Structure of Copolymers Derived from Polymethacrolein by the Cannizzaro Reaction
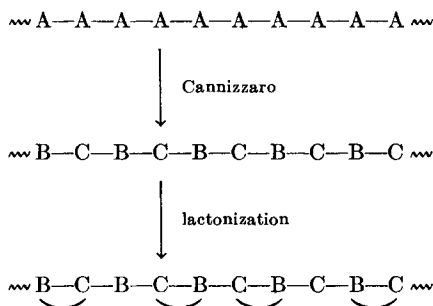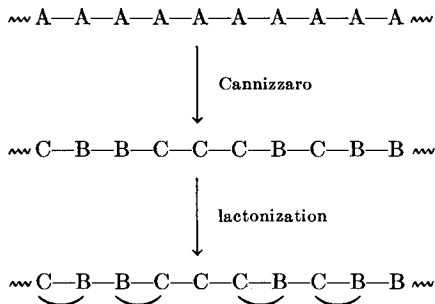
When polymethacrolein is subjected to the Cannizzaro reaction, a copolymer containing equimolar amounts of methallyl alcohol and methacrylic acid units is obtained in essentially quantitative yield.[1] This copolymer lactonizes spontaneously in acidic solution to form a product containing only 14% of the carboxyl groups initially present. Since this value is close to that expected[2] for the random cyclization of a strictly alternating methallyl alcohol–methacrylic acid copolymer, Smith and co-workers[1] concluded that an alternating copolymer results when polymethacrolein undergoes the Cannizzaro reaction. If A, B, and C represent aldehyde, alcohol, and acid units, respectively, Smith's interpretation of the Cannizzaro–lactonization sequence can be represented by the following equations, where lactone units are indicated by bridges:

$$\sim\!\!\sim A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A \sim\!\!\sim$$

$$\downarrow \text{Cannizzaro}$$

$$\sim\!\!\sim B\text{—}C\text{—}B\text{—}C\text{—}B\text{—}C\text{—}B\text{—}C\text{—}B\text{—}C \sim\!\!\sim$$

$$\downarrow \text{lactonization}$$

$$\sim\!\!\sim B\overset{\frown}{\text{—}C}\text{—}B\overset{\frown}{\text{—}C}\text{—}B\overset{\frown}{\text{—}C}\text{—}B\overset{\frown}{\text{—}C}\text{—}B\text{—}C \sim\!\!\sim$$

It seemed that the result of Smith et al. could also be explained by the following reactions:

$$\sim\!\!\sim A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A\text{—}A \sim\!\!\sim$$

$$\downarrow \text{Cannizzaro}$$

$$\sim\!\!\sim C\text{—}B\text{—}B\text{—}C\text{—}C\text{—}C\text{—}B\text{—}C\text{—}B\text{—}B \sim\!\!\sim$$

$$\downarrow \text{lactonization}$$

$$\sim\!\!\sim C\overset{\frown}{\text{—}B}\text{—}B\overset{\frown}{\text{—}C}\text{—}C\text{—}C\overset{\frown}{\text{—}B}\text{—}C\overset{\frown}{\text{—}B}\text{—}B \sim\!\!\sim$$

This alternate interpretation assumes that the Cannizzaro reaction occurs randomly between adjacent *pairs* of aldehyde units,[3] where possible. Aldehyde units that become isolated by this process are assumed to react at random with other units. Completion of the Cannizzaro reaction would thus yield a copolymer in which the acid and alcohol units tend to be associated in pairs, but there would not be any great tendency for the units to alternate.

A statistical calculation of the expected number of lactone units to form during the random lactonization of such a copolymer would seem difficult to accomplish. The Monte Carlo method was used, therefore, to simulate the Cannizzaro and lactonization reactions and to estimate the proportion of acid (and alcohol) units in the Cannizzaro product that would be unreacted in the lactonized material. Simulation of both reactions for a 216-unit cyclic polymer was accomplished in about 4 hr by tossing three dies to select monomer positions on the chain and by tossing dice to determine the course of equally likely events. (The choice was based upon whether or not the sum tossed was

greater or less than seven. Selection of monomer positions for a 104-unit polymer can be done very efficiently with a well-shuffled canasta deck.)

When the position contained an aldehyde group with two aldehyde neighbors, the dice were tossed to decide with which neighbor reaction took place. The position initially selected and the appropriate neighbor were then converted to acid and alcohol units, respectively. When the position selected had only one aldehyde neighbor, the position selected and the neighboring aldehyde position were converted to acid and alcohol sites, respectively. When an aldehyde site was selected that had no aldehyde neighbors, it was converted to an acid site, and dies were tossed to select an aldehyde site to become the corresponding alcohol site. This process was continued until all aldehyde units were converted to either acid or alcohol units. The lactonization process was simulated by an analogous procedure, except that when alcohol or acid sites were selected that had no neighbors with which to lactonize, such units were considered to be uncyclizable. The lactonization simulation was continued until no alcohol–acid junctions remained.

This simulation led to a final structure containing 15 (14%) unlactonized acid units and the same number of uncyclized alcohol units. It is interesting that more than two thirds of the uncyclized alcohol or acid units were within one or two units of positions where aldehyde units became isolated during the Cannizzaro reaction. The statistical aspects of the Cannizzaro reaction, for which Flory's analysis[2] would seem appropriate, thus have a strong influence on the outcome of the lactonization reaction.

The calculations were also done for 1000-unit polymers using an appropriately programmed IBM-360 computer and the IBM SUBROUTINE RANDU[4] to generate random numbers. The calculations were done 18 times, using randomly selected integers to initiate the RANDU routine. The average degree of lactonization obtained was 0.838 ± 0.008 (standard deviation). This value compares well with the value (0.858) obtained by Smith et al. and is also close to the value expected (0.865) for lactonization of a strictly alternating copolymer.[2]

The extent of lactonization cannot be measured accurately enough to decide between Smith's structure and ours. It seems that an intrasequence cyclization reaction (B—B or C—C) might be used for such a determination, however.

The possibility that the Cannizzaro reaction involves pairs of adjacent substituents in polymethacrolein and polyacrolein is in accord with previous work on polyacrolein[3,5] and model compounds[3,5] and with current concepts of the mechanism of this reaction.[6] Although a chain mechanism,[3] such as that shown below, might be envoked to explain the formation of an alternating structure, the formation of such would require that very long blocks of the polymer be in a polyacetal form, and this does not seem reasonable. We prefer to believe that the Cannizzaro reaction on polymethacrolein yields a product in which most of the acid and alcohol units are present as pairs, oriented randomly.
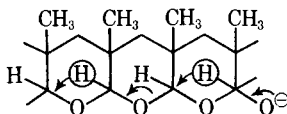
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