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Schiff bases of polyvinylbenzaldehyde and chemical release of amines

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Summary

Polyvinylbenzaldehyde reacts with primary amines with an acidic catalyst to give polymeric Schiff bases. The hydrolyses of these imines have been studied in acidic medium at pH = 1,2 or in pure water at pH = 6,5.

Introduction

In a previous report 1) it was shown that Schiff bases prepared by polymerization of imines of vinylbenzaldehyde 1 underwent hydrolyses under acidic conditions in water at pH = 1,2 with different behaviours. The vinylbenzaldehyde has been chosen as a starting monomer because constituted by a phenyl group as a spacer and an al-dehyde group to attach various amines. We may also use polyvinylbenzaldehyde which can react with primary amines to give polymeric imines.Polyvinylbenzaldehyde 2 can be prepared according to various procedures : oxydation of polychloromethyla-ted styrene 2) or polymerization of vinylbenzaldehyde. As polyvinylbenzaldehyde has numerous applications its polymerization and copolymerization reactions have been widely studied. By using a radical initiator it was generally observed chain transfer reaction broadening the molecular weight distribution of the resulting pro-ducts 3). Polyvinylbenzaldehyde with narrow molecular weight distribution can be synthesized by means of the anionic living polymerization of 1,3 dimethyl-2 (4-vinyl-phenyl) imidazoline 4) followed by the removal of the imidazoline ring from the resulting polymer. In spite of the broad molecular weight distribution a radical initiator has been used to prepare the polyaldehyde 2.

The chemical modifications of aldehyde 2 with aniline, benzylamine, phenylethylami-ne and phenylpropylamine and the hydrolysis reactions of corresponding imines are now described.

Experimental

Molecular masses of polymers have been measured with a Knauer apparatus and Ultrastyragel columns 10^4-10^5 Waters (0,7 ml / min). Polystyrene standards have been used for the calibration. Glass Transition temperatures have been measured with D.S.C. 101 Setaram : mass samples 10-15 mg, heating rate 10° / min. The amine release study has been carried out in water at pH = 1,2 prepared as previously des-described 1) and the rate of amine release from the polymer has been measured by using a U.V. Spectrometer Hitachi U1100. Infra-red spectra have been recorded with a Beckmann apparatus (KBr). Vinylbenzaldehyde 1 has been synthesized from vi-nylbenzylchloride (mixture of meta and para isomers ; 60 /40) according to a known procedure 5) by using the Sommelet reaction. Polyvinylbenzaldehyde has been pre-pared by heating vinylbenzaldehyde 1 with 1 % in weight of azobisisobutyronitrile in a sealed tube during 20 hours at 70° C. The solid material is dissolved in chloroform and precipitated by petroleum ether. After two precipitations the product is dried under vacuum during two days. The polymeric Schiff bases 3 have been prepared by

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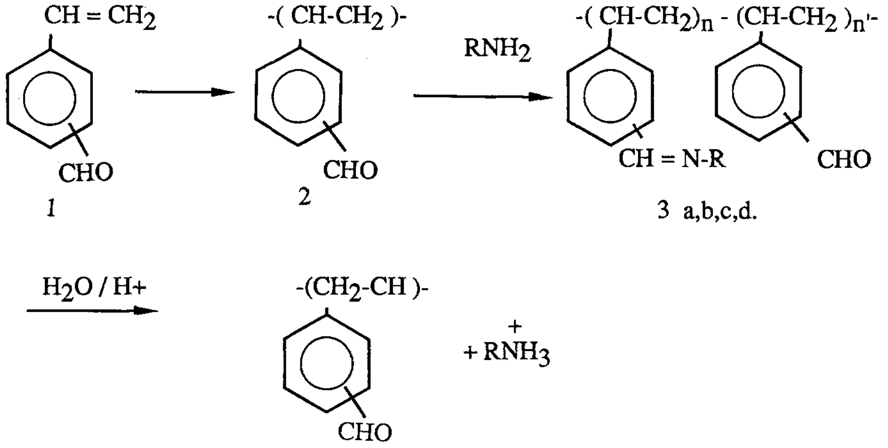
*To whom offprint requests should be sent heating a mixture of 2 (0,05 M), with a primary amine (0,05 M) and 50 mg of p. toluensulfonic acid as a catalyst in a chloroform solution. After removal of water during 8 hours the solution is cooled then neutralized with 10 ml of NaOH(1N) dried with sodium sulfate and the chloroform is evaporated. IR : 1640cm^{-1} (CH = N).

The percentages of modified polymer have been calculated by microanalyses of products 3 a, b, c, d, (percentages of oxygen and nitrogen). These results, with the molecular masses of polymers 3, their glass transition temperature are given in tabl.



a) $R=C_6H_5$ b) $R=C_6H_5CH_2$ c) $R=C_6H_5CH_2CH_2$ d) $R=C_6H_5CH_2CH_2CH_2$

Fig 1 : Preparation of modified polyvinylbenzaldehyde and hydrolysis reactions

Tab. 1 : Molecular masses of polymers 2, 3 a, b, c, d. Glass transition temperatures (T_G) and percentages of modifications of polyaldehyde 2 (n %).

Polymers	$\overline{Mn}$	$\overline{Mw}$	$\overline{Mw}/\overline{Mn}$	T_G	n %
2	14000	65000	4,65	132	
3a	36000	124000	3,5	94	90
3b	20000	43000	2,15	49	91
3c	32000	54000	1,69	46	95
3d	20000	40000	2	24	97

The abnormal variations of molecules masses observed for polymers 3 a, b, c, d, result from the high polymolecularity of product 2. Polymers 3 a, b, c, d, are twice dissolved in chloroform and precipitated with petroleum ether, therefore the low molecular masses are removed from the mixture of polymers.

Results and discussion

The hydrolyses reactions of polymeric Schiff bases have been carried out in an heterogeneous medium by soaking a sample of polymer 3 a, b, c, d (50 mg) in 100 ml of water at pH = 1,2 and in pure water (pH = 6,5). The main results of hydrolyses studies are given in tab. 2

Tab. 2 Percentages of released amine by hydrolysis of polymers 3 a, b, c, d in acidic medium (pH = 1,2) and in pure water (pH = 6,5).

Polymers	pH	Time (hours)	0,5	1	2	3	4	5	6	7	8
3a	1,2		14	22	33	43	51	59	67	68	70
3a	6,5		3,7	5,5	8,5	11	12	13	13,5	14	15
3b	1,2		35	56	73	80	84	85	86	87	88
3b	6,5		5,7	7	8,7	10	11,5	13	14	15,5	17
3c	1,2		43	53	62	69	71	72,5	73	74	74,5
3c	6,5		6,7	8,7	10,5	12	12,5	13	14	15	16
3d	1,2		8	13	18	22	24	26	27	28	31
3d	6,5		4,5	5,5	7,5	8	9	9,2	9,5	9,7	10

The kinetics of released amines from polymers 3 a, b, c, d at pH = 1,2 are given in Fig. 2

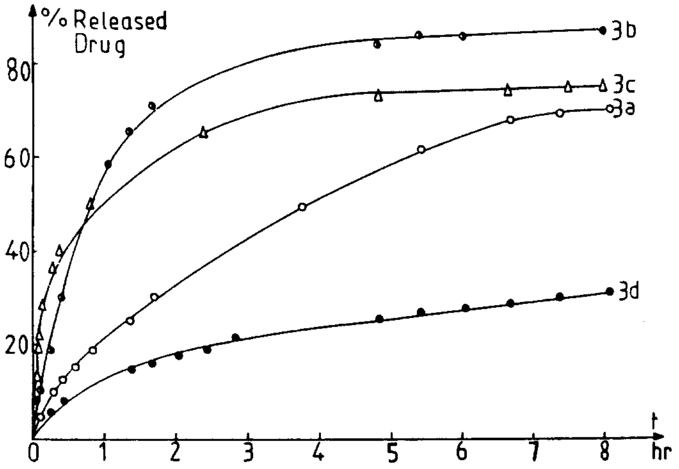


Fig. 2 : Kinetics of released amines from polymers 3 a, b, c, d in acidic medium at pH = 1,2. T = 37°C

In Fig. 3 a plot of released amine, in acidic medium, versus to the square root of the time is given.

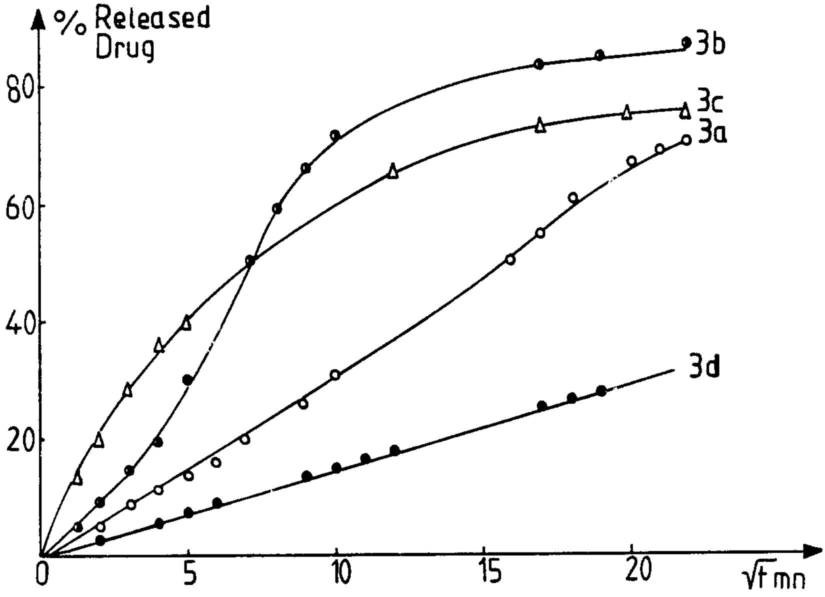


Fig. 3 : % Released drug as a function of the square root of time for 3 a, b, c, d at pH = 1,2 . T = 37°C

These experimental kinetics of release cannot be expressed by first or second order reactions. In fact the process is more complex, as the release of the amine is partially controlled by diffusion of the liquid into and diffusion of the amine out of the polymer (6,7).The whole process can thus be described in terms of a three-step process (8) :
i - Diffusion of the liquid into the polymer, with subsequent swelling of the polymer yielding to a gel.
ii- Reaction between the liquid and the active part of the polymer, releasing the amine.
iii- Diffusion of the amine through the liquid located into the swollen polymer.
Of course, the diffusivity for the liquid may vary with time, as the amount of liquid rises up to a high extent. Moreover, the diffusivity of the amine depends largely on the concentration of the liquid located in the polymer (9,10). Diffusion studies are extremely difficult in the present case for the following two reasons :
i- a double matter transfer takes place through the polymer, the transfer of amine being coupled with the transfer of liquid.
ii- a swelling of the polymer is observed, as well as a gel formation. The polymer, initially in state of solid grains with a distribution of the size of these grains, turns into an homogeneous gel.Similar results have been observed when the polymeric Schiff bases are soaked in pure water (pH = 6,5) but the durations of hydrolyses are longer. This observation is in good agreement with the known mechanism of hydrolysis of Schiff bases with acidic catalysis [11], but a good correlation

$$-CH{=}N\text{-}R + H^+ \rightleftharpoons -CH = \overset{+}{N}H\text{-}R$$

$$-CH = \overset{+}{N}H - R + H_2O \rightleftharpoons -CHOH\text{-}NH\text{-}R + H^+$$

$$-CHOH\text{-}NH\text{-}R \rightleftharpoons -CHO + RNH_2$$

between the nature of released amine or corresponding cation and the rates of hydrolyses was not observed and the cause of the relatively slow hydrolysis rate of imines with phenylpropylamine has not so for been explained.

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