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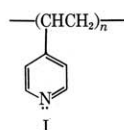
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# Uses of a Vinylpyridine Polymer in Undergraduate Organic Syntheses

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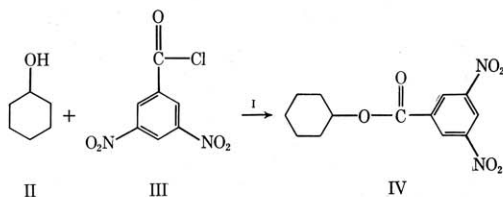
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Polymer chemistry is becoming an increasingly important aspect of industrial and synthetic chemical processes. Yet many undergraduate chemistry curricula provide little exposure to polymeric reagents and their diverse applications for organic syntheses. One recently introduced polymeric reagent that can be adapted to the parameters of the undergraduate laboratory is poly-4-vinylpyridine (PVP, I), a crosslinked 4-vinylpyridine copolymer (R-8050, Reilly Tar and Chemical Co.<sup>2</sup>) that can be used instead of pyridine or other tertiary amines in a wide variety of reactions. The granular nature of this polymer and its insolubility in all organic solvents allows for its isolation by simple filtration. After washing with the reaction solvent, the polymer or its derivatives may be recycled or regenerated repeatedly with no apparent loss of activity. Also the solid nature of the polymer obviates the use of liquid pyridine, thereby avoiding the objectionable odor, flammability, and toxicity associated with the liquid reagent. We have investigated a number of reactions that can be carried out conveniently in undergraduate laboratory courses and report the results.

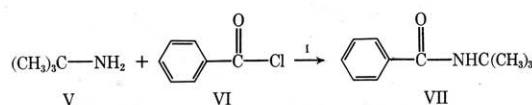


## Discussion of Chemistry

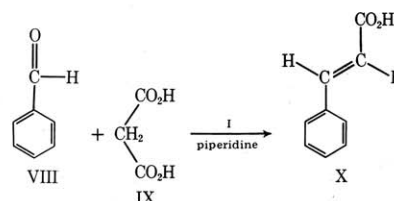
The polyvinylpyridine polymer was used instead of pyridine as a base for acyl halide esterification. Cyclohexanol (II) reacted with 3,5-dinitrobenzoyl chloride (III) to form the ester, cyclohexyl 3,5-dinitrobenzoate (IV), in a slurry of the PVP polymer and dichloromethane. Product isolation involved suction filtration and washing of the polymer with dichloromethane. The reaction mixture and washings were combined and then evaporated to give the product (IV).



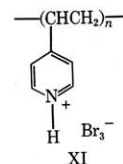
Similarly, *tert*-butylamine (V) and benzoyl chloride (VI) formed *N-tert*-butylbenzamide (VII) using the polymer as a base. In both cases, when proper stoichiometry was used, the dichloromethane solution did not need to be washed since impurities such as carboxylic acids remain on the polymer. The polymer was regenerated by washing with an aqueous sodium hydroxide solution followed by a water rinse.



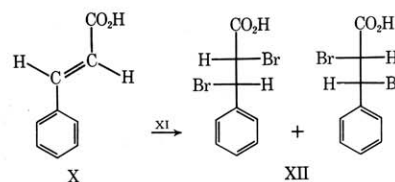
The PVP polymer is a useful catalyst for the Knoevenagel reaction. Benzaldehyde (VIII) and malonic acid (IX) were condensed in refluxing 1-propanol using the PVP polymer and piperidine as catalysts to produce (*E*)-cinnamic acid (X). The reaction is almost complete after 2 h and thus can conveniently be carried out in a 3-h laboratory period.



Simple derivatives of the PVP polymer have valuable synthetic applications. Frechet and coworkers<sup>3</sup> reported using the polymer to prepare a polymeric brominating agent that resembles pyridinium hydrobromide perbromide in specificity. This solid reagent, polyvinylpyridinium hydrobromide perbromide (XI) effectively brominates olefinic compounds and avoids the direct use of liquid bromine.



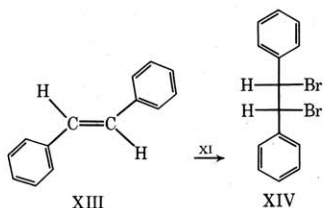
(*E*)-cinnamic acid (X) was brominated in refluxing methanol by this polymeric reagent to produce the racemic trans addition products, (2*RS*, 3*RS*)-2,3-dibromo-3-phenylpropanoic acid (XII). The progress of this reaction can conveniently be followed by observing the color change of the polymeric brominating agent, as it changes from a bright orange to a light yellow color. Product isolation involved removal of the spent polymer by filtration, washing the polymer to remove all of the product and then removal of the solvent from the product. The spent polymer could be regenerated for further use by the addition of bromine. Similarly, (*E*)-stilbene (XIII) was brominated by a trans addition mechanism to give the meso isomer, (1*R*, 2*S*)-1,2-dibromo-1,2-diphenylethane (XIV).



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<sup>3</sup> Frechet, J. M. J., Farrall, M. J., and Nuyens, L. J., *J. Macromol. Sci., Chem.*, **A11**, 507 (1977).



Refluxing reaction mixtures containing the polymer generally do not bump excessively as the polymer slowly degases and acts as boiling chips. However, **if refluxing is halted during the reaction, serious bumping may occur when the reaction is reheated.** Addition of a small amount of fresh polymer will decrease bumping in this case.

## Experimental Section

**Cyclohexyl 3,5-Dinitrobenzoate (IV).** To a dry, 100-mL round-bottomed flask containing 1.0 g (10 mmole) of cyclohexanol (II), 2.0 g of polyvinylpyridine (I) and 20 mL of dichloromethane was added 2.3 g (10 mmole) of 3,5-dinitrobenzoyl chloride (III). The flask was then fitted with a condenser and refluxed for 30 min. The dichloromethane solution was decanted from the polymer and then filtered. The polymer was then washed with 10 mL of dichloromethane. This washing was decanted, filtered, and added to the first filtrate. The dichloromethane was removed by distillation on a steam bath, yielding 2.8 g of crude product. Recrystallization from 15 mL of 95% ethanol gave 1.3 g of the ester, mp 111–112° (lit. mp = 112–113°).

**N-tert-Butylbenzamide (VII).** To a dry Erlenmeyer flask containing 1.4 g (10 mmole) of benzoyl chloride (VI), 2.0 g of polyvinylpyridine (I) and 20 mL of dichloromethane was added 0.74 g (10 mmole) of *tert*-butylamine (V) in five equal portions over several minutes. **(CAUTION: This reaction is exothermic and should be cooled in an ice bath if the solution boils.)** After all of the benzoyl chloride had been added the slurry was swirled occasionally for 15 min. The polymer was removed by filtration and washed with 20 mL of dichloromethane. The original filtrate and washings were combined, and the dichloromethane was removed by distillation on a steam bath. Crude yield 1.4 g. The product was recrystallized from 4 mL of ethanol, yield 0.9 g, mp = 134° (lit. mp = 134°).

**Regeneration of Polyvinylpyridine (I).** The polymer recovered from the above reactions was regenerated by treatment with excess aqueous sodium hydroxide. The resulting free base was filtered and washed with water until the filtrate was neutral. The polymer was then dried in an oven (110°).

**(E)-Cinnamic Acid (X).** Into a 50-mL round-bottomed flask were introduced 2.1 g (20 mmole) of benzaldehyde (VIII), 2.6 g (25 mmole) of malonic acid (IX), 3.0 g of polyvinylpyridine (I), five drops of pi-

peridine and 25 mL of 1-propanol. The flask was fitted with a condenser and the slurry refluxed for 2 h. The hot solution was decanted from the polymer and filtered. The polymer was then washed for several minutes with 10 mL of hot 1-propanol. This was then decanted, filtered, and added to the original solution. The combined filtrates were then added to 100 mL of water. After crystals appeared, the mixture was cooled in an ice bath. The crude product was then collected by suction filtration: crude yield 1.0 g. Recrystallization from 20 mL of a 2:1 mixture of water:ethanol gave 0.6 g of (*E*)-cinnamic acid; mp = 132–133° (lit. mp = 133°).

If the polymer is to be used for additional Knoevenagel reactions with the same reactants it does not have to be regenerated. If the polymer is to be used for other purposes it can be regenerated as previously described.

**Polyvinylpyridinium Hydrobromide Perbromide (XI).** Six grams of liquid bromine were slowly added to a stirred slurry of 4.5 g of polyvinylpyridine (I) and 9.0 mL of 48% HBr in 20 mL of water. The polymer turned bright orange and swelled considerably. The polymer was then filtered, washed with 150 mL of water, and air dried overnight in a fume hood. The polymer had a slight bromine odor while drying; yield 12.0 g (2.8 mmole Br<sub>2</sub>/g polymer). **Caution: Contact of this material with metal spatulas for more than a few minutes causes reaction of the metal with bromine.**

After use the polymeric brominating agent may be regenerated by the addition of bromine or it can be converted to polyvinylpyridine with aqueous sodium hydroxide, as previously described.

**(2R,3R)-2,3-Dibromo-3-Phenylpropanoic Acid (XII).** Into a 50-mL round-bottomed flask was introduced 1.0 g (6.75 mmole) of (*E*)-cinnamic acid (X), 2.6 g (equivalent to 7.3 mmole Br<sub>2</sub>) of polyvinylpyridinium hydrobromide perbromide (XI), and 20 mL of methanol. The flask was fitted with a condenser and the slurry refluxed until the bright orange polymer was a light yellow color (1.5 h). The methanol solution was decanted from the polymer and filtered. The spent brominating agent was washed with 10 mL of methanol and this solution was decanted, filtered, and added to the first filtrate. The methanol was removed by distillation on a steam bath to give 2.0 g of crude product. Recrystallization from 4.0 mL of ethyl acetate gave 0.9 g of final product; mp = 202–204° (lit. mp = 203–204°).

**(1R,2S)-1,2-Dibromo-1,2-Diphenylethane (XIV).** A slurry of 0.7 g (3.9 mmole) of (*E*)-stilbene (XII), 1.8 g (equivalent to 5.0 mmole Br<sub>2</sub>) of polyvinylpyridinium hydrobromide perbromide (XI), and 50 mL of methanol was refluxed until the polymer was a light straw color (15 min). The methanol solution was decanted from the polymer, the polymer was washed twice with 25 mL of dichloromethane and the original solution and washing combined and filtered. The solvent was removed by distillation on a steam bath and gave 1.0 g of crude product. Recrystallization of this material from methanol gave 0.5 g, mp = 234–236° (lit. mp = 237°).