

Synthesis of Water-Soluble Poly(Vinyl Dye)

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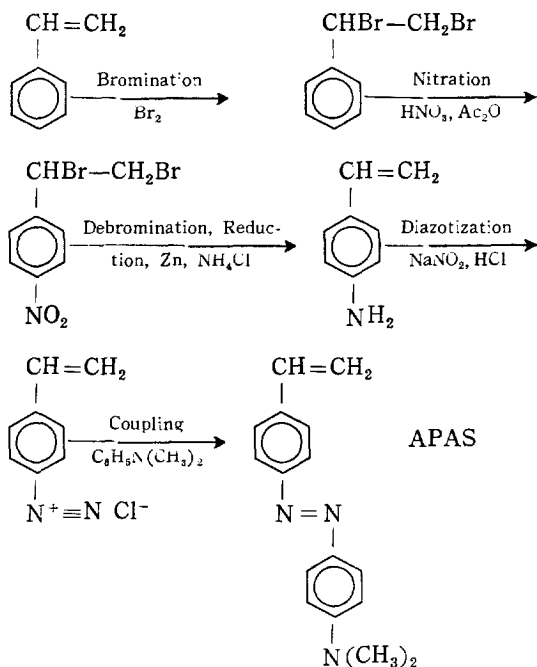
Water-soluble polymeric dyes which are of great interest for their nontoxicity due to the inability to cross membranes have been little studied¹. It is difficult to find suitable "reactive" polymers which can serve as starting materials for the preparations of polymeric dyes. Most of reported polymeric dyes were prepared by the reactions of polymers^{2,3} or by the attachment of chromophores to polymer⁴.

By copolymerization of vinylic dyes with vinyl monomers, polymeric dyes can also be prepared. We now like to report the synthesis of a vinylic dye, *p*-(4-N,N-dimethylaminophenylazo)styrene (APAS) and its copolymerization with acrylamide to prepare a water-soluble polymeric dye.

A vinylic dye has been synthesized as follows: Styrene was brominated to give styrene dibromide⁵, and then the latter was nitrated⁶, reduced and debrominated⁷ to give *p*-aminostyrene. Through diazotization and coupling reaction, *p*-aminostyrene was converted into APAS.

Thus prepared APAS was copolymerized with acrylamide in water to give a water-soluble colored polymer.

In order to ascertain that the APAS was copolymerized with acrylamide, the purified colored polymer was extracted with acetone for a few days. However no change in its color was observed. Acetone is solvent of vinylic dye, APAS. The UV-visible spectrum (Varian Cary



219 Spectrophotometer) of washed colored polymer I (Fig. 1) was compared with that of methyl orange which has the structure similar to APAS. The λ_{max} of the colored polymer was 515nm at pH=2.

In another method⁸, the colored polymer I was treated with alkaline sodium hydrosulfite in water to give colorless polymer II, and the latter was purified by reprecipitation into acetone. By diazotization and coupling reaction, the colorless polymer II was converted to colored polymer III. This change of color can be seen

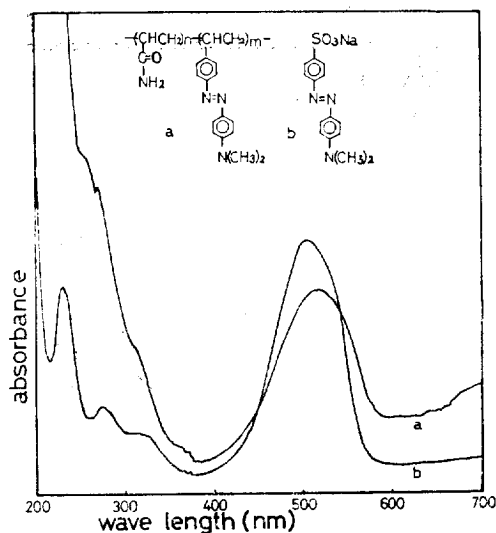


Fig. 1. UV-visible spectra of colored polymer I (a) and methyl orange (b) at pH=2.

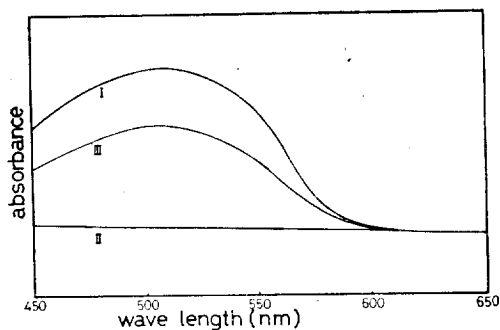


Fig. 2. UV-visible spectra of polymers, I(colored) II(colorless) and III(colored) at pH=3.

from the UV-visible spectra(Shimadzu Digital Double-Beam Spectrophotometer, UV-210A)(Fig. 2). The colorless polymer II did not exhibit any absorbance in visible region. The colored polymer III showed λ_{max} at 510nm at pH=3 which was same to that of the colored polymer I. So it can be considered that the colored polymer III had the structure same to that of colored polymer I.

In Fig. 3, the presence of phenyl ring in colored polymer was confirmed by NMR(Varian EM 360L NMR Spectrophotometer) and UV spectrum(280nm) (Fig. 1).

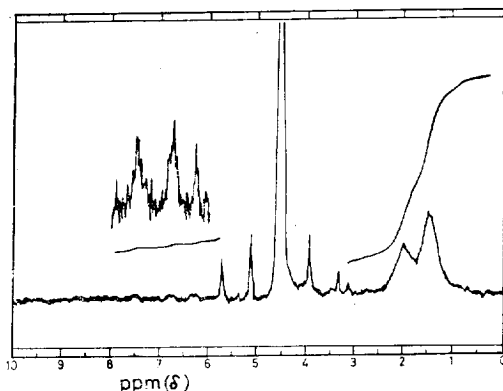


Fig. 3. NMR spectrum of colored polymer I in D_2O .

From above results, it was concluded that the vinylic dye, APAS was copolymerized with acrylamide.

However the APAS has not been separated from synthesis reaction mixture due to the experimental difficulties, and further study is now in progress.

References

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