

# SYNTHESIS OF ALCOHOL ESTER OLIGOMERS AND THEIR REACTIONS WITH ACID ESTERS\*

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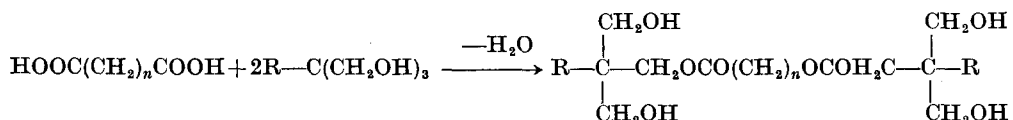
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THE synthesis of stereoregular polymers has received much attention in recent years [1-3]. The previous communication [4] described the synthesis of trifunctional acid ester oligomers with carboxyl end groups on the branches having the general formula  $RC[CH_2OCO(CH_2)_nCOOH]_3$ , in which  $R=CH_3$ , or  $C_2H_5$ . From these oligomers and the diglycidyl ester of 4,4'-dihydroxydiphenylpropane were produced polymers with a regular structure network having specific properties, differing from those of polymers with the same chemical composition but with an irregular structure.

This work deals with the synthesis of tetrafunctional alcohol ester oligomers with hydroxyl groups at the end of the branches and the production of polyesters with a crosslinked structure having a regular alternation of chain elements; these were produced by polycondensing the alcohol ester oligomers and acid esters containing the hydroxyl and carboxyl functional groups respectively.

The alcohol ester oligomers were produced by reacting dibasic aliphatic acids, such as glutaric, adipic, sebacic and azelaic, with trihydric alcohols, such as 1,1,1-trimethylolethane and 1,1,1-trimethylolpropane according to:



Earlier we found [2, 4] that the formation of acid ester oligomers with carboxyl groups at the end of the branches took place where the reaction was carried out with at least a twofold excess of acid. To clarify the conditions of synthesis, 1,1,1-trimethylolethane was reacted with dibasic acids using stoichiometric proportions as well as a twofold excess of the alcohol.

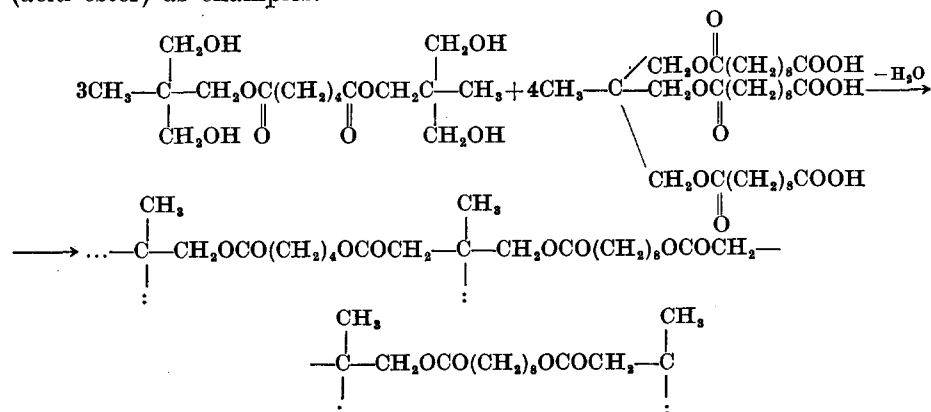
The tests showed that the alcohol esters formed already where stoichiometric quantities of alcohol and acid were used, and that the reaction progress was quantitative in such a case. The elemental analysis, molecular weight, content of functional groups, and other characteristics of the products did not differ from

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those of alcohol esters synthesized with an excess of alcohol present. All subsequent reactions were therefore carried out with stoichiometric quantities of alcohol and acid.

The properties of the tetrafunctional alcohol esters are given in Table 1. The infrared spectra analysis of these compounds (carried out by N. P. Gashnikova) established that absorption line intensities appeared in the range  $1055\text{ cm}^{-1}$ , which are direct confirmation of the presence of primary alcohols. The presence of the alcohol OH group is also indicated by the strongly displaced  $3500\text{ cm}^{-1}$  absorption line, representing to a larger extent the alcohol hydroxyls rather than those of acids. The absorption lines representing the valence oscillations of the hydroxyls of carboxyl groups were not found in the spectrum. These findings, together with the results of elemental and functional analysis, molecular weights, ester and acid values, are given in Table 1 and confirm the composition of the produced alcohol esters; these were viscous liquids soluble in methanol and ethanol, acetone, methylethylketone, dioxane, cyclohexanone, ethyl cellosolve. The glass temperatures of the alcohol esters ranged from  $-15$  to  $-37^\circ\text{C}$  and depended on the nature of the alcohols and acids used as starting materials. As Table 2 shows, the glass temperature of the compounds produced from 1,1,1-trimethylolpropane were lower by  $3-8^\circ\text{C}$  than those produced from 1,1,1-trimethylolethane. An increase of the number of methylene groups in the original acid reduced the glass temperature and this was evident to a larger extent where the number of methylene group was odd.

The synthesized tetrafunctional alcohol ester oligomers were used to produce polyesters with a stereoregular structure by polycondensing them with the earlier produced [4] trifunctional acid esters having carboxyl terminal groups as branches. The reaction was examined by using the reaction of bis-(1,1,1-trimethylolethane) adipate (alcohol ester) and 1,1,1-trimethylolethane trisebacate (acid ester) as examples:



The above scheme shows that the result of the reaction of alcohol ester oligomers with acid esters gave a mixed polyester (copolyester) with regularly alternating units between the branching points.

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