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POLYMERIZATION OF BENZYL ALCOHOL AND ITS DERIVED COMPOUNDS WITH AN ION EXCHANGE RESIN

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Benzyl alcohol, benzyl chloride and dibenzyl ether polymerize in certain conditions in the presence of ion exchange resins in the H^+ form to give a polymer of the general formula $(C_6H_4CH_2)_n$. Independently of the reactant, this result allows to establish reaction mechanism based solely on the acid-base equilibrium in the Brönsted or Lewis meaning and independently of the catalyst type: sulfuric acid, stannic chloride or ion exchange resin.

Бензиловый спирт, хлористый бензил и дибензиловый эфир полимеризуются в определенных условиях в присутствии ионообменной смолы в форме H^+, давая при этом полимер с общей формулой $(-C_6H_4CH_2-)_n$. Независимо от реактивности, этот результат позволяет установить реакционный механизм, основанный на кислотно-основном равновесии по Брёнстэду или Льюису, для любого типа катализатора: серная кислота, четыреххлористое олово или ионообменная смола.

INTRODUCTION

Benzyl alcohol(I), benzyl chloride(II) and dibenzyl ether(III) can polymerize in the presence of concentrated sulfuric acid (a) or stannic chloride (b) /1, 2/.

This paper reports the comparable results obtained on an ion exchange resin in the H^+ form (c).

Furthemore, the consideration of the problem from the thermodynamic aspect, these observations allow to suggest a general description of the polymerization phenomenon. This interpretation is independent of the reactant(I), (II) or (III) and of catalyst (a), (b) or (c) used.

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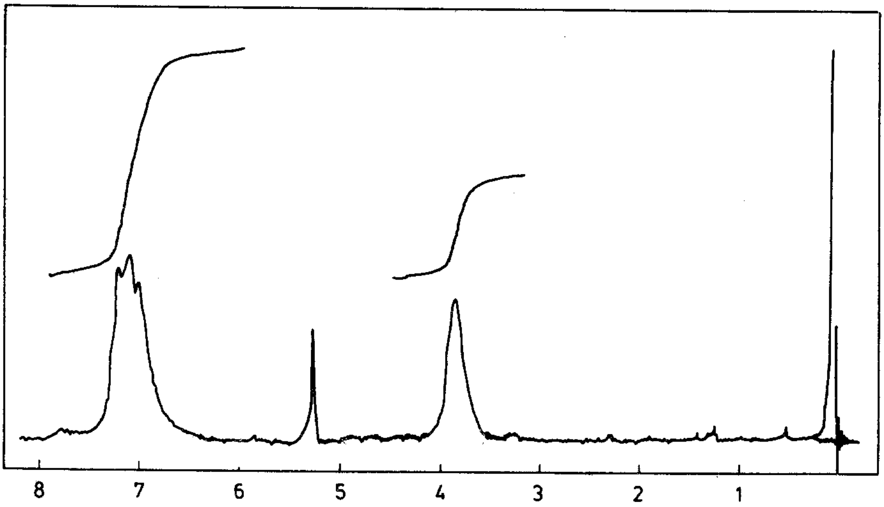


Fig. 1. Nmr (^1H) spectrum of the polymer: $H(C_6H_4-CH_2)_n R$; The abscissa represents the chemical shift (δ) relative to tetramethylsilane

RESULTS AND DISCUSSION

The syntheses are carried out in a 250 ml three-necked bottle supplied with:

- a Dean Stark apparatus for eliminating the water formed,
- a magnetic stirrer,
- a thermometer.

They are carried out at the boiling temperature of toluene used as solvent. The ion exhange resins are Lewatit SP 120 or Amberlyte 15.

Before each synthesis, toluène (100 ml) and the resin (5 g) are kept boiling in order to eliminate completely the residual water of the resin. Then, the reactant (20 ml) of the general formula $C_6H_5CH_2R$ (with R = OH (I), R = Cl (II) or R = $O-CH_2C_6H_5$ (III) is added.

Upon applying the resin in the H^+ form as catalyst, a precipitate is quickly formed. If the resin is in a metal cation form (e.g. Ag^+, Na^+) no precipitation is observed.

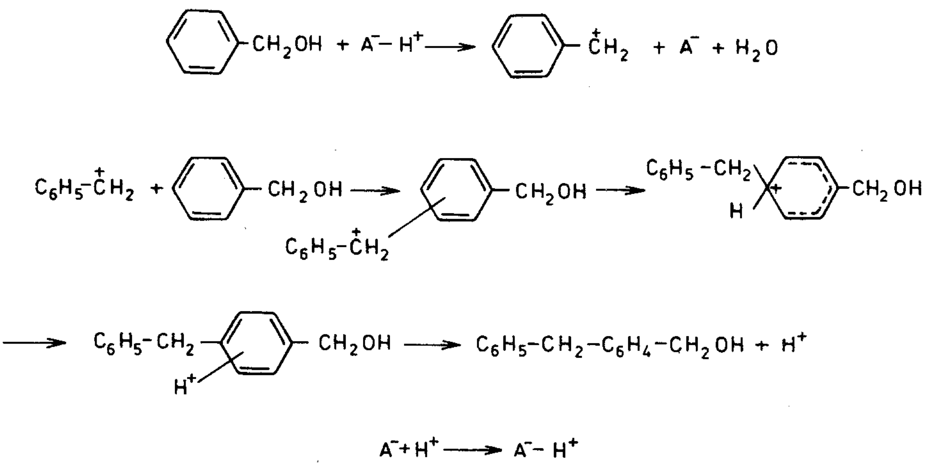
With an anion exchange resin in the Cl^- form, a slow reaction is observed. No results are observed with a resin in the OH^- form.

In the presence of the ion exchange resin, the appearance of a solid polymer corresponds to the formation of a second solid phase. These two phases are separated by decantation with dichloromethan. The fraction of polymer dissolved in the dichloromethan may be recovered after the evaporation of this solvent.

The evolution of the synthesis reaction is followed by chromatography on OV 101 Varian column.

The obtained solid polymer is studied by elementary analysis, infrared spectroscopy and proton NMR (Fig. 1). Together, these results confirm that the composition of the solid corresponds to the form $H -C_6H_4CH_2-_n R$ and it is comparable, in all respects, to that obtained from concentrated sulfuric acid (a) or stannic chloride (b) /1, 2/.

The degree of polymerization is determined by cryoscopy in benzene /3, 4/ and it varies between 12 and 25.



Scheme:

Polymerization mechanism with an ion exchange resin in the H^+ form

Scheme represents the reaction mechanism of polymer synthesis, when the catalyst is anion exhcange resin in the H^+ form. The ion exchange resin is noted A^--H^+, A^- symbolizing the macromolecular net of the resin.

Reaction mechanisms proposed in the literature differ in the catalyst used /1, 2, 5–7/ but, taking into account the results obtained with anion exchange resin used as catalyst, it is possible to suggest reaction mechanisms valid for reactants (I), (II) and (III) and catalysts (a), (b) or (c).

This thermodynamic interpretation makes use only of classic types of reactions comparable to those proposed by Brönsted or Lewis /8, 9/ and applies classic equilibria in solution.

Step 1 is the appearance of a solvate carbocation.

The competition of two molecular species, $C_6H_5CH_2R$ and R^-, to form this carbocation gives respectively the entities $C_6H_5CH_2^+$, $C_6H_5CH_2R$ and $C_6H_5CH_2R$:

$$2C_6H_5CH_2R \rightleftharpoons C_6H_5CH_2^+, \; C_6H_5CH_2R + R^-$$

In Step 2, the catalyst interacts with the substrate, being a Brönsted acid ((a) and (c)) or a Lewis acid (b):

$$\text{(a)} \qquad H_2SO_4 + 2\,R^- \rightleftharpoons 2\,HR + SO_4^{--}$$

$$\text{(b)} \qquad SnCl_4 + 2\,R^- \rightleftharpoons SnCl_4,\ 2\,R^-$$

$$\text{(c)} \qquad 2\,A^-{-}H^+ + 2\,R^- \rightleftharpoons 2\,HR + 2\,A^-$$

Stage 3 is the process of polymerization. First of all the dimer is formed:

$$\text{(a)} \quad 2C_6H_5CH_2,\ C_6H_5CH_2R^+ + SO_4^{--} \rightleftharpoons 2C_6H_5CH_2C_6H_4CH_2R + H_2SO_4$$

$$\text{(b)} \quad 2C_6H_5CH_2,\ C_6H_5CH_2R^+ + SnCl_4, 2R^- \rightleftharpoons 2C_6H_5CH_2C_6H_4CH_2R + SnCl_4, 2HR$$

$$\text{(c)} \quad 2C_6H_5CH_2,\ C_6H_5CH_2R^+ + 2A^- \rightleftharpoons 2C_6H_5CH_2C_6H_4CH_2R + 2A^-{-}H^+$$

Finally, the dimer gives rise to the formation of a new carbocation $C_6H_5CH_2C_6H_4CH_2^+$ in accordance with the description proposed in stage 1.

The process can thus continue.

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