

# Chemical Modification of Chloromethylated Polystyrene with Pyridylazo- $\beta$ -Naphthol

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**ABSTRACT:** Chloromethylated polystyrene was chemically modified through alkylation of pyridylazo- $\beta$ -naphthol (PAN) in the presence of a phase-transfer catalyst. The chemical modification was achieved through *O*-alkylation as well as *N*-alkylation of PAN, leading to formation of polymer-supported quaternary ammonium salt in the latter case. Both types of a polymer-supported PAN moiety were detected by FTIR spectroscopic analysis. The complexation behavior of the polymer-supported PAN as an ion-exchanger toward some metal ions was studied. Thermogravimetric and differential thermogravimetric analyses data were used to study the kinetics of the thermal decomposition process of the ion-exchanger. Some thermodynamic parameters for the ion-exchanger were calculated by applying the rate theory of the first-order reaction. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3044–3048, 2000

**Key words:** chloromethylated polystyrene; chemical modification; PAN; ion-exchange resins; thermal analysis

## INTRODUCTION

Polymer-supported organic compounds play an important role in many applications. Some of these organic compounds, especially those serving as chelating agents, can be used as polymer-supported materials in waste-water treatment as well as in selective sensing and separation of some heavy metal ions.<sup>1</sup> On the other hand, pyridylazo- $\beta$ -naphthol (PAN) is a well-known compound that has a strong ability to form a complex with many metal ions.<sup>2–4</sup> Also, a sulfonic acid derivative of PAN supported to some ion-exchanger was used for preconcentration of different heavy metals such as copper, zinc, cadmium, and nickel ions.<sup>5</sup> Some other analytical applications of PAN were reported.<sup>6–8</sup> The present work was aimed at supporting PAN onto chloromethylated polystyrene through an alkylation reaction

under phase-transfer-catalyzed conditions. The complexation behavior of the polymer-supported PAN toward some metal ions was studied. Also, some preliminary investigations for some thermodynamic parameters were performed.

## EXPERIMENTAL

### Materials and Techniques

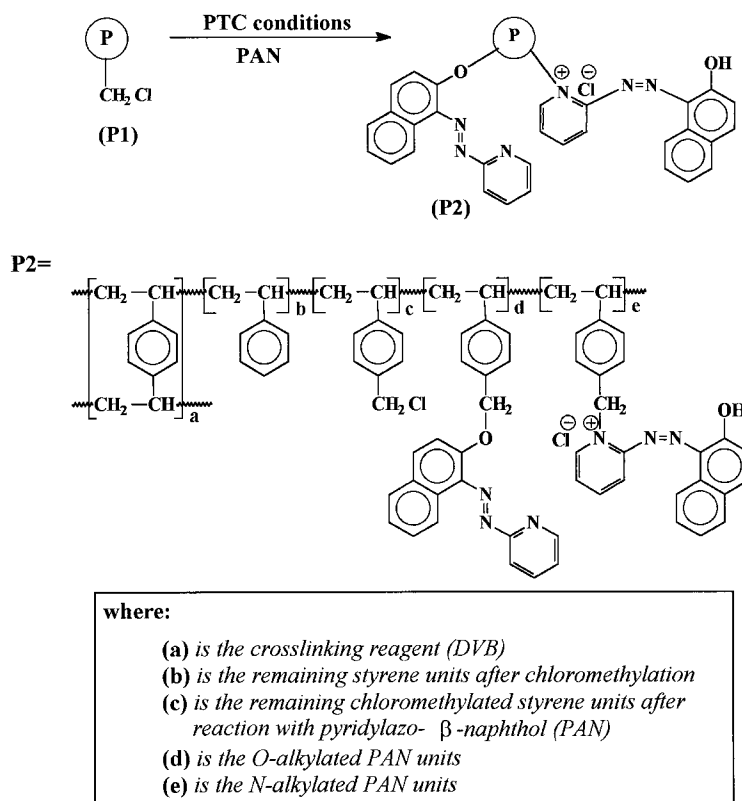
Commercial chloromethyl polystyrene-*co*-DVB (P1) [MP-500 A; Bayer Co. (Leuerkusen, Germany); 2% DVB; specific surface area (BET) is 66 m<sup>2</sup>/g and 4.6 mequiv Cl/g resin] was used. PAN, cetyltrimethylammonium bromide (CTMA), and the salts of the used metal ions (Aldrich, Milwaukee, WI, USA) were used as supplied. The reaction was followed up in all experiments using a Mattson 5000 FTIR spectrophotometer.

### Reaction of P1 with PAN

In a 50-mL round-bottom flask, 200 mg (0.92 mequiv Cl) P1 was soaked 3 days in 20 mL of

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**Scheme 1** Alkylation reaction of PAN with P1.

chloroform as a swelling medium. To the swollen polymer, 650 mg (2.5 mmol) PAN, 70 mg (0.2 mmol) CTMA as a phase-transfer catalyst, and 15 mL of a 30% aqueous solution of sodium carbonate were added. The reaction mixture was refluxed in a water bath and stirred magnetically for 96 h. After cooling, the modified polymeric product was filtered off and washed thoroughly with acetic acid, methanol, distilled water, acetone, and, finally, diethyl ether. The polymeric product [polymer-supported PAN (P2)] was then dried at 40°C overnight and characterized using FTIR spectroscopic analysis.

#### Reaction of P2 with Metal Ions

P2, 20 mg, was stirred for 20 min with 5 mL of a 10 mg/L concentration of the tested metal ion, namely, Fe(III), Mn(II), and Au(III), at the desired pH and at room temperature (~25°C). The pH of the solutions was adjusted by 0.1N HCl and 0.5N NaOH. The loaded P2 was filtered off, washed with bidistilled water, and eluted with 5 mL of 0.5M hot nitric or hydrochloric acid. The resulting solution was completed to 10 mL and

the metal ion concentration was determined by a Perkin–Elmer 2380 atomic absorption spectrometer.

#### Thermal Analysis of the Polymer-supported Products

Thermal studies were carried out using a DTA-50, TGA-50 Shimadzu thermogravimetric analyzer (Japan) with a heating rate of 10°C/min using a platinum crucible fitted with a Pt–Pt, Rh (10%) thermocouple. The weight of the samples varied from 2.0 to 3.2 mg.

## RESULTS AND DISCUSSION

The reaction of P1 (2% divinylbenzene, 4.6 mequiv Cl/g) with PAN as a nucleophile under formation of the corresponding P2 was carried out under solid–liquid–liquid (SLL) phase-transfer-catalyzed (PTC) conditions (Scheme 1). Excess amounts of PAN were used in the presence of catalytic amounts of CTMA as a phase-transfer catalyst. Chloroform was used as a solvent, as it

**Table I**  $\log k_d$  and  $R\%$  at Different pHs of Some Metal Ions

Parameter	Metal Ion					
	Fe(III)		Mn(II)		Au(III)	
	pH					
	2.3	8.0	2.0	10.5	3.0	8.0
$\log k_d$	3.7	5.4	2.8	5.2	4.7	3.0
$R\%$	67	99	20	98	95	29

was used in the reaction of P1 with 4-hydroxybenzaldehyde in a previous study.<sup>9</sup> P2 was roughly investigated as to its ability to form a polymer-supported complex with some metals such as iron, manganese, and gold. A polymer-supported complex with such metal ions was proved through the change in color after the reaction with such metal ions. Also, it was characterized by an IR spectroscopic investigation as well.

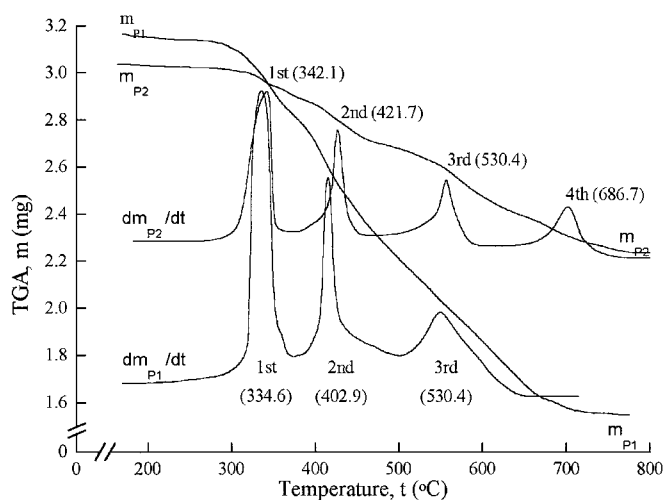
### Characterization of P2

The modified polymeric samples were subjected to infrared spectroscopic analysis that showed absorption peaks characteristic for P2 units. The absorption peaks at 385 and 1640  $\text{cm}^{-1}$  in addition to the shoulder at 1575  $\text{cm}^{-1}$  are related to the 2-substituted pyridine ring. The absorption at 1539 and 375  $\text{cm}^{-1}$  is related to the azo group of

PAN ( $-\text{N}=\text{N}-$ ). Also, the absorption at 3600–3700  $\text{cm}^{-1}$  corresponds to the phenolic OH group. In addition, the absorption at 2350–2380  $\text{cm}^{-1}$  and at 1420–1425  $\text{cm}^{-1}$  indicates the presence of  $\text{C}=\overset{\oplus}{\text{N}}$  formed during the alkylation of PAN through the formation of *N*-pyridinium quaternary salt. Also, addition of silver nitrate to P2 leads to the precipitation of silver chloride. This indicates also the *N*-alkylation of PAN with P1. On the other hand, the absorptions at 1240  $\text{cm}^{-1}$  corresponding to the aryl–O– bond and at 1050  $\text{cm}^{-1}$  corresponding to  $\text{CH}_2\text{--O--}$  bond are evidence of the *O*-alkylation of PAN with P1.<sup>10a</sup> Therefore, it can be concluded that PAN reacted with P1 through *N*-alkylation as well as *O*-alkylation reaction as represented in Scheme 1.

### Characterization of Metal-complexed P2

P2 was allowed to react with the chloride salt of iron, manganese, and gold. The complexes formed from this reaction were proved through different ways, such as by the change of color according to the complexed metal ion. The IR spectroscopic investigation of the formed complexes as well as the determination of some kinetic and thermodynamic parameters were also used to prove the formation of such complexes. The inclusion of the metal ion in a complexed form may be indicated by the absorption peak at about 1630–1640  $\text{cm}^{-1}$  as well as by shifting the absorption peaks of the organic functionalities due to the polarizing effect of such metal ions.<sup>10b</sup> The distribution of metal

**Figure 1** TGA and DTG curves of P1 and P2.

**Table II Analysis of TG Curves of Thermal Decomposition of P1 and P2**

Stage	P1			P2		
	Range (°C)	Midpoint (°C)	Wt Loss (%)	Range (°C)	Midpoint (°C)	Wt Loss (%)
1st	163.45–374.20	334.61	10.8	199.85–375.22	342.1	4.97
2nd	374.2–425.12	402.7	9.2	375.22–467.7	421.9	7.13
3rd	425.12–711.05	548.8	30.44	467.7–592.82	530.4	8.88
4th	—	—	—	592.82–780.29	686.7	7.89

ions between the solution and the polymer matrix (P2), referred to as the distribution coefficient  $k_d$  and the recovery %,  $R\%$ , of these metal ions were determined (Table I). They reflect the possibility of using P2 in some analytical applications such as in preconcentration. The distribution coefficient  $k_d$  in  $\text{cm}^3/\text{g}$  and the recovery %,  $R\%$ , of the metal ions are calculated by the following equations<sup>11,12</sup>:

$$k_d (\text{cm}^3/\text{g}) = C_{\text{P2}}/C_{\text{sol}} \quad (1)$$

where  $C_{\text{P2}}$  and  $C_{\text{sol}}$  are the concentration of the metal ion in the polymer matrix P2 in  $\mu\text{g}/\text{g}$  and that in the solution in  $\mu\text{g}/\text{cm}^3$ ;

$$R \% = k_d W_{\text{P2}} \times 100 / (k_d W_{\text{P2}} + V) \quad (2)$$

where  $W_{\text{P2}}$  is the weight of the polymer P2 used and  $V = 50$ , which is the volume in milliliters of the solution used.

### Thermal Study

The thermal decomposition of P1 and P2 is represented in Figure 1. It appears that during heating of the studied compounds the corresponding TG and DTA curves undergo a series of three steps for P1 and four thermal steps for P2 associated with weight loss in both cases. TG curves started at 163.5°C for P1 and at 200°C for P2. The analysis of the TG curves of the compounds under investigation is given in Table II.

### Kinetic Study

This was based on Chatterjee's method<sup>13</sup> using the following general equation for the rate of the heterogeneous kinetics ( $V$ ):

$$V = \frac{-dm}{dt} = km^n \quad (3)$$

where  $k$ ,  $m$ ,  $n$ , and  $t$  are, respectively, the specific reaction rate constant, the active mass of the decomposing material in milligrams, the reaction order = 1, and the time in minutes elapsed from the start of the experiment.

Substituting  $k$  from the Arrhenius equation into the last one gives

$$\log V = \log A - n \log m - \frac{E_a}{2.303RT} \quad (4)$$

where  $A$  is the frequency factor and  $R$  is the gas constant. This equation gives the relationship between the reaction rate and temperature. The energy of activation,  $E_a$ , can be calculated from the slope  $S$  of the straight line from the plot of  $\log V$  versus  $1/T$ , where  $E_a = 2.303RS$ .

The evaluated values of the specific rate constant and the energy of activation are given in Tables III and IV, respectively. It is obvious that the order of the decomposition reaction for all cases is nearly equal to unity. This indicates that the decomposition reactions have the same mechanism.<sup>14</sup>

**Table III Kinetic Parameters of P1 and P2 Using Chatterjee's Method (Order = 1)**

Stage	P1		P2	
	$K \times 10^2$ ( $\text{min}^{-1}$ )	$t^{1/2}$ (min)	$K \times 10^2$ ( $\text{min}^{-1}$ )	$t^{1/2}$ (min)
1st	7.48	9.3	9.87	7.0
2nd	42.49	1.6	22.98	3.0
3rd	5.72	12.1	15.39	4.5
4th	—	—	10.46	6.6

**Table IV** Evaluated Values of the Activation Energy and Thermodynamic Parameters of the Thermal Decomposition Stages of P1 and P2

Parameter	Polymer	Stage				Total
		1st	2nd	3rd	4th	
$E_a$ (kJ mol <sup>-1</sup> )	P1	18.99	159.20	34.75	—	212.44
	P2	26.60	93.55	85.61	81.84	287.60
$\Delta H^*$ (kJ mol <sup>-1</sup> )	P1	13.94	153.58	27.92	—	195.44
	P2	21.49	87.77	78.93	73.86	262.12
$-\Delta G^*$ (kJ mol <sup>-1</sup> )	P1	5.05	5.61	6.83	—	17.49
	P2	5.11	5.77	6.68	7.97	25.53
$\Delta S^*$ (J K <sup>-1</sup> mol <sup>-1</sup> )	P1	31.25	235.60	42.28	—	309.13
	P2	43.24	134.63	106.56	85.27	360.70

### Thermodynamic Parameters Calculation

By using the values of the specific rate constant of the thermal decomposition process in each stage according to the rate theory<sup>15</sup> and the Arrhenius equation,<sup>16</sup> the thermodynamic parameters  $\Delta H^*$ ,  $\Delta G^*$ , and  $\Delta S^*$  for the thermal decomposition process were calculated. The obtained values are summarized in Table IV. From this table, the values of  $\Delta H^*_{\text{total}}$  and  $\Delta S^*_{\text{total}}$  for all cases are positive, which means clearly that the decomposition process is endothermic and is accompanied by an increase in the disorder of the decomposition steps. It is clear also that P2 has the total activation energy  $E_a$  and other thermodynamic parameters such as  $\Delta H^*_{\text{total}}$ ,  $-\Delta G^*_{\text{total}}$ , and  $\Delta S^*_{\text{total}}$ , higher than that of P1. Thus, the calculated thermodynamic parameters confirm the formation of P2. This has not been reported previously. The negative values of  $\Delta G^*$  indicate that the decomposition process is a spontaneous reaction. However, at temperatures of 300–700°C, the nonspontaneity of the decomposition process may be apparent. This can be attributed to the fragmentation accompanying the decomposition process increasing the system disorder. This means that the values of  $T\Delta S^*$  are, consequently, still higher than those of  $\Delta H^*$  in Gibb's equation, leading to negative values of  $\Delta G^*$ . The obtained data in the present study are in a good agreement with similar findings reported earlier in the literature.<sup>17–20</sup>

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