

# Synthesis of Poly(vinyl alcohol) Phosphorylate–Dicyandiamide–Formaldehyde Resin Complex and Its Adsorption of Rare Earth Ions

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**ABSTRACT:** Poly(vinyl alcohol) phosphorylate was prepared and its complex with dicyandiamide–formaldehyde resin was used for adsorption and separation of  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Er}^{3+}$  ions. The factors that affect the adsorption and separation of these ions on the polyacid–polybase complex, such as the acidity of the sample solution, adsorption capacity, and conditions of desorption, were investigated by means of spectrophotometry and inductively coupled plasma optical emission spectrometry. IR spectrometry and X-ray photoelectric spectrometry were used to study the adsorption mechanism, and the probably coordination structure was given. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 962–968, 2002; DOI 10.1002/app.10197

**Key words:** polyacid; polybase; adsorption; rare earth element

## INTRODUCTION

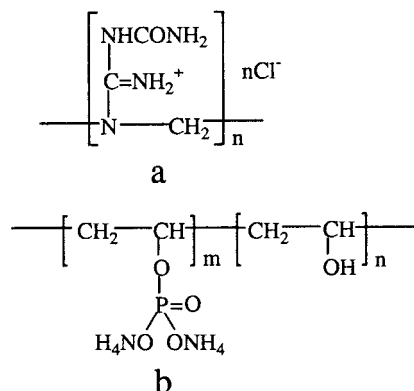
It is well known that polyelectrolytes (PECs) form complexes with metal ions. Under some conditions, two kinds of PECs with different charges can form a complex with a certain ratio. Polyanion and metal ions form a complex by coordination bonds and electrostatic attraction; they then form a stable polyacid–metal ions–polybase triple complex with a polycation by electrostatic attraction, coordination bonds, hydrophobic interaction, hydrogen bonds, and van der Waals forces.<sup>1</sup> Metal ions can be separated from the triple complex. It is mainly controlled by the acidity. The binary complex that the metal ions have eluted can be reused for concentration and separation. For

example, a poly(acrylic acid)–poly(vinyl pyrrolidone) complex was used to adsorb  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ .<sup>2,3</sup>

Ion exchange and precipitation are often used for preconcentration and separation of rare earth elements,<sup>4–7</sup> but PEC complexes used for concentration and separation of rare earth elements have not been reported. We studied the diethylenetriamine copolymer of a sodium acrylate and maleic anhydride system that was used for concentration and separation of  $\text{Au}^{3+}$ ,  $\text{Ru}^{3+}$ ,  $\text{Bi}^{3+}$  and  $\text{Hg}^{2+}$ .<sup>8</sup> In this article we synthesized poly(vinyl alcohol) phosphorylate (PVAP). It and dicyandiamide–formaldehyde resin (DCAF, Fig. 1) were used for adsorption and separation of  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Er}^{3+}$  ions by forming a polymer–metal ions–polymer triple complex. The results were satisfactory. We also studied its mechanisms.

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**Figure 1** (a) Dicyandiamide-formaldehyde resin and (b) phosphorous polyacid-phosphorylate poly(vinyl alcohol) (PVAP).

## EXPERIMENTAL

### Instruments, Reagents, and Standards

An ICP/6500 spectrometer (model 175-5X, Perkin-Elmer), FTIR spectrometer, and PHI-5702 XPS/AES system (equipped with a customization workstation) for X-ray photoelectron spectrometry (XPS) were used. The conditions for analysis by XPS were a vacuum tightness overmatch of  $10^{-7}$  Pa, a  $\text{MgK}\alpha$  radiation source at 1253.6 eV, 15-kV voltage, and 250-W power; the energy through the energy analyzer was 29.35 eV. All XPS spectra were energy referenced to the  $\text{C}_{1s}$  photoemission peak at 284.6 eV.

A standard solution consisted of 1 g/L of  $\text{Sm}^{3+}$ ,  $\text{Nd}^{3+}$ ,  $\text{Gd}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Er}^{3+}$ . A mixed standard solution contained 100 mg/L of  $\text{Sm}^{3+}$  and  $\text{Nd}^{3+}$  and 10 mg/L of  $\text{Gd}^{3+}$ ,  $\text{Ho}^{3+}$ , and  $\text{Er}^{3+}$ .

### Synthesis of PVAP

Five grams of PVA (compound 1799: molecular weight =  $77,000 \pm 2000$  g/mol, alcoholysis degree = 99%) were dissolved in hot water. Eight and one-half grams of urea were dissolved in 15 g of concentrated phosphoric acid with heating. This was poured into the PVA solution. After 4.5 h of

**Table II** Effect of Pretreatment Acidity of Binary Complex on Recovery

Acidity	Recovery (%)				
	0.1N	1N	2N	3N	4N
$\text{Er}^{3+}$	56.2	98.3	98.7	98.9	69.0
$\text{Gd}^{3+}$	60.4	98.4	98.9	99.1	70.3
$\text{Ho}^{3+}$	57.3	98.3	99.0	98.8	69.4
$\text{Sm}^{3+}$	65.6	100.0	99.8	100.0	76.7
$\text{Nd}^{3+}$	63.2	99.3	99.2	99.4	73.2

reaction with stirring at  $90^\circ\text{C}$ , a double volume of water was added to the system when it was cooled. The solution was poured into an excess of methanol with stirring, which was followed by the precipitation of a large amount of floc. The dissolving and precipitating procedure was repeated. The precipitate was dried and ground into a powder. We repeated the experiment using PVA (compound 1788: molecular weight =  $77,000 \pm 2000$  g/mol, alcoholysis degree = 88%).

### Determination of Percentage of Phosphorus

The product was decomposed with a strong nitric acid and perchloric acid mixture. The solution was diluted with water so that the concentration of the phosphoric acid radical of the solution could be determined by inductively coupled plasma optical emission spectrometry.

### Optimum DCAF/PVAP Ratio of Binary Complex

A solution of 8 g/L of PVAPs 1788 and 1799 and the DCAF was prepared. Two kinds of solutions were mixed in different ratios. The absorbency was determined by a spectrophotometer. The results are shown in Table I.

### Effect of Pretreatment Acidity of Binary Complex

The effect of the pretreatment acidity of the binary complex was investigated in a HCl concen-

**Table I** DCAF/PVAP Ratio of PVAP-DCAF Complex (1799)

DCAF	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
PVAP	5	5	5	5	5	5	5	5	5	5
Absorbency	0.221	0.379	0.432	0.480	0.488	0.501	0.496	0.429	0.366	0.328
Ratio	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16	0.18	0.20

**Table III Effect of Acidity on Adsorption**

pH	Recovery (%)						
	1.0	1.5	2.1	2.5	3.1	4.1	6.0
Er <sup>3+</sup>	0	15.8	66.9	97.9	100	100	100
Gd <sup>3+</sup>	0	22.4	75.6	99.5	100	100	100
Ho <sup>3+</sup>	0	16.8	67.5	98.0	100	100	100
Sm <sup>3+</sup>	1.1	23.8	83.2	99.4	100	100	100
Nd <sup>3+</sup>	0	23.8	81.0	99.2	100	100	99.8

**Table IV Effect of Acidity on Elution**

[H <sup>+</sup> ]	Elute Rate (%)						
	4N	3N	2N	1N	0.32N	0.1N	0.01N
Er <sup>3+</sup>	25.6	40.3	48.0	74.1	79.0	93.0	72.0
Gd <sup>3+</sup>	12.6	21.6	29.8	62.7	82.8	81.3	71.0
Ho <sup>3+</sup>	20.6	45.1	55.3	74.4	73.7	92.9	75.3
Sm <sup>3+</sup>	15.6	31.0	39.8	74.6	89.1	98.0	77.5
Nd <sup>3+</sup>	30.1	40.6	55.7	78.5	88.7	100	77.1

tration range of 0.1–4.0N. The mixing standard solution (1 mL) was added after shaking for 1 h. The acidity was adjusted to pH 4.0. The results are presented in Table II.

#### Effect of Acidity on Adsorption

The adsorption experiments were done under different acidities after pretreatment, and the results are summarized in Table III.

#### Effect of Acidity on Elution

The resins were eluted with different concentrations of hydrochloric acid after adsorption. Table IV contains the results.

#### Static Adsorption Capacity

Five 0.05-g pretreated pieces of the binary complexes were added to 5.21 mg/L of rare earth ions.

**Table V Static Adsorption Capacity (mg/g R\*)**

	Ions				
	Er <sup>3+</sup>	Ho <sup>3+</sup>	Gd <sup>3+</sup>	Sm <sup>3+</sup>	Nd <sup>3+</sup>
Capacity	154.8	155.2	155.8	155.8	155.8

**Table VI Effect of Different Interferential Ions on Adsorption Rate**

Interference Ions	Recovery (%)						
	Ba <sup>2+</sup>	Zn <sup>2+</sup>	Cu <sup>2+</sup>	Fe <sup>3+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Al <sup>3+</sup>
Er <sup>3+</sup>	100	100	73.0	59.0	100	100	80.0
Gd <sup>3+</sup>	98.0	97.0	70.0	61.0	97.0	99.1	70.0
Ho <sup>3+</sup>	100	100	70.0	56.0	100	100	71.3
Sm <sup>3+</sup>	100	100	88.1	59.7	100	100	74.3
Nd <sup>3+</sup>	100	99.2	87.5	59.7	100	99.4	73.1

The adsorption experiment was done under optimum conditions. A certain amount of solution (1.5 mL) was taken out until the concentration was unchanged. The results are given in Table V.

#### Effect of Different Interference Ions on Adsorption Rate

Different interfering ions were added to the rare earth standard solutions. The analytes were adsorbed and determined as described. The results are summarized in Table VI.

#### Sample Preparation for IR Spectrometry Analysis

Four compounds were prepared for IR spectrometry: PVAP, the PVAP–DCAF binary complex, the PVAP–Nd<sup>3+</sup>–DCAF triple complex, and DCAF.

#### Preparation of XPS Sample

In compound 1 the PVAP (7.0% P) was dried for 48 h. For compound 2, 5 g of DCAF resin (drying weight: 52%) was diluted with 5 g of water. Sodium hydroxide solution was added dropwise until no deposition was formed. Then the deposition was dissolved with the HCl solution. The process was repeated 3 times. The deposition was dried for 48 h. Compound 3 is the PVAP–Nd<sup>3+</sup>–DCAF triple complex. PVAP and DCAF solutions were

**Table VII XPS Data (C<sub>1s</sub>) of Compounds 2 and 3**

Sample Functional Group	Compound 2		Compound 3	
	E <sub>B</sub> (eV)	Atomic Conc	E <sub>B</sub> (eV)	Atomic Conc
C=N <sup>+</sup> H <sub>2</sub>	399.81	61.51	400.55	16.32
C–N	398.32	38.49	399.60	83.68

**Table VIII XPS Data (C<sub>1s</sub>) of Compounds 1–3**

Sample Functional Group	Compound 1		Compound 2		Compound 3	
	$E_B$ (eV)	Atomic Concn	$E_B$ (eV)	Atomic Concn	$E_B$ (eV)	Atomic Concn
C=N <sup>+</sup> H <sub>2</sub>			287.85	27.38	288.03	4.79
C=O			286.05	27.70	286.80	9.96
C—O	286.10	33.99			285.95	17.99
C—H	284.62	66.01	284.56	44.92	284.66	67.25

mixed in the optimum ratio, then an excess of Nd<sup>3+</sup> solution was added. The deposition was separated with a centrifugal machine. The process was repeated 3 times.

## RESULTS AND DISCUSSION

The phosphorus content of PVAP that was synthesized from PVAP 1799 is 7.0%, which means that there is one phosphoryl group in 8.5 chain elements. The phosphorus content of PVAP that was synthesized from PVAP 1788 is also 7.0%.

Table I shows that the optimum DCAF/PVAP (1799) ratio of the binary complex is 0.12. When the ratio was >0.12, the precipitate dissolved. In this study we adopt the DCAF/PVAP (1799) ratio of 0.12 (Table I). However, with PVAP 1788 in any ratio or increased concentration, DCAF could not form a precipitate with PVAP, because the hydroxyl content of PVAP 1788 was lower than of PVAP 1799. There were not enough hydrogen bonds to form the precipitate. This showed that there were many hydrogen bonds in the binary complex.

Table II shows that the adsorption rate increased according to the increasing acidity, became flat, and then decreased. Because the binary complex has a certain stability, an increase of the acidity was good for the decomposition of the complex. The structure of the binary complex would

be destroyed if the acidity were too high, so the adsorption rate decreased. The pretreatment acidity selected in this experiment was 1*N*.

When the pH was under 2.5, the recovery increased corresponding to the increase of the acidity. In this experiment pH 3.0 was selected as the adsorption acidity, and an [H<sup>+</sup>] of 0.1 was selected as the elution acidity.

The 50–500-fold excesses of other ions such as Mg<sup>2+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, and Zn<sup>2+</sup> cause a little interference in the adsorption (Table VI); however, interference ions of Cu<sup>2+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup> caused high interference (50-fold excesses to Sm<sup>3+</sup> and Nd<sup>3+</sup>; 500-fold excesses to Er<sup>3+</sup>, Ho<sup>3+</sup>, and Gd<sup>3+</sup>).

The proposed method for adsorption of the metal ions was quick, convenient, and precise. The binary complex had a strong enrichment effect and a big adsorption capacity unlike traditional resins, which depend on time, while enriched ions and the binary complex were of anti-jam base metal ions. However, the binary complex selectivity of rare earth ions was poor, being only about 1.

The XPS data of the N<sub>1s</sub>, C<sub>1s</sub>, and O<sub>1s</sub> binding energy are shown in Tables VII–IX, respectively. In Table VII the N<sub>1s</sub> binding energy of the functional group C=N<sup>+</sup>H<sub>2</sub> in compound 2 was 399.81 eV and in compound 3 was 400.55 eV, which is an increase of 0.74 eV. The N<sub>1s</sub> binding energy of functional group C—N in compound 2 was 398.32 eV and in compound 3 was 399.60 eV, an increase

**Table IX XPS Data (O<sub>1s</sub>) of Compounds 1–3**

Sample Functional Group	Compound 1		Compound 2		Compound 3	
	$E_B$ (eV)	Atomic Concn	$E_B$ (eV)	Atomic Concn	$E_B$ (eV)	Atomic Concn
C=O(P=O)	532.53	47.76	530.9		532.47	22.15
C—O(P—O)	531.34	52.54			530.85	77.85

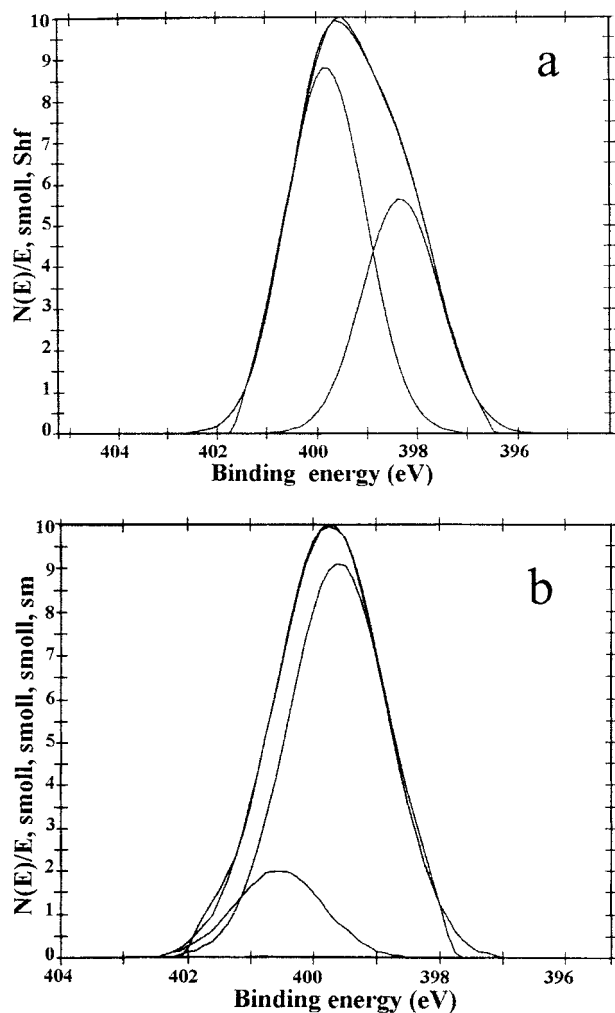
Compound 1: P=O (P—O, C—O); Compound 3: (P=O, C=O), (P—O, C—O).

**Table X** Data of IR Spectrum

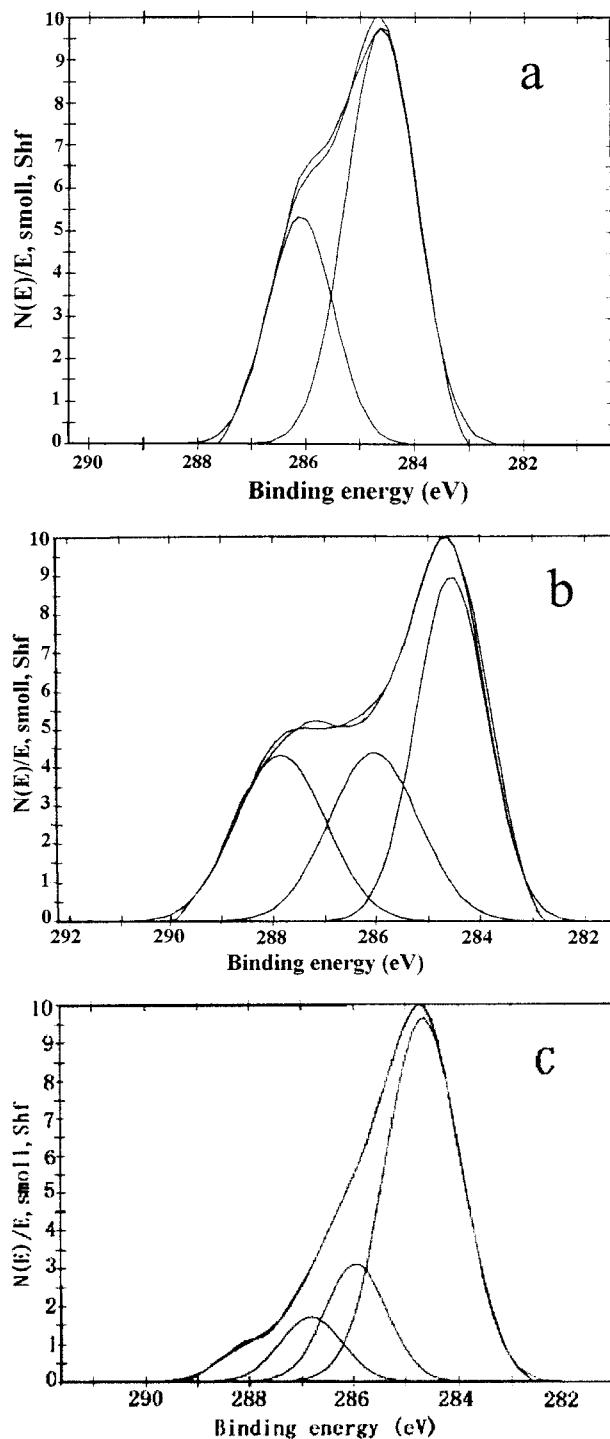
Sample	a	b	c
P=O flex	1289.2 $\text{cm}^{-1}$	1317.1 $\text{cm}^{-1}$	1383.7/1356.0 $\text{cm}^{-1a}$
P—O flex	915.9 $\text{cm}^{-1}$	978.7 $\text{cm}^{-1}$	1021.0 $\text{cm}^{-1}$
Association vibration	2370.6 $\text{cm}^{-1}$	Disappeared	

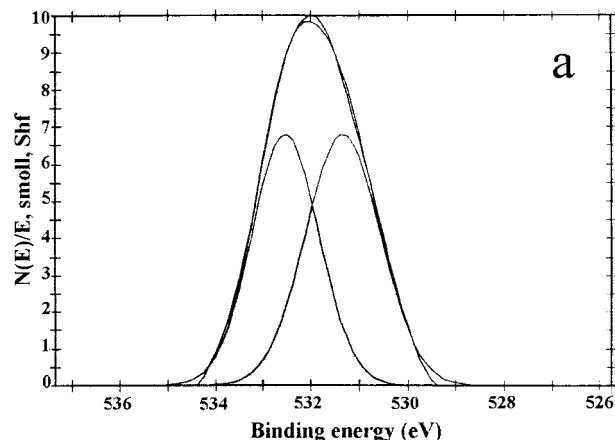
<sup>a</sup> Split.

of 1.28 eV (Fig. 2). This indicates the charge of these two kinds of N atoms changed, and chemical translocation took place. This means these two kinds of N atoms assist in coordination. This could also be deduced in Table VIII. In Table VIII the  $\text{C}_{1\text{S}}$  binding energy of functional group C—O was 286.10 eV in compound 2 and 285.95 eV in

**Figure 2** The  $\text{N}_{1\text{S}}$  XPS spectra of (a) DCAF and (b) PVAP- $\text{Nd}^{3+}$ -DCAF.

compound 3, a decrease of 0.15 eV (Fig. 3). Table IX shows that the  $\text{O}_{1\text{S}}$  binding energy of functional group C— $\text{N}^+$  was 531.34 eV in compound 1 and 530.85 eV in compound 3, a decrease of 0.49

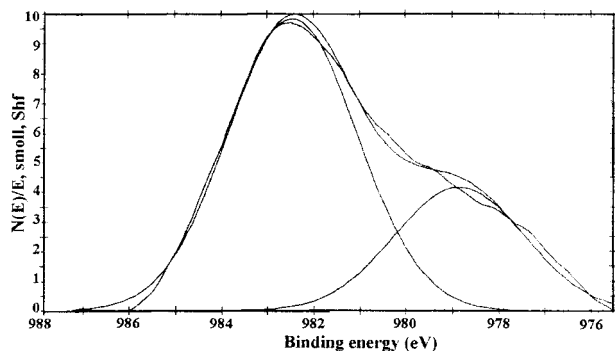
**Figure 3** The  $\text{C}_{1\text{S}}$  XPS spectra of (a) PVAP, (b) DCAF, and (c) PVAP- $\text{Nd}^{3+}$ -DCAF.



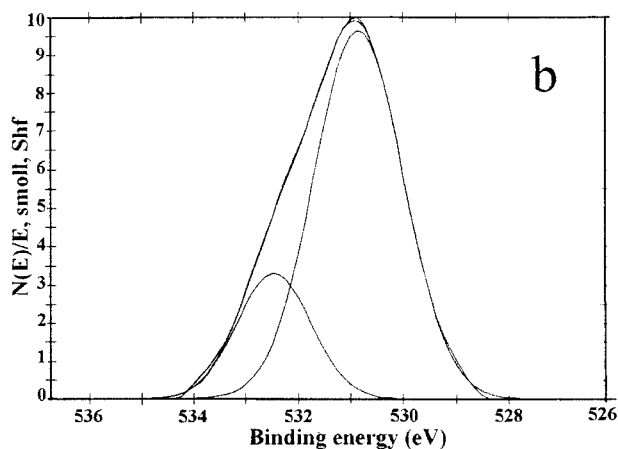
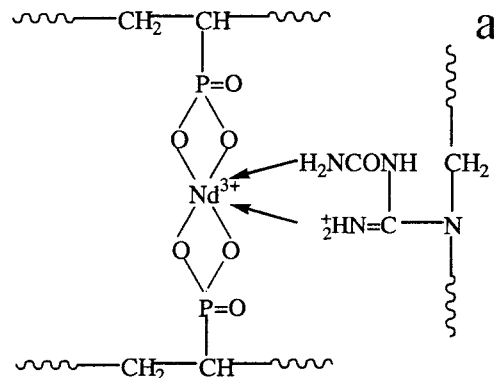
**Figure 4** The  $O_{1s}$  XPS spectra of (a) DCAF and (b) PVAP-Nd $^{3+}$ -DCAF.

eV (Fig. 4). These indicated that hydrogen bonds were formed. The  $P_{2p}$  binding energy of functional group P=O was 132.7 eV in compound 1 and 133.9 eV in compound 3, an increase of 0.2 eV. This shows that phosphoryl also assisted in bonding with rare earth ions.

In the spectra of Figure 4(a), 1289.2, 915.9, 2370.6, and 1704.1  $\text{cm}^{-1}$  are the vibration of P=O, the vibration of P—O, the absorption of the association vibration, and rocking, respectively, compared to the spectra of Figure 4(b) at 1289.2–1317.1, 915.9–978.7, and 2370.6  $\text{cm}^{-1}$  that disappeared. These indicate PVAP bonded with DCAF. Compared with the spectra of Figure 4(c) at 1317.1  $\text{cm}^{-1}$ , those of Figure 4(b) split and moved to 1783.7 and 1356.0 and 978.7–1021  $\text{cm}^{-1}$ , which means P=O and P—O—H, respectively, assist in bonding. In the spectra of Figure 4(d), 1164.6  $\text{cm}^{-1}$  is the vibration of C—N and 2173.1  $\text{cm}^{-1}$  is the vibration of C=N $^+$ H $_2$ . Compared with the



**Figure 5** The  $Nd_{3/2p}$  XPS spectrum of PVAP-Nd $^{3+}$ -DCAF.



**Figure 6** The DCAF-Nd $^{3+}$ -PVAP coordination structure.

spectra of Figure 4(c), 1164.6  $\text{cm}^{-1}$  moved to 1171.4  $\text{cm}^{-1}$  and 2173.1  $\text{cm}^{-1}$  moved to 2179.2  $\text{cm}^{-1}$ , which indicated that two kinds of N atoms assisted in binding.

## CONCLUSIONS

In this experiment some experimental phenomena proved that loops formed in the polymer chains.<sup>9</sup>

1. The binary complexes had a little selectivity on rare earth ions, and its tendency accorded with the lanthanide contraction effect. This indicated that the selectivity depended on the size of the coordinate ions.
2. The adsorption rate decreased with the pretreatment acidity's increase, because the structure was destroyed.
3. The triple complexes had colorimetry corresponding to rare earth ions, indicating

that rare earth ions coordinate loops were formed.

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