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Abstract

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PHYSICAL CHEMISTRY

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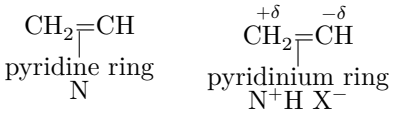
POLYMERIZATION OF 4-VINYLPYRIDINE ON POLYSTYRENESULFONIC ACID

In work ([1]) it was shown that, upon interaction of 4-vinylpyridine with haloalkyls and strong low-molecular-weight acids, a specific ionic polymerization occurs, which ensures strict selection into the polymer composition of only those 4-vinylpyridine (4-VP) molecules that have entered into the salt-formation reaction.

The mechanism of polymerization is assumed to reduce to the following. The first stage consists in neutralization of the pyridine base by an acid, with formation of a pyridinium salt (I)

$$CH_2{=}CH + HX \longrightarrow \overset{+\delta}{C}H_2{=}\overset{-\delta}{C}H \qquad (I)$$



The appearance of a positive charge on the nitrogen atom leads to strong polarization of the monomer double bond and makes it possible to initiate polymerization according to one of schemes (II) or (III)

$$\overset{+\delta}{C}H_2{=}\overset{-\delta}{C}H \longrightarrow X{-}CH_2{-}\overline{CH} \qquad (II)$$

$$2\,\overset{+\delta}{C}H_2{=}\overset{-\delta}{C}H \longrightarrow X{-}CH_2{-}CH{-}CH_2{-}\overline{CH} \qquad (III)$$

Fig. 2

Figure 1: Fig. 2

Fig. 1. IR spectra: a—4-VP; b—poly-4-vinylpyridine; c—product of interaction of previously synthesized poly-4-vinylpyridine and PSSA; d—product of interaction of 4-VP with PSSA

Figure 2: Fig. 1. IR spectra: a—4-VP; b—poly-4-vinylpyridine; c—product of interaction of previously synthesized poly-4-vinylpyridine and PSSA; d—product of interaction of 4-VP with PSSA

The active center formed can add molecules of the pyridinium salt (IV)

$$\mathrm{X{-}CH_2{-}CH{-}CH_2{-}\overline{CH}{+}CH_2{=}CH \longrightarrow X{-}CH_2{-}CH{-}CH_2{-}CH{-}CH_2{-}\overline{CH}}\ \text{and so on} \qquad (IV)$$

Addition of a molecule of 4-VP that has not entered into the neutralization reaction is considerably less probable, since, first, the electron-cloud density of its double bond is considerably higher and, second,

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Fig. 2. *a* —37,000×, *b* —37,500×, *v* —540×, *g* —147,000×, *d* —144,000×, *e* —113,000×, *zh* —209,000×.

such an act would require separation of the positive and negative charges interacting through the system of π-bonds of the pyridine ring (V)

$$\sim \mathrm{CH_2-\overline{CH}+CH_2{=}CH} \nrightarrow \sim \mathrm{CH_2-CH-CH_2-\overline{CH}} \qquad (V)$$

In this article the results are described of a study of the interaction of 4-vinylpyridine with a strong polymeric acid—polystyrenesulfonic acid—

Fig. 1. IR spectra: *a*—4-VP; *b*—poly-4-vinylpyridine; *c*—product of interaction of previously synthesized poly-4-vinylpyridine and PSSA; *d*—product of interaction of 4-VP with PSSA

—PSSA. The data of (1) and the considerations presented make it possible to hope that, in the case under consideration, only those molecules of 4-VP that prove to be bound to the PSSA chains will be able to enter into polymerization, i.e., growth of the polyvinylpyridine chains will proceed directionally along the PSSA macromolecules.

In our experiments PSSA obtained by radiation polymerization of styrenesulfonic acid was used. The reduced viscosity of PSSA in aqueous solution at a concentration of 0.084 g/100 ml is equal to 4.9.

It turned out that, upon addition to 4-VP of a 30% solution of PSSA in methanol (molar ratio 4-VP : PSSA = 10 : 1), a rapidly hardening precipitate immediately separates. An analogous phenomenon is observed if, instead of 4-VP, 2-methyl-5-vinylpyridine (2-M-5-VP) is taken. However, in this case

formation of a precipitate proceeds somewhat more slowly. When a solution of PSSA is mixed under analogous conditions with γ-picoline, which may be regarded as a nonpolymerizing model of the vinylpyridines, a salt is obtained that is readily soluble in methanol. This fact in itself indicates that the formation of vinylpyridinium ions is accompanied by polymerization.

Figure 1 presents the IR spectrum of the product of the interaction of 4-VP with PSSA (*d*). For comparison, the spectra of vinylpyridine (*a*) and poly-4-vinylpyridine (*b*) are also given there. It is characteristic that in all the spectra, except that of 4-VP, the band in the region of 926 cm^{-1}, assigned to deformation vibrations of C–H in the vinyl group, is absent. The absence of this band in spectrum *d* confirms the supposition that polymerization occurs during the formation of the salt of 4-VP with PSSA. It may be assumed that, as a result, aggregates are formed from macromolecules of polyvinylpyridinium and PSSA, linked by salt bonds (VI).

Spectrum (*c*) corresponds to a model of the proposed polymerization product, obtained by mixing solutions of previously synthesized poly-4-vinylpyridine and PSSA. This spectrum practically coincides with spectrum (*d*).

Elemental analysis of the products of the interaction of 4-VP and PSSA gave the following results:

Found, %:	N 4.6; S 10.0
Calculated for the stoichiometric salt, %:	N 4.85; S 11.07

Within the errors of determination, the value found is close to that calculated for the stoichiometric salt. This result shows that, despite a 10-fold molar excess of 4-VP, only those 4-VP molecules that have formed a salt with PSSA enter into polymerization. Consequently, the PSSA macromolecule plays the role of a selective polymeric activator, ensuring the polymerization of the vinylpyridinium ions bound to it.

$$\begin{array}{c} -CH_2-CH- \\ \left|\begin{array}{c} C_6H_4 \\ SO_3^- \\ H \\ N^+ \\ C_5H_4 \end{array}\right| \\ -CH_2-CH- \end{array} \qquad \text{(VI)}$$

It is noteworthy that polymerization also occurs when an aqueous solution of PSSA and vinylpyridine are mixed. The IR spectra of the products of interaction in aqueous solutions are analogous to that shown in Fig. 1*d*. The proposed specific ionic mechanism of polymerization is probably also realized in an aqueous medium.

It is further of interest to establish what structural forms arise during the polymerization of 4-VP on PSSA. For this purpose, methods of electron and optical microscopy were used.

Figures 2*a* and *b* (see insert on p. 1118) show electron micrographs of the product obtained in the polymerization of 4-VP in a 30% methanolic solution of PSSA, isolated and then dissolved in a mixture of concentrated hydrochloric acid and methanol (*a*–0.01% solution, *b*–0.001% solution). Upon dilution of the solution from which the specimens were prepared, it is possible to trace the transition from large globular aggregates (Fig. 2*a*) to globules of molecular dimensions (Fig. 2*b*). In methanolic solution, PSSA macromolecules are relatively weakly ionized and are coiled into globules. The 4-VP molecules penetrate inside these globules, enter into the neutralization reaction, and polymerize. As a result, disordered globular aggregates are formed. However, repeated reprecipitation of the polymerization product with water leads to the unfolding of the globules and the spontaneous appearance of ordered fibrous structures of the polymer salt. Figure 2*c* presents a photograph of one of such fibrils, taken with an optical microscope in polarized light.

A different picture is observed during polymerization in aqueous solution. In water, the macromolecules of PSSA are strongly ionized and, owing to the electrostatic repulsion of the side groups, are rigid charged rods surrounded by a cloud of oxonium counterions. Therefore, neutralization of PSSA by vinylpyridine and the subsequent polymerization of the activated monomer molecules take place on already extended macromolecules. In Fig. 2a–e are shown electron micrographs of the products of interaction of PSSA and 4-VP in aqueous solutions. The samples were prepared as follows. To a dilute (0.01–0.001%) aqueous solution of 4-VP, PSSA was added in an amount sufficient to neutralize approximately 0.1 of the 4-VP contained in the solution. Then a drop of the solution was applied to a grid with a collodion substrate. In this case, as was to be expected, ordered aggregates of the fibrillar type are formed as a result of polymerization. When samples are prepared from highly dilute solutions (0.0003%), a distinctive spiralization of the fibrils is clearly observed (Fig. 2g). This spiralization may be a consequence of the appearance of internal stresses due to redistribution of interatomic distances occurring during the growth of macromolecules from monomer molecules chemisorbed on PSSA.

Thus, using the previously discovered phenomenon of specific polymerization of vinylpyridinium salts ([1]), we have succeeded in observing the spontaneous formation of ordered structures during the synthesis of polyvinylpyridine macromolecules on PSSA macromolecules. The latter perform the function of catalytic "matrices" capable of attaching, activating, and selectively polymerizing

vinylpyridine molecules adsorbed on them.

In conclusion, the authors express their gratitude to the staff of the laboratory of M. M. Kusakov for recording the IR spectra.

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[1] V. A. Kargin, V. A. Kabanov, K. V. Aliev, E. F. Razvodovskii, *DAN*, **160**, No. 3, 604 (1965).

Note: Figure translations are in progress. See original paper for figures.