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Polymerization of Vinylpyridinium Salts. XI. Charge-Transfer Polymerization of 4-Vinylpyridinium p-Styrenesulfonate

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Polymerization of Vinylpyridinium Salts. XI. Charge-Transfer Polymerization of 4-Vinylpyridinium p-Styrenesulfonate

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ABSTRACT

The spontaneous polymerization of 4-vinylpyridinium p-styrenesulfonate or 4-vinylpyridinium chloride with sodium p-styrenesulfonate or of 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate with sodium p-styrenesulfonate produces an amphoteric, equimolar copolymer. An UV study on the interaction between 4-vinylpyridinium chloride and sodium p-styrenesulfonate indicates an absorption maximum corresponding to 1:1 charge transfer complex. From the observed results, a charge-transfer polymerization of 4-vinylpyridinium salts with electron-donating monomers is elucidated.

INTRODUCTION

In order to clarify the mechanism of spontaneous polymerization of vinylpyridinium salts that are initiated by means other than an anionic pyridylethylation reaction, studies of the polymerization

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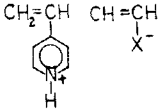
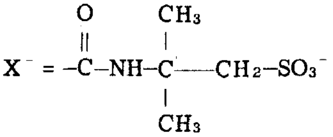
behavior of cationic-anionic monomer pairs derived from 4-vinylpyridine and a vinyl acid of form I have been undertaken [1].



I

Ia: $X^- = -SO_3^-$

Ib: 

$$X^- = -\overset{\displaystyle O}{\overset{\|}{C}}-NH-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2-SO_3^-$$

Ic: $X^- = -C_6H_4-SO_3^-$

These monomers were synthesized in order to help elucidate the existence of a radical polymerization mechanism for the spontaneous polymerization process as a variety of polymer structures could form from the polymerization of such ion pair comonomers depending on the mechanism of polymerization. During the course of our studies of the spontaneous polymerizations of Ia-Ic, it appeared that Ia yielded poly-4-vinylpyridinium vinylsulfonate (II), that Ib yielded either a polyelectrolyte complex of poly-4-vinylpyridinium poly-2-acrylamido-2-methylpropanesulfonate or a block copolymer from these monomers (III), and that Ic yielded an alternating copolymer (IV) of 4-vinylpyridinium p-styrenesulfonate [2]. These results were indeed unusual and clearly indicated a complex character to the probable existence of a radical polymerization mechanism. In the formation of II from Ia by spontaneous polymerization, only the homopolymerization of the vinylpyridinium moiety occurred, as there was no incorporation of the vinylsulfonate moieties under the conditions studied. By free-radical polymerization of Ia, again polymer II formed with no polymerization of the monomeric anion. On the other hand, the spontaneous polymerization of Ib appeared to yield either two separate homopolymers or a block copolymer, whereas in free radically initiated polymerization only a random copolymer was formed. The polymerization of Ic was perhaps the most unique. The product had the solubility characteristics of polyampholyte and an elemental analysis of equimolar concentration even when polymerization of Ic was conducted in the presence of an equivalent concentration of sodium p-styrenesulfonate.

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Since no vinylic compound has been previously incorporated into spontaneous polymerization of a vinylpyridinium compound and since the compound Ic is comprised of the vinylpyridinium moiety of apparently high electron-withdrawing character and high resonance stability [3] and the p-styrenesulfonate moiety, also of high resonance stability but of high electron-donating character, it could be anticipated that a charge transfer interaction would be possible between such aromatic compounds of opposite polarity. In this work, an investigation of this charge transfer polymerization reaction of vinylpyridinium salts was undertaken and a discussion of its possible consequences in the overall spontaneous polymerization process are presented.

EXPERIMENTAL

Sodium p-Styrenesulfonate

Monomeric sodium p-styrenesulfonate (Pfaltz & Bauer Inc.) was purified by continuous extraction with methanol as a solvent and recrystallized in a 90% methanol-water solution.

4-Vinylpyridinium p-Styrenesulfonate

The preparation and characterization of this monomeric salt have previously been described [1].

Spontaneous Polymerization of 4-Vinylpyridinium p-Styrenesulfonate

A solution of 1.45 g (5 mmole) of 4-vinylpyridinium p-styrenesulfonate in 9.5 ml of distilled water was degassed, sealed, and placed in a thermostated bath at 25°C. After 4 hr, the viscous material was dissolved in 100 ml of 1% sodium hydroxide solution and dialyzed exhaustively against deionized water followed by lyophilization to obtain an anionic polymer. NMR (D_2O) showed δ 8.8, 8.1, and 7.2 ppm (broad, protons of aromatic rings) and δ 1.9 and 1.4 ppm (broad, protons of vinyl backbone).

ANAL. Calcd for $-(C_7H_7N)_1-(C_8H_7O_3SNa)_1$: C, 57.87%; H, 4.53%; N, 4.50%; S, 10.30%. Found: C, 57.65%; H, 4.54%; N, 4.62%; S, 10.11%.

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Spontaneous Polymerization of 4-Vinylpyridinium Chloride with Sodium p-Styrenesulfonate

To 0.71 g (5 mmole) of 4-vinylpyridinium chloride and 1.03 g (5 mmole) of sodium p-styrenesulfonate was added 9 ml of distilled water. The solution was degassed, sealed, and placed in a thermostatted bath at 25°C. After 4 hr, the viscous material was dissolved in 100 ml of 1% sodium hydroxide solution, dialyzed against deionized water, followed by lyophilization to obtain an anionic polymer. NMR (D_2O) showed δ 8.8, 8.1, and 7.2 ppm (broad protons of aromatic rings), and δ 1.9 and 1.4 ppm (broad, protons of vinyl backbone).

ANAL. Calcd for $-(C_7H_7N)_1-(C_8H_7O_3SNa)_1$: C, 57.87%; H, 4.53%; N, 4.50%; S, 10.30%. Found: C, 57.77%; H, 4.48%; N, 4.55%; S, 9.98%.

Spontaneous Polymerizations of 4-Vinylpyridinium 2-Acrylamido-2-methylpropanesulfonate with Sodium p-Styrenesulfonate

In an ampule, 1.56 g (5 mmole) of 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate and 1.03 g (5 mmole) of sodium p-styrenesulfonate were dissolved in an appropriate amount of distilled water to make 10 ml of solution. The solution was degassed, sealed, and placed in a thermostatted bath at 25°C. After 4 hr, the seal was broken, and the viscous material was dissolved in 100 ml of 1% sodium hydroxide solution. The solution was then exhaustively dialyzed against deionized water followed by lyophilization to obtain the polymer.

ANAL. Calcd for $-(C_7H_7N)_1-(C_8H_7O_3SNa)_1$: C, 57.87%; H, 4.53%; N, 4.50%; S, 10.30%. Found: C, 58.01%; H, 4.61%; N, 4.83%; S, 10.07%.

Spontaneous Polymerization of 4-Vinylpyridinium Chloride with α-Methylstyrene

In an ampule, 1.14 g (8 mmole) of 4-vinylpyridinium chloride and 0.94 g (8 mmole) of α-methylstyrene were dissolved in an appropriate amount of anhydrous methanol to make 8 ml of solution. The solution was degassed, sealed, and placed in a thermostatted bath at 25°C. After 5 days, the white precipitate was filtered, washed with methanol, and dried. A part of the white precipitate was dissolved in distilled water and neutralized slowly with excess sodium carbonate solution to precipitate polymer. The polymer was filtered, washed thoroughly with distilled water, and dried in vacuo. The polymer was found to be soluble in the aromatic solvents benzene or toluene and in acidic solution. NMR (D_2O + D_2SO_4) showed δ 8.4 and 7.8 ppm (two broad

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peaks, protons of pyridinium ring), δ 6.9 ppm (broad, protons of phenyl ring), and δ 1.9-1.5 ppm (broad, protons of vinyl backbone).

ANAL. Calcd for $-(C_7H_7N)_1-(C_9H_{10})_1$: C, 86.05%; H, 7.67%; N, 6.27%. Found: C, 85.76%; H, 7.75; N, 6.33%.

UV Studies of the Interaction between 4-Vinylpyridinium Cation and p-Styrenesulfonate Anion

The UV absorption of 4-vinylpyridinium p-styrenesulfonate was studied by using the mixtures of 4-vinylpyridinium chloride and sodium p-styrenesulfonate. The mixtures were of the same total monomer concentration, but with a different comonomer ratio.

RESULTS AND DISCUSSION

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In order to investigate the possibility of a charge-transfer interaction in the spontaneous polymerization process, the reactions of several 4-vinylpyridinium salts were investigated with electron donating vinylic compounds. The former included 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate (Ib) and 4-vinylpyridinium chloride (V) as electron-withdrawing monomers. It is apparent for Ib that polymerizable gegenion is present, whereas for V only the cationic moiety is polymerizable. For the electron-donating monomers, sodium p-styrenesulfonate, α-methylstyrene, trans-stilbene and n-butyl vinyl ether were investigated. The spontaneous polymerizations were conducted by dissolving equimolar amounts of electron-donating monomer and electron-withdrawing monomer in a suitable solvent, degassing the solution, sealing under reduced pressure, and polymerizing at 25.0°C.

Previously, it had been found that the spontaneous polymerization of 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate occurs in an aqueous or organic solution when the monomer concentration is above 0.5 M. In this study, 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate was added to an equivalent of sodium p-styrenesulfonate in aqueous solution at 25°C. It was found that the polymerization was rapid and resulted in a water insoluble polymer. The polymerization was stopped at low conversion since each one of the three ionic moieties (4-vinylpyridinium cation, 2-acrylamido-2-methylpropanesulfonate anion, and p-styrenesulfonate anion) could polymerize spontaneously. The resulting polymer was dissolved in a sodium hydroxide solution and exhaustively dialyzed, followed by lyophilization to give an anionic polymer. The microanalysis of the anionic polymer showed that its composition corresponded to that obtained from the spontaneous polymerization of 4-vinylpyridinium

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p-styrenesulfonate. In addition, it was also found that this polymer was insoluble in the pH range from 0 to 6, but soluble below and above these values. It would appear, consequently, that the product obtained is that from the polymerization of the 4-vinylpyridinium moiety with that of p-styrenesulfonate moiety with the exclusion of the acrylamido anion. In order to substantiate further that the interaction of 4-vinylpyridinium cations and p-styrenesulfonate anions are of a charge transfer nature, the spontaneous copolymerization of 4-vinylpyridinium chloride with sodium p-styrenesulfonate was investigated. Interestingly, the copolymerization of 4-vinylpyridinium chloride with an equivalent of sodium p-styrenesulfonate was as rapid as that of 4-vinylpyridinium 2-acrylamido-2-methylpropanesulfonate with sodium p-styrenesulfonate. The composition, infrared and ^{1}H-NMR spectra, and the solubility properties again conformed to an equimolar polyampholyte of 4-vinylpyridinium and p-styrenesulfonate moieties.

In further support of a charge transfer, donor-acceptor polymerization discussed above, the spontaneous polymerization of 4-vinylpyridinium chloride with an equivalent of α-methylstyrene was also investigated. This reaction resulted in the formation of a precipitate which was shown to be a mixture of ionene polymer [poly(1,4-pyridiniumdiyethylene chloride)] and a smaller amount of copolymer. The copolymer (VI) was separated from the mixture by precipitation into basic solution with concommitant destruction of the ionene. The recovered polymer had spectral characteristics of both poly-4-vinylpyridine and poly-α-methylstyrene. Interestingly, the microanalysis of this product also supported an equimolar copolymer structure of 4-vinylpyridine and α-methylstyrene. Since this polymer was also soluble in acidic solution through polycation formation from the protonation of the pyridine groups, it is likely that the copolymer is also of alternating structure. The structure of the neutralized copolymer of 4-vinylpyridine and α-methylstyrene is quite interesting, since it may conceivably be the first example of an alternating copolymer of these two monomers which is obtained by changing the polarity of the pyridine functional group after polymerization (i. e., from an electron-withdrawing pyridinium group to an electron donating pyridine group).

The results discussed above suggested a UV study of the interaction of the 4-vinylpyridinium cation and the p-styrenesulfonate anion. This was accomplished through the utilization of 4-vinylpyridinium chloride and sodium p-styrenesulfonate. Three samples with the same total monomer concentration (1.0×10^{-2} $\underline{M}$) but in different donor-acceptor ratios (9:1, 5:5, 1:9 for 4-vinylpyridinium chloride to sodium p-styrenesulfonate) were prepared in aqueous solution. At the concentration employed, spontaneous polymerization was relatively slow. The UV results showed a greater absorbance for the samples with an equimolar ratio (5.0×10^{-3} $\underline{M}$ for each

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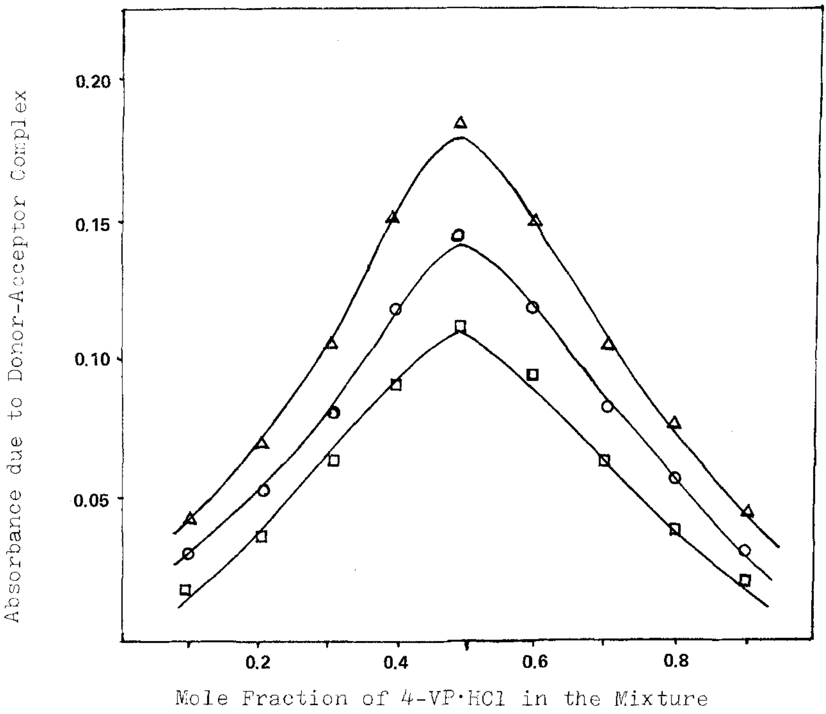

FIG. 1. UV absorption of 4-vinylpyridinium p-styrenesulfonate charge-transfer complex from the interaction of 4-vinylpyridinium chloride and sodium p-styrenesulfonate: (△) 340 nm; (○) 350 nm; (□) 360 nm. Total monomer concentration, 1 × 10^{-2} M; 1.0 cm cell.

monomer) at wavelengths longer than 320 nm. Qualitatively, this study indicated the formation of a complex which has a molar absorptivity at wavelength longer than 320 nm. The stoichiometric composition of the complex was determined by the continuous variation method in which the absorbance of the charge-transfer complex was obtained by substracting the absorbance of the monomer in excess from the total absorbance of the sample [4]. In Fig. 1 is plotted the absorption due to the complex versus the mole fraction of 4-vinylpyridinium chloride in the mixture at different wavelengths (340, 350, and 360 nm). The results obtained indicate that a maximum absorption occurs at 50% mole fraction of each monomer and that the absorbance of the complex is proportional to its concentration.

The results obtained in these spontaneous polymerization studies of vinylpyridinium salts with the p-styrenesulfonate ion and with α-methylstyrene strongly support the charge-transfer interaction of these monomers to yield alternating copolymers. In the near future we hope to report further studies on the structural characterization of these polymers.

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