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Figure 1

Figure 1: Figure 1

Abstract

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SPECIFIC POLYMERIZATION OF 4-VINYLPYRIDINE SALTS

When 4-vinylpyridine (4-VP) interacts with alkyl halides (Menshutkin reaction), instead of monomeric quaternary salts, colorless hygroscopic high-molecular-weight amorphous substances are formed, soluble in water and in methanol. These substances contain no vinyl groups or tertiary pyridine rings (as established by determination of bromine numbers and by titration with HCl) and are typical polyelectrolytes. Figure 1 presents the dependences of the reduced viscosity (η_{sp}/c) of one of the samples on concentration, measured in water and in 0.05 N KBr solution. In the region of low polymer concentrations, the increase in η_{sp}/c characteristic of polyelectrolytes is observed; it is removed when the ionic strength of the solution is increased.

Fig. 1. Dependence of the reduced viscosity of the product of interaction of 4-VP with ethyl bromide on its concentration in solution. Solvents: *1* —water, *2* —0.05 N KBr solution

The complete elemental composition of the high-molecular-weight products obtained in the interaction of 4-VP with ethyl bromide in various solvents (benzene, acetonitrile, methanol) at different molar ratios of the components (from 1:3 to 3:1) corresponds, within the limits of analytical error, to poly-4-vinylpyridinium ethyl bromide. In an excess of 4-VP, formation of the polymer ceases simultaneously with consumption of the alkyl halide: unreacted 4-VP remains in the system. This indicates a close connection between salt formation and polymerization and, together with the data on elemental composition, shows that only those 4-VP molecules that enter into the Menshutkin reaction participate in the polymerization.

Strong inhibitors of radical polymerization—benzoquinone and diphenylpicrylhydrazyl—do not inhibit the reaction and do not lower the molecular weight of the polymers. Consequently, a radical polymerization mechanism is excluded. When 4-VP interacts with ethyl bromide in a styrene medium, the polymer formed contains no styrene units. This also makes it possible to exclude the possibility of a cationic mechanism, since in styrene the electron density of the double-bond cloud ($e_1 = -0.8$) is higher than in 4-VP ($e_2 = -0.2$), i.e., in cationic polymerization a copolymer enriched in styrene should have been obtained.

All the facts listed above compel the supposition that the polymerization proceeds by a specific mechanism that ensures the selection into the polymer composition only of those 4-VP molecules that have entered into the Menshutkin reaction, which is the first stage of the process:

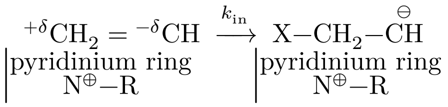
$$\text{RX}+\text{CH}_2\text{=CH} \underset{\text{pyridine ring with } N}{|} \xrightarrow{k_1} \text{CH}_2\text{=CH} \underset{\text{pyridinium ring with } N^+R}{|} \ X^- \tag{1}$$

The rate of this stage (v_1) can be expressed as:

$$v_1 = k_1 x^2, \tag{1}$$

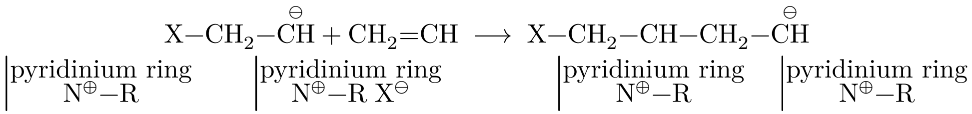
where k_1 is the rate constant of the Menshutkin reaction; x is the molar concentration of 4-VP and of the alkyl halide, which, for simplicity, are taken to be equal.

In the molecule of the monomeric salt formed, owing to the appearance of a positive charge on the nitrogen atom, a shift of the π-electrons of the double bond toward the pyridine ring occurs. In connection with this, intramolecular rearrangement may occur with some probability, leading to the formation of an ionic dipole:

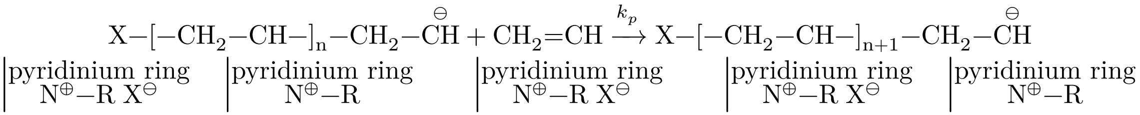


$$\underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R}}}{{}^{+\delta}\text{CH}_2 = {}^{-\delta}\text{CH}} \xrightarrow{k_{\text{in}}} \underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R}}}{\text{X}-\text{CH}_2-\overset{\ominus}{\text{CH}}} \tag{II}$$

This dipole initiates polymerization. It is capable of adding other molecules of the quaternary salt according to the scheme:



$$\underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R}}}{\text{X}-\text{CH}_2-\overset{\ominus}{\text{CH}}} + \underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R X}^{\ominus}}}{\text{CH}_2\text{=CH}} \longrightarrow \underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R}}}{\text{X}-\text{CH}_2-\text{CH}}-\underset{\substack{|\text{pyridinium ring}\\ \text{N}^{\oplus}-\text{R}}}{\text{CH}_2-\overset{\ominus}{\text{CH}}} \tag{III}$$



$$X{-}[{-}CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R\;X^{\ominus}}}{CH}{-}]_n{-}CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R}}{\overset{\ominus}{CH}} + CH_2{=}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R\;X^{\ominus}}}{CH} \xrightarrow{k_p} X{-}[{-}CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R\;X^{\ominus}}}{CH}{-}]_{n+1}{-}CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R}}{\overset{\ominus}{CH}}$$

(III')

The rate of initiation (v_{in}) can be expressed by the equation:

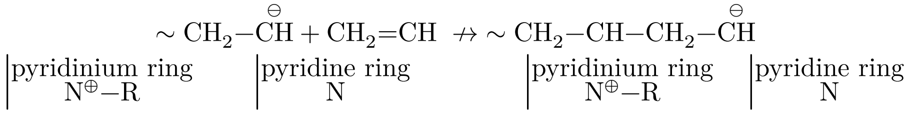
$$v_{\text{in}} = k_{\text{in}} m = \frac{da}{dt}, \tag{2}$$

where k_{in} is the rate constant; m is the molar concentration of the quaternary salt; a is the molar concentration of the initiating dipoles.* The rate of polymerization (v_{pol}) is given by the equation:

$$v_{\text{pol}} = k_p a m \simeq -\frac{dm}{dt}, \tag{3}$$

where k_p is the rate constant of chain growth.

Molecules of 4-VP that have not entered into the Menshutkin reaction cannot compete for the active center, first, because the double bond of 4-VP is characterized by a relatively high electron-cloud density in comparison with the double bond of the quaternary salt, and, second, because upon addition of 4-VP to the growing chain, separation of the opposite charges initially interacting through the system of π-bonds of the pyridine ring would have to occur:



$$\sim CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R}}{\overset{\ominus}{CH}} + CH_2{=}\underset{\substack{|\text{pyridine ring}\\ N}}{CH} \nrightarrow \sim CH_2{-}\underset{\substack{|\text{pyridinium ring}\\ N^{\oplus}{-}R}}{CH}{-}CH_2{-}\underset{\substack{|\text{pyridine ring}\\ N}}{\overset{\ominus}{CH}}$$

This is associated with a substantial increase in the energy of the system. The second reason, probably, must account for the nonreactivity of the growing chain toward most other monomers.

If the proposed reaction scheme is correct, then it should be expected that vinylpyridines in which the double bond is located in positions 3 or 5 will be less prone to polymerization by the adopted mechanism, since for them the appearance of a positive charge on the nitrogen atom should be accompanied by a smaller polarization of the double bond. Indeed, when 2-methyl-5-vinylpyridine is allowed to react with ethyl bromide under analogous conditions, a crystalline monomeric quaternary salt is formed.

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* It is possible that the initiation stage should be regarded as the totality of transformations II and III′. This question requires a special kinetic study.

Fig. 2

Figure 2: Fig. 2

Fig. 2. Dependence of the polymerization rate in the 4-VP—ethyl bromide system on the nature of the solvent. Initial concentrations of reagents 3 mol/l. 1, 2 —temperature 40°, solvents benzene and acetonitrile, respectively; 3, 4 —temperature 50°, solvents benzene and nitrobenzene, respectively

Figure 2 presents kinetic curves of polymerization in the 4-VP—alkyl halide systems. It is seen that, for the given alkyl (ethyl bromide), the polymerization rate increases on going to polar solvents (Fig. 2). In one and the same solvent (nitrobenzene) the polymerization rate increases on going from butyl bromide to ethyl bromide, i.e., with a decrease in the length of the hydrocarbon radical (Fig. 3). Polymerization is retarded if, instead of alkyl bromides, the corresponding alkyl chlorides are introduced into the reaction. Similar kinetic regularities are characteristic of Menshutkin reactions. The total activation energy, calculated from the temperature dependence of the polymerization rate in the 4-VP—ethyl bromide system (solvent benzene), proved to be equal to 15 kcal/mol. This value corresponds to activation energies usually observed in Menshutkin reactions (ˆ1). It may be assumed that formation of the quaternary salt in the present case is the rate-limiting stage of the process. Then the steady-state condition is fulfilled: $dm/dt = k_1 x^2 - k_{pam} = 0$. Assuming the absence of termination and chain transfer, the number-average degree of polymerization ($\overline{P}_n$) of the polymer formed over time t is given by the equation:

$$\overline{P}_n = \int_0^t v_{\text{pol}}\,dt \Big/ \int_0^t v_{\text{in}}\,dt = \int_0^t k_p a m\,dt \Big/ \int_0^t k_{\text{in}} m\,dt. \tag{4}$$

Expressing m from the steady-state condition, substituting a as a function of t, which can be found by integrating kinetic equations (1) and (2), and integrating the numerator and denominator of equation (4), we obtain:

$$\overline{P}_n = \frac{\sqrt{2}}{2} \cdot \frac{k_p^{1/2} x_0^{1/2}}{k_{\text{in}}^{1/2}} q^{1/2}, \tag{5}$$

where x_0 is the initial concentration of 4-VP and the alkyl halide; $q = (x_0 - x)/x_0$ is the conversion. It follows from equation (5) that the degree of polymerization should increase with conversion. The experimental dependences of the intrinsic viscosity ($[\eta]$) of polymers obtained from 4-VP and ethyl bromide in benzene on conversion are in qualitative agreement with those predicted by the theory (Figs. 3, 4). During polymerization in media with a high dielectric constant and in solvents, containing relatively mobile protons, this regularity is not observed. On the basis of data on the polymerization of quaternary salts of 4-VP with alkyl halides, we assumed that similar processes may also occur in the formation of salts of 4-VP with strong protonic acids, since addition of a proton to the nitrogen atom of the pyridine ring should likewise lead to substantial polarization of the double bond. Indeed, mixing 4-VP with sulfuric, hydrochloric, nitric, and toluenesulfonic acids in benzene, ethyl ether, and other solvents is accompanied by formation of the corresponding poly-4-vinylpyridinium salts in amounts equivalent to the acid added. In these cases subsequent

[Fig. 3 and Fig. 4 graphs]

Fig. 3. Dependence of the rate of polymerization on the nature of the alkyl halide. Initial reagent concentrations 3 mol/l. Solvent—nitrobenzene. Temperature 50°. 1—ethyl bromide, 2—butyl bromide

Fig. 4. Dependence of the intrinsic viscosity of polymers obtained by the interaction of 4-VP with ethyl bromide in benzene on the degree of conversion. Initial reagent concentrations 3 mol/l. Polymerization temperatures: 1—20°, 2—50°. Viscosities were measured in a 0.05 N KBr solution at 20°.

treatment of the polymer with dilute alkalis converts polyvinylpyridinium into polyvinylpyridine. By slow addition of sulfuric acid to a benzene solution of 4-VP at 20°, poly-4-vinylpyridine with an intrinsic viscosity in methanol equal to 2.3 was obtained in this way. It is noteworthy that in these cases also, when acid is added to solutions containing equimolar amounts of 4-VP and styrene, in accordance with the reaction scheme proposed above, styrene does not enter into the reaction. Only the salt of 4-VP that is formed undergoes polymerization. However, unlike Menshutkin reactions, formation of salts of 4-VP with strong acids proceeds very rapidly. Therefore the steady-state condition is apparently not fulfilled, and the kinetic description of the process must differ from that given above.

Thus, polymerization of salts of 4-VP is characterized by very high chemical specificity. Chain growth, owing to the special nature of the active centers, is able to "select" in the reaction system and add only those monomer molecules that have entered into the salt-formation reaction. The implementation of such processes opens interesting possibilities for specific syntheses of macromolecules and for biological modeling.

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