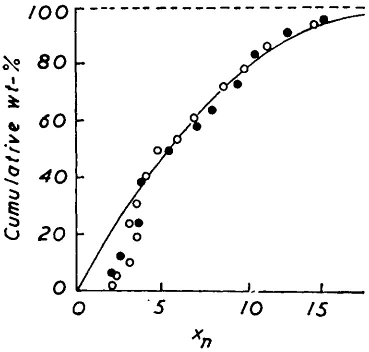


FIG. 5. *Molecular-weight distribution in two polymers of the same average molecular weight,* 570, *but prepared at different temperatures. The full line is a theoretical most probable distribution drawn to be a good fit with experiment.*



Distribution of Molecular Weight in the Polyesters.—Details of the method of polymer analysis are given elsewhere.[3,5] The molecular-weight distributions of the higher-molecular weight polymers agree well with theory (Fig. 4). The deviations from the most probable distribution in the lower polymers is such that low-molecular weight material has been lost at the expense of higher-molecular weight polymers. This is the distribution to be expected if the earlier stages in the reaction are faster than the later.

Because the differences in kinetics at different temperatures were so marked (Fig. 2) we analysed polymers of the same number-average molecular weight but prepared at different temperatures. Fig. 5 shows that we were unable to see any differences in the molecular-weight distributions.

[5] Baker and Williams, *J.*, 1956, 2352.

DISCUSSION

The present work confirms Flory's,[1] in so far as the kinetics of formation of polyesters are given by his equation $C_0C_{\text{cat}}kt = x_n + 1$ over the range of polymers of molecular weight from some hundred to several thousand. The equation implies that the reactivity of the end groups is unaltered by the changes in the medium during reaction. The molecular-weight distributions of the low-molecular weight polymers are not those expected from equal reactivity of the end groups. The deviations in distribution from the most probable distribution and the kinetics at 140° both show that the low-molecular weight polymers react most rapidly. Moreover the same distribution is observed for polymers prepared at lower temperatures where the kinetics (Fig. 2) indicate a slower reaction rather than a faster one at low degrees of polymerisation. Flory [1] also observed that the initial stages of reaction were slower than the later, and he pointed out that this was common to simple esterification also. He concluded that the changes in kinetics were due to changes in the characteristics of the medium and that there were no changes in the reactivity of the functional groups. Although we cannot agree with the latter conclusion we are unable to offer any alternative explanation to an effect of the medium for the changes in kinetics of reaction with temperature and time in the early stages. If we are correct the changes in medium on increase of molecular weight serve to increase the reactivity.

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