

## Studies of the Water-Soluble Polymers. XVI. Azo Dyes of Poly-*N*-Vinylimidazole

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### Synopsis

Homopolymer of 2-methyl-*N*-vinylimidazole and copolymer of the monomer with acrylamide were coupled with some aromatic diazonium compounds to give polymeric azo dyes. The dyestuff prepared from the homopolymer was soluble in water only when it was coupled with diazonium component containing sulfonic acid group, but the dyestuffs prepared from the copolymer were soluble. The reactivity, chemical structure, color, and dyeability of the polymeric dyes are discussed by comparing them with those of the corresponding monomeric dyes. The color fastness of the polymeric dyes was found to be in a high class; the rubbing and dry-cleaning fastness were especially excellent.

### Introduction

It has been shown that homopolymer of 2-methyl-*N*-vinylimidazole<sup>1</sup> and copolymer of the monomer with acrylamide<sup>2</sup> are soluble in water and serve as cationic polyelectrolytes in hydrochloric acid solution. Some poly-*N*-vinylimidazoles have been utilized as levelling agents in dyeing<sup>3</sup> and as finishing agents for textile fibers<sup>4,5</sup> and anion-exchange resins.<sup>6</sup>

The present paper reports the application of these polymers to dyestuffs. Some aromatic diazonium compounds were coupled with the imidazole groups of the polymers to give polymeric azo dyes. The reactivity, chemical structure, color, and dyeability of the polymeric dyes are discussed by comparing them with those of the corresponding monomeric dyes.

## EXPERIMENTAL AND RESULTS

### 1. Materials

2-Methyl-*N*-vinylimidazole (MVI) was distilled under reduced pressure; b.p. 193°. Acrylamide (AA) was recrystallized from acetone; m.p. 84.5°. 2-Methylimidazole (2MI) was recrystallized from benzene; m.p. 143-144°.

1,2-Dimethylimidazole (DMI) and 1-ethyl-2-methylimidazole (EMI) were prepared from 2MI by Balaban and Pyman's method;<sup>7</sup> DMI b.p. 59.4-60.4° (3-4 mm. Hg), picrate m.p. 180-181.2°; EMI b.p. 209.5-210°, picrate m.p. 184.5-185°.

Aromatic amines used as diazonium components were obtained commercially.

## 2. Synthesis of Monomeric Dye

The aromatic amines listed in Table I were diazotized and coupled with 2MI and DMI by the usual method. After the reaction the solution was concentrated to dryness and extracted with methanol. The methanolic solution was concentrated to dryness. The crude dye was purified by being passed through a cellulose column with a solution of *n*-butanol-ethanol-water (6:2:3 v./v.) as developer. The monomeric dye prepared, for example, with naphthionic acid as the diazonium component was tested by visible and infrared absorption spectra. The results are shown in Figures 1 and 2.

TABLE I  
Aromatic Amines Used for Synthesizing Dyes

(A) Aniline	(B) Sulfanilic acid
(C) <i>p</i> -Aminobenzoic acid	(D) <i>p</i> -Aminophenol
(E) <i>p</i> -Nitroaniline	(F) <i>o</i> -Toluidine HCl salt
(G) <i>p</i> -Anisidine	(H) 2-Aminophenol-4-sulfonic acid
(I) Naphthionic acid	(J) $\alpha$ -Naphthylamine
(K) Anthranilic acid	(L) 1,7 Cleve's acid
(M) Benzidine	(N) Dianisidine
(O) 2-Diazonaphthol-4-sulfonic acid	(P) 2-Diazonaphthol-6-nitro-4-sulfonic acid
(Q) Diacelliton F. Violet	(R) Diacelliton F. Orange

## 3. Synthesis of Polymeric Dye

### 3.1. Synthesis of MVI Polymer

MVI was polymerized in water at 65–70° with 0.5 wt.-% (to monomer) of azobisisobutyronitrile as initiator under an atmosphere of nitrogen for half an hour.<sup>1</sup> The polymer was separated by pouring the solution into acetone and was purified by reprecipitation. Conversion was 40%. The intrinsic viscosity of the polymer, determined in 0.1*N* hydrochloric acid solution at 30 ± 0.1°, was 3.20.

### 3.2. Synthesis of MVI-AA Copolymer

A mixture of 60 mole-% of MVI and 40 mole-% of AA was copolymerized in acetone with 0.5 wt.-% (to monomer) of azobisisobutyronitrile as initiator under an atmosphere of nitrogen at 60° for an hour. More acetone was added to the reaction mixture, for separating the copolymer from monomer. The copolymer was filtrated and dried. Conversion was 57.2%. By the analytical data (N, 21.61%) the copolymer was found to contain 31 mole-% of MVI component. The intrinsic viscosity of the

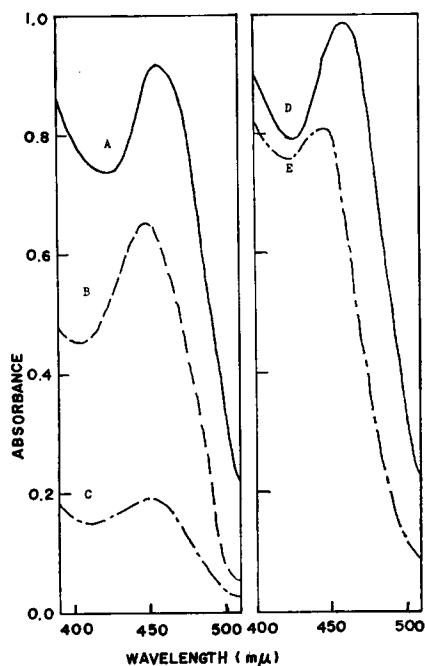


Fig. 1. Visible spectra of polymeric dyes and monomeric dyes: (A) polymeric dye of MVI-AA copolymer with naphthionic acid; (B) monomeric dye of DMI with naphthionic acid; (C) monomeric dye of 2MI with naphthionic acid; (D) polymeric dye of MVI polymer with naphthionic acid; (E) monomeric dye of 2MI with naphthionic acid.

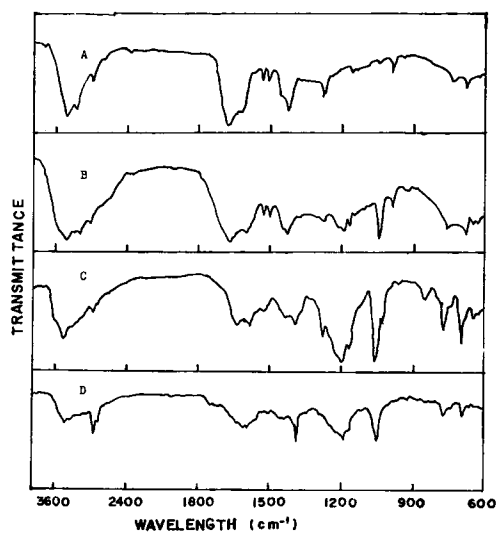


Fig. 2. Infrared spectra of copolymer, polymeric dye, and monomeric dyes: (A) MVI-AA copolymer; (B) polymeric dye of MVI-AA copolymer with naphthionic acid; (C) monomeric dye of 2MI with naphthionic acid; (D) monomeric dye of DMI with naphthionic acid.

copolymer determined in 0.2*N* hydrochloric acid solution at  $30 \pm 0.1^\circ$  was 2.30.

### 3.3. Synthesis of Polymeric Dye

Twice an equimolar amount of aromatic diazonium compound to that of imidazole group in the polymer chain was added to a 1% solution of MVI polymer or MVI-AA copolymer. The pH value of the coupling solution was adjusted to 9–12 by adding dilute sodium hydroxide solution. The coupling reaction was completed in about 10 hr. at room temperature; this was ascertained by potassium iodide starch paper. The solution was concentrated and poured into acetone, to precipitate the azo dye, which was filtrated and dried.

The dyestuff prepared from MVI polymer was soluble in water only when it was coupled with diazonium component containing a sulfonic acid group in the molecule, such as sulfanilic acid and naphthionic acid. The dyestuffs prepared from MVI-AA copolymer, however, were generally soluble enough in water for dyeing condition. The water-soluble polymeric dyes were dissolved in water and purified by being passed through a Sephadex column.<sup>8</sup>

## 4. Color and Absorption Spectra of Polymeric Dye

Visible, ultraviolet, and infrared spectra of MVI polymer, MVI-AA copolymer, and some polymeric azo dyes synthesized from them were observed. The results obtained are shown in Figures 1, 2, and 3, where they are compared with the corresponding monomeric dyes.

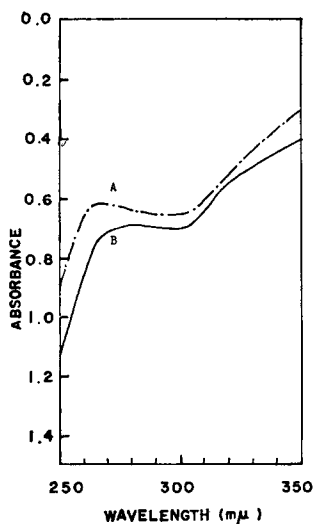


Fig. 3. Ultraviolet spectra of polymeric dye and monomeric dye: (A) monomeric dye of 2MI with naphthionic acid; (B) polymeric dye of MVI-AA copolymer with naphthionic acid.

On the visible and ultraviolet spectra both monomeric and polymeric dyes show the absorption band at similar wavelengths, which signifies their similar chemical structures.

The infrared spectra of the polymeric dye synthesized by being coupled with the diazonium component containing a sulfonic acid group show the absorption band at  $1045\text{ cm.}^{-1}$ , which is assigned to the sulfonic acid group; the bands at  $1200 \pm 20\text{ cm.}^{-1}$  assigned to the aryl sulfonic acid group are also shown.

Some amide groups in the MVI-AA copolymer were found to be converted into carboxylate groups in the coupling reaction.

Some colors of the azo dyes in aqueous solution change with changing pH values. The color changes of the dyes synthesized from MVI-AA copolymer by being coupled with sulfanilic acid, naphthionic acid and 1,7 Cleve's acid, for example, are shown in Table II.

TABLE II  
Color Changes of Polymeric Dyes (MVI-AA Copolymer) and  
Monomeric Dyes (2 MI) with pH

Diazonium component	Dyes	Color changes and pH
Sulfanilic acid	polymeric	yellow (8.0-9.5) red
	monomeric	yellow (8.0-9.5) red
Naphthionic acid	polymeric	reddish violet (6.0-8.0) orange, brown
	monomeric	reddish violet (6.0-8.0) yellowish orange
1,7 Cleve's acid	polymeric	reddish (6.5-9.0) red-orange
	monomeric	red (6.5-9.0) concd. red

## 5. Dyeability of Polymeric Dye

### 5.1. Dyeing

Nylon cloth was dyed with the water-soluble polymeric dye in acidic solution. The dyeing conditions were as follows:

Dyestuff:	5% (to cloth)
Bath ratio:	1:50
Temperature:	95-98°
Time:	1 hr.

After the dyeing the cloth was soaped as usual. For comparison, the dyeing was carried out by using the corresponding monomeric dye in the same condition. The colors of the dyed cloths are shown in Table III.

The dyeing by means of the two-bath method reported in a previous paper<sup>9</sup> was also carried out, and similar results were obtained. Water-insoluble polymeric dyes, however, were not found applicable in the dyeing mentioned above. Utilization of the water-insoluble polymeric dyes as dispersion dyes was also unsatisfactory.

TABLE III  
Colors of the Cloths Dyed with Polymeric Dyes and Monomeric Dyes

Diazonium component	Polymeric dyes	Monomeric dyes
	MVI polymer:	(2MI)
Naphthionic acid	reddish violet	red
2-Diazonaphthol-6-nitro-4-sulfonic acid	brown	brown
2-Aminophol-4-sulfonic acid	orange-brown	orange
	MVI-AA copolymer	
Aniline	yellow	bitter-orange
Sulfanilic acid	white-yellow	yellow
<i>p</i> -Nitroaniline	brown (basic)	reddish brown (basic)
	orange (acidic)	reddish orange (basic)
<i>p</i> -Aminophol	soil yellow	brown
<i>p</i> -Aminobenzoic acid	concd. yellow	concd. yellow
$\alpha$ -Naphthylamine	concd. violet	red
Naphthionic acid	reddish violet	red
1,7 Cleve's acid	reddish violet	orange-red
2-Diazonaphthol-4-sulfonic acid	concd. pink	concd. brown

TABLE IV  
Color Fastness of Polymeric Dyes

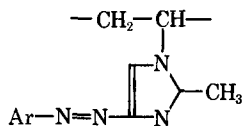
Diazonium component	Wash- ing	Hot water	Fill- ing	Rubbing		Light		Dry clean- ing	Hot press- ing	Color fade
				Dry	Wet	20 hr.	50 hr.			
MVI polymer:										
1,7 Cleve's acid	2			4-5	4-5	3-4	2-3	4	160	4 Br
Naphthionic acid	2			4-5	4-5	3	2	4	140	4 D
2-Aminophenol-4-sulfonic acid	4			5	5	4	4	5	140	4 D
2-Diazonaphthol-4-sulfonic acid	4-5			5	5	3	2	5	5	5
2-Diazonaphthol-6-nitro-4-sulfonic acid	3-4			5	5	4-5	3	5	180	4 Br
MVI-AA Copolymer:										
Aniline	3	3	5	5	5	3	2	5	180	4 Br
<i>p</i> -Nitroaniline	3	4	5	5	5	4	2	5	180	4 Br
<i>p</i> -Aminophenol	3	4	5	5	5	3	2	5		5
<i>p</i> -Aminobenzoic acid	3	3	5	5	5	3	2	5	180	4 D
<i>o</i> -Toluidine HCl salt	3	5	5	5	5	3	2	5		5
<i>p</i> -Anisidine	3	3-4	5	5	5	3	2	5		5
$\alpha$ -Naphthylamine	3	3	4	5	5	3	2	4		5
1,7 Cleve's acid	3	1	4-5	5	4-5	3	2	4-5		5
2-Diazonaphthol-4-sulfonic acid	3	3-4	5	5	4	3	2	5		5
Diacelliton F. Violet	2	4	5	5	5	4	2	5		5

## 5.2. Fastness

The color fastness of the dyed fabric was tested by means of Japanese Industrial Standards.<sup>10</sup> The results obtained are shown in Table IV.

## DISCUSSION

An imidazole ring having an aromatic character is capable of coupling with aromatic diazonium salt to give an azo compound. According to the classic exposition, imidazoles, in order to be capable of coupling, must contain a free imino group and also a hydrogen atom or an other displaceable group, such as the carboxyl group, in one or two 2, 4, or 5 positions.<sup>11</sup> The arylazoglyoxalines hitherto prepared are carbon azo compounds. The 1,2-disubstituted imidazole compounds used in the present investigation are protonized in aqueous solution and show the strong basic character, as reported in a previous paper.<sup>1</sup> Since the 2 position of the compound has been taken by a methyl group, the coupling reaction takes place at the 4 or the 5 position. In the polymer reaction the coupling would be considered to take place at the 4 position, considering steric factors.



To obtain a water-soluble dye from MVI polymer, the amine containing the sulfonic acid group must be used as the diazonium component, but the dyes from MVI-AA copolymer are generally soluble in the dyeing condition, and the solubility is able to be regulated by the ratio of acrylamide component in the first copolymer. To take more soluble polymeric azo dyes, the diazonium component containing water-soluble groups, such as the sulfonic acid group, was more satisfactory.

In a previous paper<sup>9</sup> the polymeric dyes of styrene copolymers having diazonium components were reported. Unlike the previous dyes, the polymer chain serves as coupling component in the dyestuff prepared in the present experiment. The dyestuff obtainable is more soluble in water and convenient for dyeing. The coloring is rather rich in variety: yellow, red, orange, brown, violet, and so on. The relation between the diazonium component and the coloring of the dye has not yet been investigated.

The color-fastness of the polymeric dyes is of a high class; the rubbing and dry-cleaning are especially excellent. The polymeric dyestuff is applicable to dyeing not only nylon but also polyacrylonitrile.

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