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The Polymerization of Propargyl Chloride Activated by Interaction with Poly(4-vinylpyridine)

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ABSTRACT

The reaction between poly(4-vinylpyridine) and propargyl chloride was studied in methanol. It was shown that, independently of the ratio of reactants to each other, the end products of the reaction are polymers with conjugated bond systems formed by the opening of the propargyl triple bond which was activated by interaction with poly(4-vinylpyridine). It was shown that "normal" quaternization of poly(4-vinylpyridine) by propargyl chloride precedes accelerated polymerization of propargyl chloride which begins at 6 to 8% alkylation. It was established that the solution becomes structured before accelerated polymerization begins. A possible mechanism for this reaction has been proposed.

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INTRODUCTION

If the chemical interaction of monomer with the medium brings about an increase in the rate of polymerization, then we call such an interaction chemical activation and the corresponding monomer chemically activated.

The chemical activation of monomer can be caused by the redistribution of the electron density of its bonds by the interaction between the monomer and the medium.

In Ref. 1 it was established that the chemical activation of 4-vinylpyridine by its interaction with alkyl halides in organic media and the forming of quarternary salts brings about the spontaneous polymerization of the quarternary salts

Another example is the polymerization of pyridine and quinoline activated by interaction with zinc chloride [2, 3].

4-Vinylpyridine in the presence of polystyrenesulfonic acid, polyethylenesulfonic acid, and polyacrylic acid undergoes matrix polymerization [4-7].

It was also discovered [8] that pyridine reacts with propargyl chloride to form propargylpyridinium chloride which polymerizes spontaneously at the triple bond of quarternized propargyl chloride. This process takes place in mild conditions to form a polymer containing a conjugated bond system in the main chain.

Therefore we expected to observe unusual effects during the interaction of poly(4-vinylpyridine) and propargyl chloride as a result of intermolecular and intramolecular chemical activation.

EXPERIMENTAL

4-Vinylpyridine (4-VP) "Lawson" (England) was redistilled five times under vacuum. The fraction we worked with was kept in a dark glass bottle fitted with a tight fitting glass stopper in an argon atmosphere at 5°C. In order to attain good reproducible results we redistilled 4-VP additionally before the experiment.

Literature constants [9]: boiling point = 64-67°C/15-17 mm; $n_D^{20} = 1.5495$. Found: boiling point = 65°C/15 min; $n_D^{20} = 1.5491$.

Propargyl chloride (PC) "Schuchardt" (West Germany) was preliminarily distilled under vacuum. Afterwards it was carefully distilled in a separating column ($h = 720$ cm) over a small quantity of P_2O_5 . The fraction we worked with was gathered in the interval $56.5 \pm 0.5^\circ C$. The sensitivity of the reaction to the way PC is purified is of particular importance. The PC purified in the above way contains a small amount of HCl (about 0.25%) that was responsible

for a surprising effect which helped us to understand the nature of the mechanism of the polymerization of PC.

Literature constants [10]: boiling point = 56-56.8°C; $n_D^{20} = 1.4329$.

Found: boiling point = 56.5°C; $n_D^{20} = 1.4328$.

Propargyl alcohol "Fluka" (Switzerland) was carefully distilled and kept in an argon atmosphere at low temperature.

Literature constants [11]: boiling point = 115°C; $n_D^{20} = 1.4310$.

Found: boiling point = 115°C; $n_D^{20} = 1.4310$.

Propyl chloride was purified by the method contained in Ref. 12.

Literature constants [13]: boiling point = 46.5°C; $n_D^{20} = 1.3886$.

Found: boiling point = 46.5°C; $n_D^{20} = 1.3886$.

Methanol (CP; 0.9 liter) was poured into a round-bottom flask fitted with a reflux cooler after 5 g of magnesium filings, 0.5 g of iodine, and 60 ml of methanol were heated on a water bath and all the magnesium turned into magnesium methylate. Then the methanol was refluxed 1 to 2 hr, and after that it was distilled, separating the first 25 ml of distillate from the rest of the absolute methanol.

Literature constants [11]: boiling point = 64.5°C; $n_D^{20} = 1.3268$.

Found: boiling point = 64.5°C; $n_D^{20} = 1.3284$.

Toluene was shaken many times in a separating funnel with 10% (by volume) concentrated sulfuric acid. Then the toluene was shaken with water and 10% NaOH solution until there was a neutral reaction. The toluene was first dried with anhydrous CaCl_2 and then distilled over metallic sodium. For our work we collected the fraction which boiled in the temperature range $109.5 \pm 0.5^\circ\text{C}$.

Literature constants [13]: boiling point = 110.63°C; $n_D^{20} = 1.4969$.

Found: boiling point = 109.5°C; $n_D^{20} = 1.4966$.

Diethyl ether was purified by the method suggested in Ref. 12.

Literature constants [13]: boiling point = 34.5°C; $n_D^{20} = 1.3527$.

Found: boiling point = 34.5°C; $n_D^{20} = 1.3527$.

Allyl chloride was purified by distillation and kept in a dark glass bottle, fitted with a ground glass plug, in an argon atmosphere at low temperature.

Literature constants [13]: boiling point = 45.1°C; $n_D^{20} = 1.4154$.

Found: boiling point = 45°C; $n_D^{20} = 1.4154$.

The synthesis of poly(4-vinylpyridine) (PVP) was carried out in a 100 ml ampule in a 10% toluene solution of 4-VP. Recrystallized azobisisobutyronitrile was used as the initiator. Before sealing, the ampule was filled with an argon atmosphere. After sealing, the

ampule was placed in a thermostat at $50 \pm 0.1^\circ\text{C}$ for 120 hr. After the reaction was completed the polymer was separated from the solvent and unreacted monomer by washing the white precipitate in diethyl ether several times. Then the PVP was reprecipitated from a methanol solution by a mixture of methyl ethyl ketone and hexane in 15:1 volumetric proportion and dried in a vacuum at 60°C and 5 Torr to constant weight.

The purity of the polymer was confirmed by IR spectra. PVP was kept in a desiccator containing NaOH. The molecular weight was determined by the formula $[\eta] = 2/5 \times 10^{-4} M^{0.68}$ as given in Ref. 14. The PVP we used had a molecular weight of 500,000.

Reaction Kinetics

The reaction between propargyl chloride and PVP was carried out in a series of standard ampules prepared in the following way.

With an exact medical syringe inject the needed dosage of PVP in methanol solution into the ampoule. Then inject the needed dosage of propargyl chloride in a methanol solution into the ampule. After this, bubble argon through the ampule 15 min and seal the ampule.

To obtain good reproducibility we used standard solutions of PVP and propargyl chloride where the concentration was known exactly, and these standard solutions were used for a kinetic run.

When argon was blown into the reaction solutions the ampule was kept at 0°C to prevent the blowing out of any volatile propargyl chloride.

The ampules were then placed in a thermostat at $50 \pm 0.1^\circ\text{C}$. At various intervals the ampules were taken out of the thermostat, opened, and the contents poured into ethyl ether. The precipitate was washed several times with ethyl ether and dried in a vacuum until the weight of the reaction product remained constant. The extent of the reaction was calculated by determining the amount of chlorine in the reaction product by a standard method [15].

From these data we plotted the graphic dependency of the percent of reacted pyridine rings (in PVP) on the reaction time.

IR Spectra

IR spectra were recorded on a UR-10 spectrophotometer (GDR). The samples were measured in tablet form.

UV Spectra

UV spectra were recorded on a EPS-03 spectrophotometer (Hitachi, Japan). The samples were measured in methanol solution in the concentration range from 1×10^{-4} to 4×10^{-4} mole/liter.

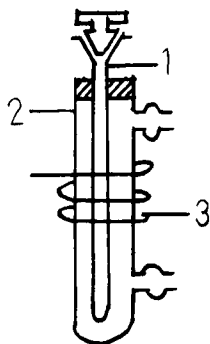


FIG. 1. Device for measuring viscosity during the reaction. (1) Glass tube, (2) thermostating jacket, and (3) electromagnetic coil.

Viscosity Measurements During the Reaction

Because we could not study the viscosity of the reaction products in the usual way (after precipitation they are insoluble), we constructed a device (shown in Fig. 1) which allowed us to overcome the difficulty.

The device consists of a glass tube (150 cm long and 5 mm in diameter) fitted with a ground glass joint at the top; a thermostating jacket; and an electromagnetic coil.

First we injected the reactants into the tube. Then we dropped a ballbearing ($d = 1$ mm) into the tube and filled the system with argon. Then water ($50 \pm 0.1^\circ\text{C}$) was sent through the thermostating jacket and we studied the dependency of the time it took for the ballbearing to fall down the tube on the reaction time.

RESULTS AND DISCUSSION

During the reaction between PVP and PC taken in equimolar quantities ($C = 0.3$ mole/liter) in methanol in an inert gas atmosphere at 50°C , we found the following regularities: during heating the reaction system remained colorless for 3 hr and then during 1 min turned dark brown. This was accompanied by gel formation. The reaction products were precipitated and would not dissolve either in water or in any organic solvent. These facts prompted us to study the reaction in greater detail.

In Fig. 2 the IR spectra of the products of reaction of PVP and PC are given for different degrees of conversion of the initial products. As seen from Fig. 2, the adsorption band at 2140 cm^{-1} , corresponding to the $-\text{C}\equiv\text{C}-$ bond in propargyl, is absent. During the reaction the

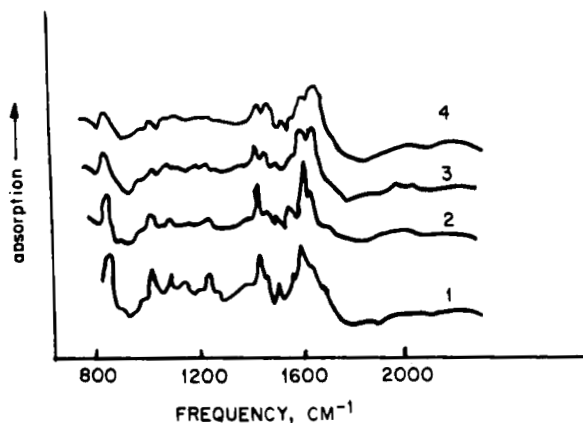
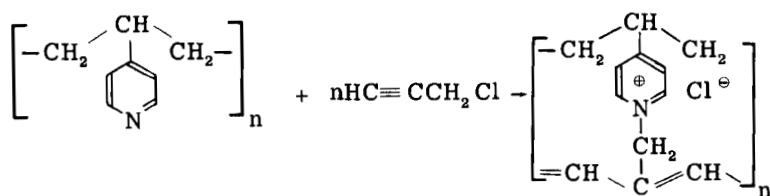


FIG. 2. IR products of the reaction between PVP and PC. [PVP] = [PC] = 0.3 mole/liter in methanol at 50°C. (1) After 0.5 hr (colorless), (2) after 1 hr (colorless), (3) after 3 hr (dark brown, and (4) after 15 hr (dark brown).

band at 1640 cm^{-1} , characteristic of quarternized PVP salts, grows in relationship to the 1600, 1420, and 1000 cm^{-1} bands characteristic of free pyridine rings. This proves that the pyridine rings are being alkylated during the reaction.

These facts allow us to suggest that the IR spectra correspond to different stages of the following reaction:



This means that the reaction of PC with PVP takes part in two steps: the alkylation of PVP and the polymerization on the $\text{---C}\equiv\text{CH}$ bonds, chemically activated by propargyl, bringing about the formation of a polymer with a conjugated bond system.

Next we studied the reaction kinetics. The kinetic curve is shown on Fig. 3 (Curve 1). This curve has an initial linear "induction period" which corresponds to the usual alkylation kinetics of PVP [16].

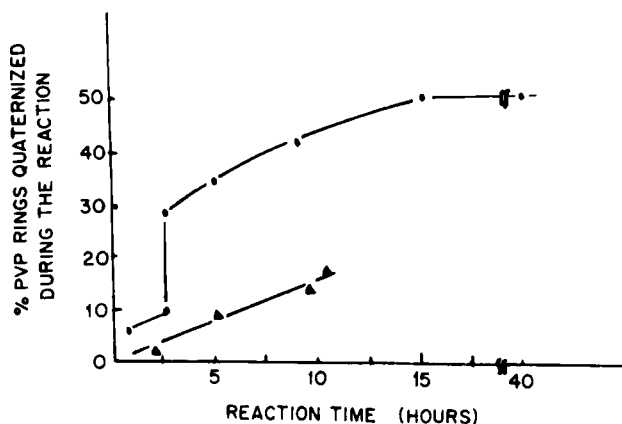


FIG. 3. Reaction kinetics. (1) $[PVP] = [PC] = 0.3$ mole/liter. (2) $[PVP] = [allyl\ chloride] = 0.3$ mole/liter.

But after reacting to a degree of about 8% alkylation, we noticed a sharp reaction acceleration, and just at this moment the system changes from colorless to dark brown.

After this acceleration the kinetic curve reaches a stage of slowing down and the degree of alkylation of PVP tends to limit itself at 50%.

The kinetics depends on the way the PC is purified. The PC we used contained about 0.25% HCl. If the HCl is not present, the initial linear "induction period" is absent. The reason for this is discussed later on.

These regularities are unusual for the quaternization of PVP by alkyl halides, the speed of which, up to 20% alkylation, obeys second-order kinetics and then slows down because of the difficulty of nucleophile attack due to the blocking effect of positively charged pyridine cycles surrounding the nucleophile [16]. The usual alkylation of PVP by PC was confirmed by studying the reaction of alkylation of PVP by allyl chloride (Curve 2) where even at degrees of alkylation of 14% no acceleration of the reaction is noticed.

We thought that these effects could be explained if, during the reaction acceleration, a (PVP.PC) complex reacted giving the end reaction products.

In order to find out whether this was so, we studied the viscosity of the reaction system during the reaction of PC with PVP (Fig. 4). Initially we found a linear growth of viscosity simultaneously with the first part of the kinetic curve. But after reaching a degree of

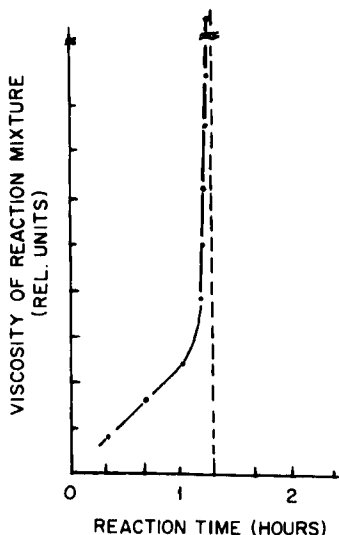


FIG. 4. Viscosity of reaction mixture PVP and PC during the reaction. $[PVP] = [PC] = 0.7$ mole/liter.

quarternization of 8%, the viscosity of the systems grows sharply, the system becomes structured, and in the next moment we observe reaction acceleration accompanied by the dark brown coloring of the system.

To explain the structuring of the system, several proposals were made. One was that the factor responsible for the structure formation was chemical "cross-links" of $-C=C-$ in PC reacting with PVP. However, this is not true because the colorless gel, when taken out of the reaction, dissolves in methanol.

Another hypothesis was that after reaching a certain "critical" charge resulting from alkylation, the chains of PVP begin to unfold which, in turn, make it easier for a (PC.PVP) complex to be formed. However, if this is true, then why do we not observe such an acceleration with allyl chloride? We can suggest that the acceleration, connected with the changing structure as a result of chain charging, is specific for the interaction between PC and PVP.

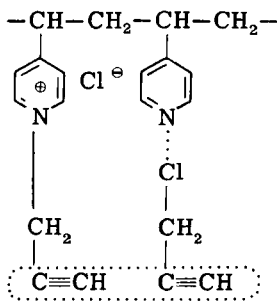
To find out whether this is true, we made the following experiment: PVP was preliminarily alkylated to 8% with propyl chloride and then reacted with PC. We found that the "induction period" grew larger and that the gel became structured later. The polymer prepared this way did not have as deep a brown color and contained less

alkylated pyridine cycles than the polymer prepared from PC and unalkylated PVP.

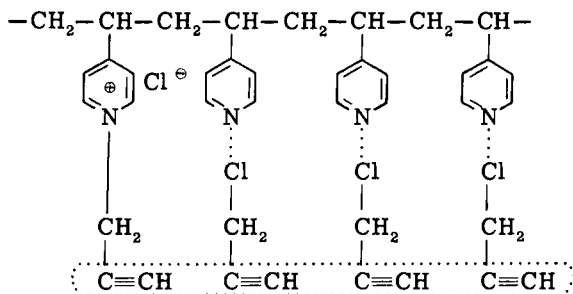
Suppose that the factor responsible for gel structure is the formation of a complex between PC and pure PVP (without PC, which reacted with PVP).

UV spectra of PVP (not shown) with different quantities of PC, less and more than stoichiometric, were almost identical, which shows that no complex is formed between PC and pure PVP.

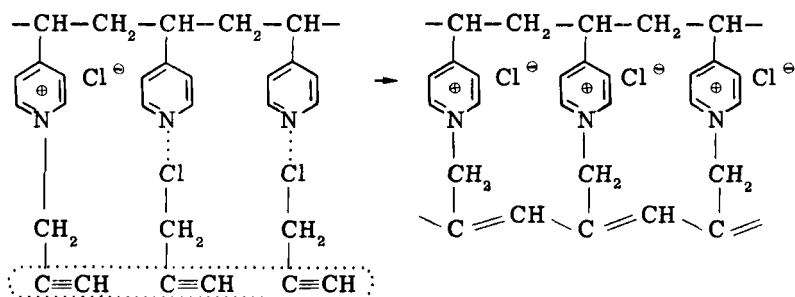
All these facts suggest that the reaction mechanism begins with "normal" alkylation of PVP, and every act of alkylation stabilizes the formation of a complex:



Stuart models show that the most favorable conditions for the energy interaction of $\text{---C}\equiv\text{CH}$ in PC alkylated into PVP with $\text{---C}\equiv\text{CH}$ in PC complex occur only in interchain interactions; therefore the reason for gel structure formation becomes clear. It is possible that after 7 to 8% alkylation and chain unfolding, "microcrystalline areas" are formed consisting of a series of continuous energy reacting $\text{---C}\equiv\text{CH}$ bonds according to



Because the electron density is reached in "knots" in such a series, it is possible upon reaching a "critical" number of interacting triple bonds that it becomes energetically more favorable for delocalization of the electron cloud, bringing about the opening of the triple bonds with simultaneous alkylation:



If this mechanism is true, we can understand why the 0.25% HCl would produce such an induction period. The HCl would react much faster than the PC, and it would take time for the PC to displace the HCl from the PVP and form a critical number of interacting triple bonds in the series.

This hypothesis is supported by the fact that at no stage in the reaction does the IR spectra record triple bonds.

In Fig. 5 the UV spectra of the reaction products are shown.

Curve 1 is before reaction acceleration (colorless products), Curve 2

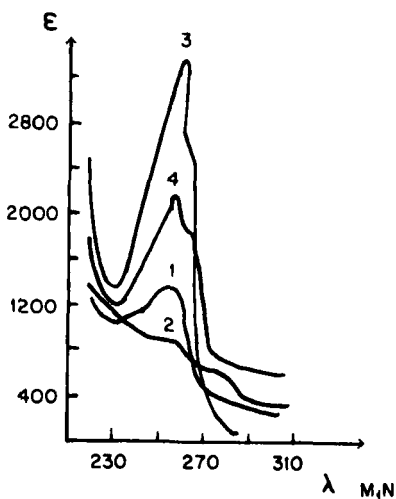


FIG. 5. UV spectra of reaction products. (1) PVP with PC (colorless, 7% alkylation), (2) PVP with PC (dark brown, 50% alkylation), (3) PVP, and (4) PVP with propyl chloride (8% alkylation).

is after reaction acceleration (dark brown products), Curve 3 is the reaction products of 8% alkylated PVP with propyl chloride, and Curve 4 shows PVP.

It is apparent that although the degrees of alkylation of the product before reaction acceleration and in the 8% alkylated PVP are about the same, the spectrum of the diluted colorless gel resembles the spectrum of the dark brown reaction product more closely, which we think is due to the interaction shown in preceding scheme. Propargyl alcohol injected into the system loosens the gel structure before reaction acceleration and greatly dampens the acceleration. We can explain this by the competition of propargyl alcohol and PC for a place beside the PC which had already reacted with PVP.

Nevertheless, this mechanism needs further study.

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