

# Chemical Modification of PVC into Polymer-Supported Oxazolinones and Triazoles

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**ABSTRACT:** PVC (**P1**) was converted into polymer-supported oxazolinone and triazole derivatives after sequential chemical assembly of the reactive groups onto PVC. First, poly(vinyl chloride-co-vinylaminoaniline) (**P2**) was prepared by the reaction of PVC with *p*-phenylenediamine. The primary aromatic amino group in **P2** was diazotized and reacted with hippuric acid to form the supported oxazolinone derivative (**P3**) which could be converted into supported triazole derivatives (**P4**)–(**P6**) on further interaction with substituted

anilines. The involved ring opening and preferred cyclization reactions have been clearly addressed based on spectroscopic and elemental analyses of the products. Also the ability for metal uptake has been roughly tested through the interaction with Cu(II) ions. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2304–2309, 2007

**Key words:** functional polymers; PVC; oxazolinone; chemical modification; triazole

## INTRODUCTION

Chemical modification of polymers has widespread applications, as the obtained functionalized polymers acquire the reactivity of the introduced functionality while keeping the main features of the base polymeric matrix.<sup>1–5</sup> Hence, many functional polymers have been prepared through the reaction of a base polymer with different chemically reactive species such as aldehydes,<sup>6,7</sup> phenols,<sup>8</sup> and ketones.<sup>9</sup> Functionalization can also be achieved through physical blending of some organic compounds such as phenolic compounds.<sup>10</sup> Some heterocyclic compounds showed stabilizing efficiency for rubber mixes<sup>11</sup> and their ability for metal uptake is expected as well. Considering the problems in the case of physical blending, which cause the additives to bloom to the surface of the blend, chemical blending or functionalization would be beneficial in comparison. Oxazolinones and triazoles are known as common classes of organic compounds and a lot of work, from the middle of the last century,<sup>12</sup> has been done to synthesize different oxazolinones and 1,2,4-triazoles either through solution- or through solid-phase synthesis strategy. However, little work has been reported in the light of supporting them onto polymer matrices.<sup>13–15</sup> The supported organic compounds in the current work are the first to

be synthesized in the last decade and since that time no bulk work has been done.<sup>11</sup>

The present work deals with the chemical modification of **P1** into polymer-supported oxazolinone and triazole derivatives through sequential chemical assembly of the reactive species onto the **P1** matrix. Characterization of the obtained modified polymers as well as estimation of the reaction efficiency has been achieved and the possible ability for metal uptake has been also roughly tested through the interaction with Cu(II) ions.

## EXPERIMENTAL

All chemicals were purchased from Aldrich, unless otherwise mentioned, and used without further purification. The low molecular weight analogues as model compounds have been synthesized and characterized previously by our group.<sup>11</sup>

### Conversion of **P1** into poly(vinyl chloride-co-vinylaminoaniline) (**P2**)

**P1** has been converted into poly(vinyl chloride-co-vinylaminoaniline) (**P2**) through chemical modification with *p*-phenylenediamine (**1**), according to the method reported before.<sup>11</sup> Elemental and FTIR spectroscopic analyses have concluded the formation of the above-mentioned copolymer (**P2**) with 70% conversion. The reaction conversion has been calculated from the elemental analysis on the basis of mole fraction concept.<sup>16</sup>

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TABLE I  
Elemental Analysis Data and Metal Uptake for the Chemically Modified (P1)

Sample	Elemental analysis data				Conversion (%)	Overall Yield (%)	Metal uptake (mg/g)
	C (%)	H (%)	N (%)	Cl (%)			
P1	38.38	4.78	–	56.80	–	–	–
P2	69.32	7.08	17.44	9.39	70	70	285
P3	65.18	4.45	17.07	5.69	64	45	150
P4	66.11	5.12	19.06	4.78	78	35	200
P5	66.94	4.88	16.66	4.88	71	32	205
P6	68.68	4.92	19.48	5.08	67	30	105

### Conversion of PVC copolymer P2 into oxazolinone-supported polymer (P3)

A cold suspension of finely powdered P2 (16.1 g, 0.1 mol Ar–NH<sub>2</sub> group) in 100 mL of 0.5M HCl was diazotized with sodium nitrite (35 g, 0.5 mol). The reaction mixture was coupled with hippuric acid (2) (22 g, 0.12 mol) in 70 mL acetic anhydride containing 3 g of freshly fused sodium acetate. After stirring the suspension for 1 h while the temperature was kept at 0–5°C, the reaction mixture was then filtered off and washed successively with water, ethanol, acetone, and finally with ether. The yellowish green product (P3) was dried under vacuum at 40°C to constant weight

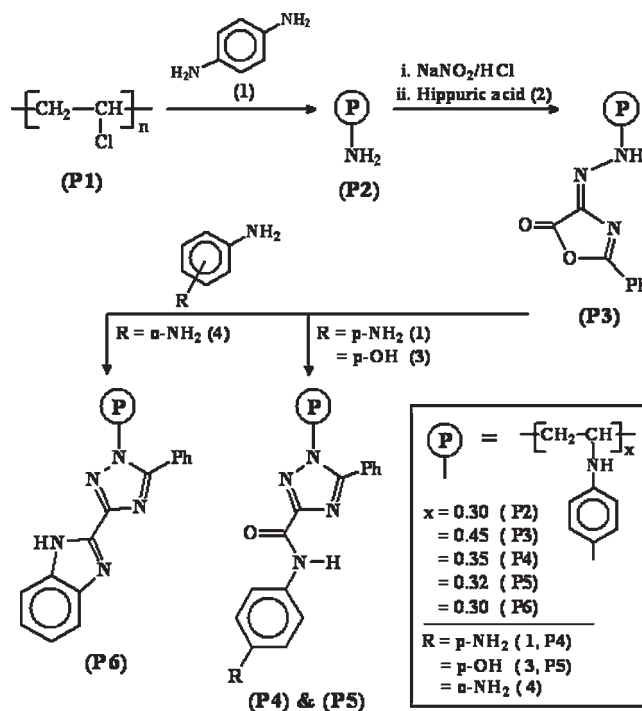
and then subjected for elemental and FTIR spectroscopic analyses.

### Conversion of P3 into triazole-supported polymers triazole (P4)–(P6)

A mixture of P3 (19 g, 0.1 mol of the oxazolinone residue) and the investigated substituted aromatic amines (1), (3), and (4) (0.12 mol) was soaked for 12 h in 70 mL glacial acetic acid and refluxed with stirring for further 8 h. The reaction mixture was kept overnight at room temperature. The modified polymeric product was filtered off and washed thoroughly with water,

TABLE II  
FTIR Spectroscopic Data for the Chemically Modified (P1)

Sample	Metal-unloaded polymer		Metal-loaded polymer	
	$\nu$ (cm <sup>-1</sup> )	Description	$\nu$ (cm <sup>-1</sup> )	Description
P1	705	–C–Cl	705	–C–Cl
	1675	–C=C–	1673	–C=C–
P2	2850	–CH–N–	3460	Shift of NH <sub>2</sub> absorption peak due to possible chelating
	3480	–NH <sub>2</sub>		
P3	3350	–NH		
	1590	C=C aromatic		
	3320	–NH	1572	–N=N–
	1621	–C=N–	1675	–C=C–
	1050	–C–O–C–	1658	–C=C–O <sup>-</sup> . <sup>+</sup> Metal
	3500	–OH		
	1590	C=C aromatic		
P4	3350	–NH	1612	–N=C–O <sup>-</sup> . <sup>+</sup> Metal
	1670	–CONH–	3460	Shift for NH <sub>2</sub> absorption peak
	1620	–C=N–		
	3480	–NH <sub>2</sub>		
	3500	–OH		
P5	1590	C=C aromatic		
	3350	–NH–	1613	–N=C–O <sup>-</sup> . <sup>+</sup> Metal
	1670	–CONH–	3482	Ph–O <sup>-</sup> . <sup>+</sup> Metal
	1622	–C=N–		
	3500	–OH		
P6	1590	C=C aromatic		
	3300	–NH–	3289	Shift of NH– absorption peak due to possible chelating
	1624	–C=N– absence of C=O, NH <sub>2</sub>		



**Scheme 1** Modification of P1 into polymer-supported oxazolinone and triazole P2–P6.

acetone, and finally with ether. The reaction products (P4)–(P6) were dried under vacuum at 40°C to constant weight and then subjected for elemental and FTIR spectroscopic analyses.

#### Loading of the dentate polymers P2–P6 with Cu(II) ions

To about 0.5 g of finely powdered modified PVC samples (P2)–(P6), a solution of copper acetate (50 mL, 0.1M) was added and stirred for 12 h at room temperature. The mixture was filtered off and washed thoroughly with distilled water and the metal-loaded modified P1 samples were separated off. The metal uptake by the modified PVC samples was determined through back determination of the excess Cu(II) in the filtrate and the raw data are listed in Table I. The metal-loaded samples P2M–P6M were subjected to FTIR spectroscopic analysis.

Characterization results for all the modified P1 samples are summarized in Table I for the elemental analysis, reaction conversion percentage, and the overall reaction yield percentage and in Table II for FTIR spectroscopic analysis.

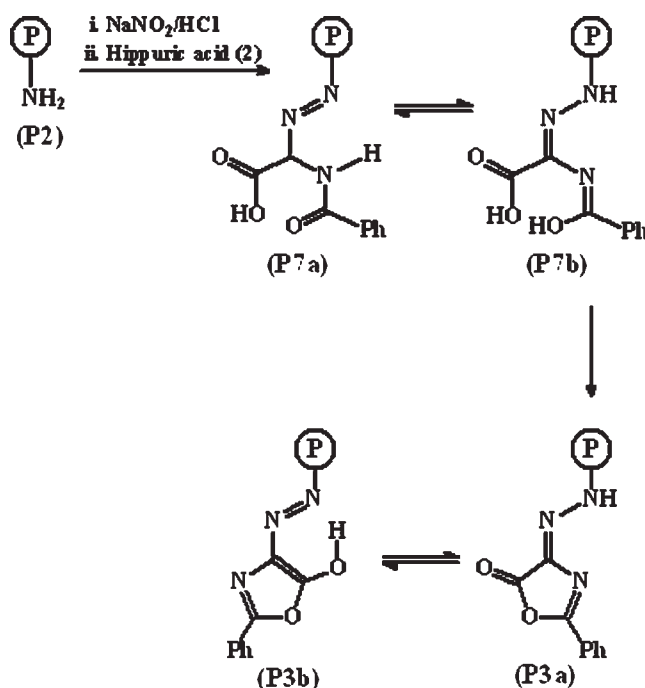
## RESULTS AND DISCUSSION

The chemical modification of polyvinyl chloride (P1) is of great importance as it can be used in many applications. In the present work, P1 has been modified into polymer-supported oxazolinone and triazole

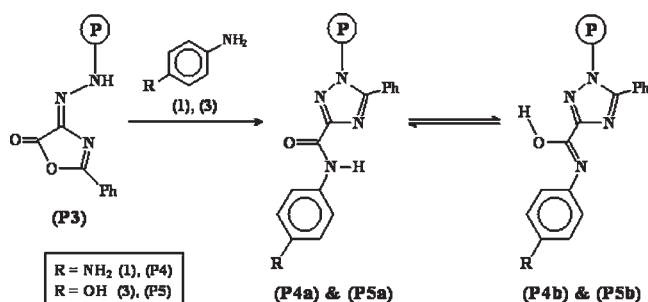
derivatives through sequential chemical assembly of the reactive species onto the P1 matrix.

#### Characterization of poly(vinyl chloride-co-vinylaminoaniline) (P2)

Scheme 1 represents the overall reaction sequence. Accordingly, P1 was converted into poly(vinyl chloride-



**Scheme 2** Formation of the polymer-supported oxazolinone derivative P3.



Scheme 3 Reaction of P3 with 1 and 3.

co-vinylaminoaniline) (P2) through the reaction with *p*-phenylenediamine (1), according to the previously reported method,<sup>11</sup> and the formation of the copolymer (P2) with 70% conversion has been concluded from elemental and FTIR spectroscopic analyses. P2 showed absorption at 2850  $\text{cm}^{-1}$  corresponding to CH—N bonding formed by alkylation of 1 with P1. The unreacted  $\text{NH}_2$  groups and the obtained NH bonds in P2 are responsible for the absorption shown at 3480  $\text{cm}^{-1}$  and 3350  $\text{cm}^{-1}$ , respectively. Also, insertion of the aniline residues was confirmed by the absorption at 1590  $\text{cm}^{-1}$  corresponding to C=C aromatic in P2. Comparison of FTIR spectrum of P2 with that of P1 clearly proves such a modification of P1, as it showed absorption bands only at 705  $\text{cm}^{-1}$  corresponding to C—Cl bond in addition to the absorption at 1675  $\text{cm}^{-1}$  for C=C bonds that mostly occurred in P1 or during the chemical reactions and thermal treatment as well (see Table II).

On the other hand, elemental analysis was also used to prove the success of the reaction as well as to esti-

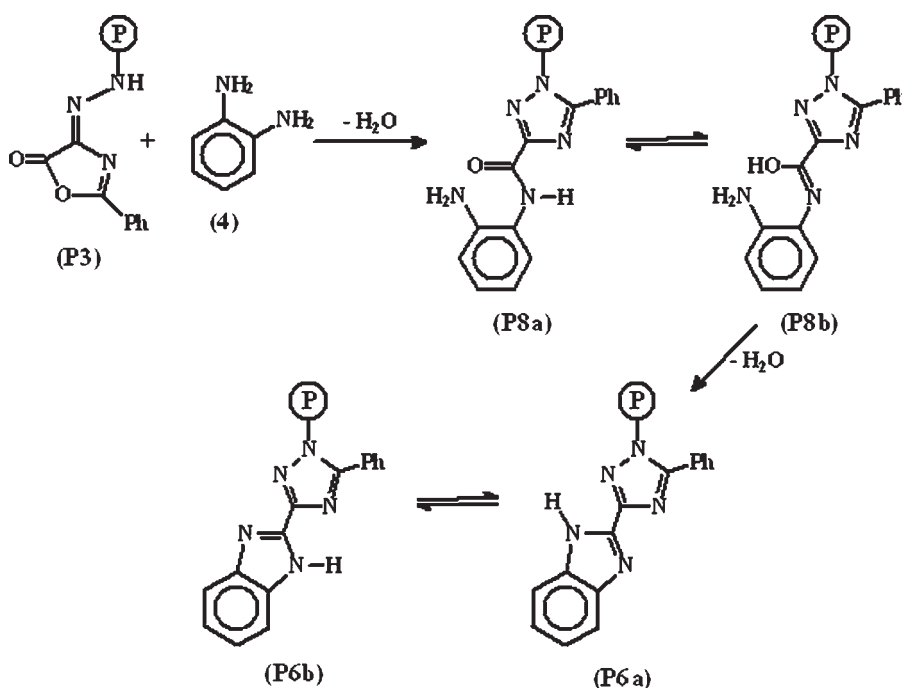
mate the reaction yield based on the mole fraction concept where the carbon content increased from 38.38% to 69.32% and decreased from 56.8% to 9.39% for chlorine while nitrogen appeared in 17.44% content. These data correspond for both the conversion percentage and the overall reaction yield (70%, see Table I).

#### Characterization of oxazolinone-supported polymer (P3)

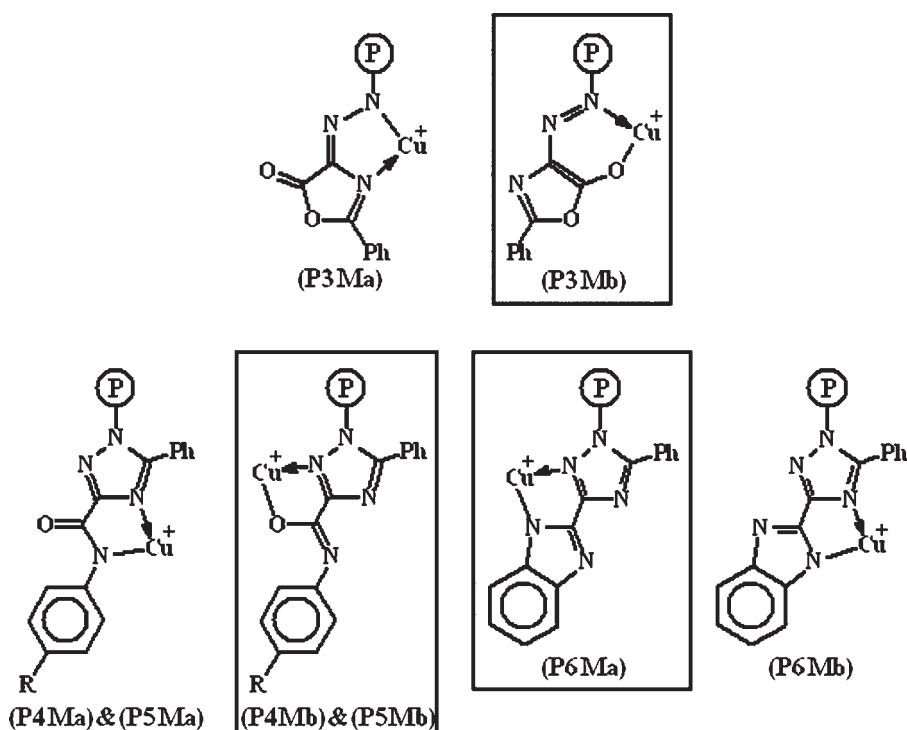
The primary aromatic amino groups in P2 were diazotized and reacted with hippuric acid (2) to form the supported oxazolinone derivative (P3) as a yellowish green product. During the reaction of diazotized P2 with hippuric acid (2), the obtained product undergoes azo-hydrazo tautomerism resulting in formation of P7a and P7b. Absorption at 3320  $\text{cm}^{-1}$  and at 1050  $\text{cm}^{-1}$  for NH and C—O—C, respectively, were observed for P3 confirming the formation of 5-oxazolinone derivative P3a in addition to the absorption at 3500  $\text{cm}^{-1}$  and 1565  $\text{cm}^{-1}$  related to OH and N=N groups justifying the formation of the tautomer 5-oxazolol derivative P3b as represented in Scheme 2.

#### Characterization of triazole-supported polymers P4 and P5

After the preparation and characterization of the polymer-supported oxazolinone (P3), the obtained product has been further reacted with different aniline derivatives, 1 and 3. Under the reaction conditions, the primary aromatic amino group of 1 and 3 may attack the intramolecular ester functionality in the polymer-supported oxazoli-



Scheme 4 Chemical transformation of P3 into P6.



Scheme 5 Possible interaction of the obtained polymeric samples P3–P6 with Cu(II).

none (P3), resulting in the formation of the corresponding polymer-supported 1,2,4-triazolyl-3-carboxanilides P4 and P5 in the amide form (a) or in the imine-ol form (b).

This reaction may undergo simultaneous ring opening amidation of the oxazolinone ring followed by condensation cyclization, resulting in the formation of polymer-supported triazolyl tautomers P4a, P5a, P4b, and P5b. Characterization of the obtained products P4 and P5 with the aid of elemental and FTIR spectroscopic analyses showed their chemical structure. Both P4 and P5 showed approximately similar absorption at  $3350\text{ cm}^{-1}$  (NH),  $1670\text{ cm}^{-1}$  (CONH),  $1620\text{ cm}^{-1}$  (C=N), and  $3500\text{ cm}^{-1}$  (OH) in addition to the absorption at  $1590\text{ cm}^{-1}$  for C=C aromatic. P4 showed further absorption at  $3480\text{ cm}^{-1}$  corresponding to *p*-NH<sub>2</sub> functionality. Occurrence of hydroxyl group absorption in P4 in addition to the amide functionality concludes the presence of P4 in the two tautomeric forms P4a and P4b and the same holds true also for the obtained product (P5) as represented in Scheme 3. Elemental analysis data of P4 (C; 66.11%, H; 5.12%, N; 16.66 and Cl; 4.78) and P5 (C; 66.94%, H; 4.88%, N; 19.06 and Cl; 4.88) concluded that P4 was obtained in 78% conversion and 35% overall reaction yield, while P5 was obtained in 71% conversion and 32% overall reaction yield (see Table I).

#### Characterization of polymer-supported 2-benzimidazolyl-1,2,4-triazole (P6)

On the other hand, by using 4 instead of 1 or 3, the ortho amino group in the corresponding polymer-sup-

ported 1,2,4-triazolylcarboxanilide derivative (P8a,b) can undergo further dehydration to produce the corresponding polymer-supported 2-benzimidazolyl-1,2,4-triazolyl derivative P6 as represented in Scheme 4. FTIR analysis of P6 showed absorption at  $3300\text{ cm}^{-1}$  and  $1624\text{ cm}^{-1}$  corresponding to NH and C=N functionalities, whereas absorption of either carbonyl or NH<sub>2</sub> group is absent (see Table II). This confirms the intramolecular amidation of the ortho amino group in the corresponding triazole derivative (P8) during the reaction of P3 with 4, resulting in formation of the corresponding polymer-supported 2-benzimidazolyl-1,2,4-triazolyl derivative P6. Also, elemental analysis (C; 68.68, H; 4.92, N; 19.48 and Cl; 5.08) confirmed the formation of P6 in 67% conversion and 30% overall reaction yield as shown in Table I (Scheme 4).

#### Application of P2–P6 for metal uptake of Cu(II) ions

The obtained modified PVC samples P2 to P6 were treated with an aqueous solution of copper acetate to check roughly their ability to uptake Cu(II) ions. The metal uptake by the modified PVC samples was determined through back determination of the excess Cu(II) ions in the filtrate while the metal-loaded samples P2M–P6M were subjected to FTIR spectroscopic analysis (see Table II). The raw data for metal uptake by these polymers are listed in Table I. FTIR characterization of the metal-loaded samples (P2M)–(P6M) proved their ability for Cu(II) uptake. The absorption peaks involved are shifted after treatment with the metal ion solution as

shown in Table I. Scheme 5 represents the possible interaction of the investigated samples **P3** to **P6** with Cu(II) ions, and the more favorable forms that may be involved in the metal uptake have been framed.

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