



Molecular Recognition Characteristics of Cobalt(II)-Complex Molecularly Imprinted Polymer

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(Received: 24 November 2010;

Accepted: 24 June 2011)

AJC-10076

Using Co-2,2'-dipyridyl complex as template, 4-vinylpyridine as the functional monomer and triallyl isocyanurate as the cross-linking monomer, a cobalt(II)-complex template polymer was prepared by molecularly imprinting technology. The regulation effect of cobalt(II) to the selective recognition of polymer was studied. The results showed that the ability of selective recognition for 2,2'-dipyridyl by the polymer was distinctly enhanced in certain cobalt(II) acetate solution through equilibrium-binding experiment.

Key Words: Molecularly imprinted polymer 2,2'-Dipyridyl molecular recognition cobalt(II).

INTRODUCTION

Molecularly imprinted technology is that with some molecular as template, function monomer combined with it through covalent bond or no covalent bond, then crossing-link is added to polymerization. When the reaction is over, template is washed away from polymer, which is a kind of macromolecule compound which has some cavities and can recognize template molecular, which is called molecularly imprinted polymer (shortening MIP). With the characteristic of predetermination, recognition and practicability, MIP is used in many fields, such as chiral separation of enantiomer and isomer¹, clinical drug analysis², enzyme-mimic catalyzed reaction³, solid phase extraction^{4,5}, chemical bionics sensor and film separation⁶. Interactions between molecularly imprinted polymer and template molecular mostly are ionic bond, hydrogen bond or metal complex. It is found that binding between drugs and metal ion is specific, which is important in the system of biological recognition. So, using cobalt(II)-2,2'-dipyridyl complex as template molecular, a kind of metal-complex template polymer was prepared, whose characteristics of specific and selective binding to 2,2'-dipyridyl by cobalt(II) ion mediated recognition in the polymer was studied in detail.

EXPERIMENTAL

4-Vinylpyridine was purchased from chemical factory in Beijing, China and was freshly distilled prior to using for removing inhibitors. Triallyl isocyanurate was purchased from Laiyu Company, China and was freshly distilled prior to using for removing inhibitors. Azobis-isobutyronitrile was purchased from Beijing chemical company, China. Cobalt(II) acetate was

purchased from chemical experiment factory of Tianda in Tianjin, China. 2,2'-Dipyridyl and 2,2'-dipyridylamine was purchased from the first reagent factory in Shanghai, China. 2,2'-diquinolyl was purchased from chemical reagent factory in Shanghai, China. 4,4'-Dipyridyl was purchased from chemical factory in Beijing, China. All the other organic solvents were analytical.

All spectrophotometric measurements were made with an ultraviolet visible recording spectrophotometer (UV-265, Shimadzu, Japan). Super constant temperature bath (Chongqing Experimental Instruments Factory, China) was used for controlling temperature (60 ± 0.01 °C).

Procedure: Cobalt(II)-complex molecularly imprinted polymer [shortening P(Co-2,2'-dipyridyl)] preparation 2,2'-dipyridyl (10 mmol) and cobalt(II) acetate (10 mmol) were dissolved in methanol (50 mL) for 2 h 4-vinylpyridine (40 mmol), Triallyl isocyanurate (200 mmol) and Azobis-isobutyronitrile (400 mg) were added and the mixture was supersonic and deoxygenated with nitrogen for approximately 15 min. The tube was sealed and then heated in a shaking water bath at 60 °C for 30 h.

The hard polymer was smashed, passed through the sieve of 76 μm and deposited in methanol again to discharge superfine particles. The sieved and deposited polymer was transferred to a filter funnel and washed with methanol/acetic acid (9/1 v:v) until without 2,2'-dipyridyl was monitored at $\lambda = 279$ nm, with EDTA solution (0.10 mol/L) for 5 h to remove survivals metal ion and with water at last. Dry the polymers for stand by.

Two reference polymer systems were similarly prepared, P(2,2'-dipyridyl), without cobalt(II) acetate and P (blank), without cobalt(II) acetate and 2,2'-dipyridyl.

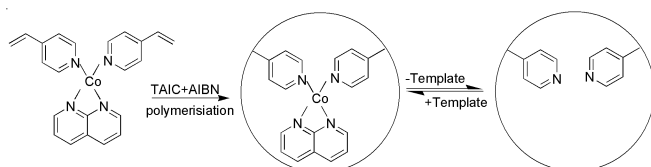


Fig. 3. Preparation of the molecularly imprinted polymer

Standard curve of 2,2'-dipyridyl: In six test tubes, 0.00, 0.20, 0.40, 0.60, 0.80, 1.00 mL 2,2'-dipyridyl/methanol solution, whose concentration was 5.00 mmol/L, were added in turn. The mixture was diluted with methanol to 10 mL and monitored at $\lambda = 279\text{nm}$ with UV-265. Standard curve was made according to absorbency.

Binding capacity of polymers to 2,2'-dipyridyl: 100.0 mg P(Co-2,2'-dipyridyl), 100 mg P(2,2'-dipyridyl) and 100 mg P(blank) were weighted to three glass tubes respectively and 10.00 mL 2,2'-dipyridyl/ methanol solution, whose concentration was 5.00 mmol/L, was added too. The mixture was shaking for 5 h at room temperature and was disposed with centrifuge. 0.50 mL centrifugal solution was diluted into 5.00 mL with methanol and monitored at $\lambda = 279\text{ nm}$ with UV-265. Balanceal concentration of 2,2'-dipyridyl was calculated in according to the standard curve and binding capacity Q of polymers was calculated in according to the change of the concentration.

$$Q = \frac{(C_i - C_f)V_s \times 1000}{M_{\text{MIP}}}$$

where Q is binding capacity of MIP ($\mu\text{mol/g}$), C_i the initial 2,2'-dipyridyl concentration (mmol/l), C_f the final 2,2'-dipyridyl concentration (mmol/l), V_s the volume of solution tested (mL), M_{MIP} the mass of dried polymer (mg).

Binding capacity of polymers to Co-2,2'-dipyridyl: 100.0 mg P(Co-2,2'-dipyridyl), 100 mg P(2,2'-dipyridyl) and 100 mg P(blank) were weighted to three glass tubes respectively and 10.00 mL 2,2'-dipyridyl/ methanol/cobalt(II) acetate (cobalt(II) acetate concentration was 2.00 mmol/L) solution, whose concentration was 5.00 mmol/L, was added too. The mixture was shaking for 5 h at room temperature and was disposed with centrifuge. 0.50 mL centrifugal solution was diluted into 5.00 mL with methanol and monitored at $\lambda = 279\text{ nm}$ with UV-265. Balanceal concentration of 2,2'-dipy was calculated in according to the standard curve and binding capacity Q of polymers was calculated in accord with the change of the concentration.

Effect of Co^{2+} concentration on recognition of P(Co-2,2'-dipyridyl): 100.0 mg P(Co-2,2'-dipyridyl) was weighted to seven glass tubes respectively and 10.00 mL 2,2'-dipyridyl (concentration was 5.00 mmol/L) / methanol/ cobalt(II) acetate (concentration was 0.00~5.00 mmol/L) solution, was added too. 100.0 mg P(blank) was weighted to seven glass tubes respectively and 10.00 mL 2,2'-dipyridyl (concentration was 5.00 mmol/L) / methanol/ cobalt(II) acetate (concentration was 0.00~5.00 mmol/L) solution, was added too. The mixture was shaking for 5 h at room temperature and was deposited with centrifuge. 0.50 mL centrifugal solution was diluted into 5 mL with methanol and monitored at $\lambda = 279\text{ nm}$ with UV-265. Balanceal concentration of 2,2'-dipy was calculated

according to the standard curve and binding capacity Q of polymers was calculated in accord with the change of the concentration. Fig. 2 was drawn according to Q versus concentration of cobalt(II) acetate.

Dynamic binding capacity of polymer: 100 mg of P(Co-2,2'-dipyridyl) was weighted to three glass tubes respectively and 10 mL 2,2'-dipyridyl (concentration was 5 mmol/L)/ methanol/cobalt(II) acetate (concentration was 2 mmol/L) solution, was added too. 100 mg P(blank) was weighted to three glass tubes, respectively and 10 mL 2,2'-dipyridyl (concentration was 5 mmol/L) / methanol/cobalt(II) acetate (concentration was 2 mmol/L) solution, was added too. At different time 0.50 mL centrifugal solution was diluted into 5 mL with methanol and monitored at $\lambda = 279\text{ nm}$ for binding capacity Q.

RESULTS AND DISCUSSION

Regulation of Co^{2+} to the recognition of polymer: As can be seen from Table-1 that binding capacity of P(Co-2,2'-dipyridyl), P(2,2'-dipyridyl) and P(blank) to 2,2'-dipyridyl is same approximately, but different to Co-2,2'-dipyridyl, that of P(Co-2,2'-dipyridyl) is bigger than P(2,2'-dipyridyl) and P(blank). This shows P(Co-2,2'-dipyridyl) can recognize Co-2,2'-dipyridyl, not to 2,2'-dipyridyl. In another word, Co^{2+} can mediate recognition of P(Co-2,2'-dipyridyl) to 2,2'-dipyridyl. This can be explained as follows: When there was Co^{2+} in solution, it can form Co-2,2'-dipyridyl complex with 2,2'-dipyridyl, which is the template of P(Co-2,2'-dipyridyl) and P(Co-2,2'-dipyridyl) just can recognize its template. This shows the unique characteristic of molecularly imprinted polymer. In other ways, 2,2'-dipyridyl or blank is the template of P(2,2'-dipyridyl) or P(blank), so binding capacity to Co-2,2'-dipyridyl is less than P(Co-2,2'-dipyridyl).

TABLE-1
BINDING CAPACITY OF POLYMERS

Samples	Q of P(Co-2,2'-dipyridyl) (μmol)	Q of P(2,2'-dipyridyl) (μmol)	Q of P(blank) (μmol)
2,2'-dipyridyl	4.30	4.05	3.74
Co-2,2'-dipyridyl	26.33	3.96	3.10

It is seen (Table-1) that 2,2'-dipyridyl is the template of P(2,2'-dipyridyl), but binding capacity of P(2,2'-dipyridyl) to 2,2'-dipyridyl isn't bigger than that of P(blank). It is possible that 2,2'-dipyridyl can be bound with 4-vinylpyridine (functional monomer) only when there is Co^{2+} . Without Co^{2+} , 2,2'-dipyridyl can not be imprinted in polymer; didn't take the role of template in the process of synthesis. So, binding capacity of P(2,2'-dipyridyl) to 2,2'-dipyridyl is same approximately with P(blank). This just inosculates with the figure of forming P(Co-2,2'-dipyridyl), which we designed.

Selectivity of polymer: It can be seen from Table-2 that binding capacity of P(Co-2,2'-dipyridyl) to 2,2'-dipyridyl was bigger than to other materials. This can be explained as follows: there were many rooting arrange solid cavities in molecularly imprinted polymer P(Co-2,2'-dipyridyl), whose size, shape and binding radical were accord with template molecular Co-2,2'-dipyridyl, so, molecularly imprinted polymer P(Co-2,2'-

dipyridyl) can shapely recognize its template molecular Co-2,2'-dipyridyl. In addition, molecularly imprinted polymer is specific as enzymes in theory, but it also recognized other molecular in practical, whose structures are resemble to template molecular, as can be seen from Table-2. P (blank) with the same chemical composition as P(Co-2,2'-dipyridyl) didn't selectively bind to four material as P(Co-2,2'-dipyridyl) did. It is because arrange of functional monomer in P(blank) was disorder and there weren't solid cavities which were according to the structure of four material, binding capacity of P(blank) to them was same approximately, without selective.

Samples	Q of P(Cu-2,2'-dipyridyl) (μmol)	Q of P(blank) (μmol)	Ratio
2,2'-dipyridyl	26.33	3.10	8.49
4,4'-dipyridyl	5.10	3.20	1.59
2,2'-dipyridylamine	7.40	3.09	2.39
2,2'-diquinolyl	3.80	3.60	1.05

Effect of Co^{2+} concentration on recognition of P(Co-2,2'-dipyridyl): As can be seen from Fig. 1. that, first, with improving Co^{2+} concentration, binding capacity of P(Co-2,2'-dipyridyl) to 2,2'-dipyridyl is increasing and declining as followed. This is the reason why there was Co^{2+} in solution, it can be formed Co-2,2'-dipyridyl complex with 2,2'-dipyridyl, which is the template of P(Co-2,2'-dipyridyl) and P(Co-2,2'-dipyridyl) just can recognize its template. This shows the unique characteristic of molecularly imprinted polymer. When Co^{2+} concentration reaches to 2 mmol/L, binding capacity is the most. After saturation of polymer sites, higher concentration of Co^{2+} can compete for 2,2'-dipyridyl with polymer, which leads to declining binding capacity of P(Co-2,2'-dipyridyl) to 2,2'-dipyridyl. Second, with improving Co^{2+} concentration, binding capacity of P(blank) to 2,2'-dipyridyl is increasing slightly. This can be explained that with increasing concentration of cobalt(II) acetate, ionic intension increasing, which effects the binding capacity of polymer.

Dynamic binding capacity of polymer: From adsorption dynamic curves (Fig. 2.) it can be seen that binding capacity of P(Co-2,2'-dipyridyl) to Co-2,2'-dipyridyl was remarkably increasing in 2 h, followed by becoming mild little by little and was stable after 5 h. The reasons probable were that binding template first was done on surface and then done at depth after the former was saturation and there was resistance for the latter. So binding capacity was changing from more to less, at last stable as time increases.

It can be seen from curves that binding capacity of P(blank) to Co-2,2'-dipyridyl was stable after 2.5 h and which was smaller than that of P(Co-2,2'-dipyridyl). It is because there weren't order solid cavities on P(blank), binding to Co-2,2'-dipyridyl which can only be done on surface, which belongs to no selection.

Conclusion

From the experiments it is suggested that the metal-complex template molecular imprinted polymer was of characteristics of specific and selective recognition, which can be mediated by metal ion, as can be applied to sensors of biology and recognition system of enzymes that were made by man. In addition, metal- complex polymer can also be used to the system where hydrogen bond was destroyed or disturbed easily, such as recognition in water.

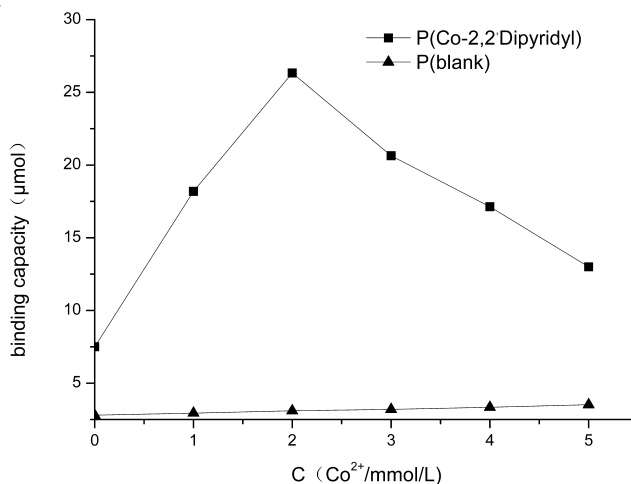


Fig. 1 Effect of Co(AC) 2 concentration on binding capacity of P(Co-2,2'-dipyridyl) and P (blank)

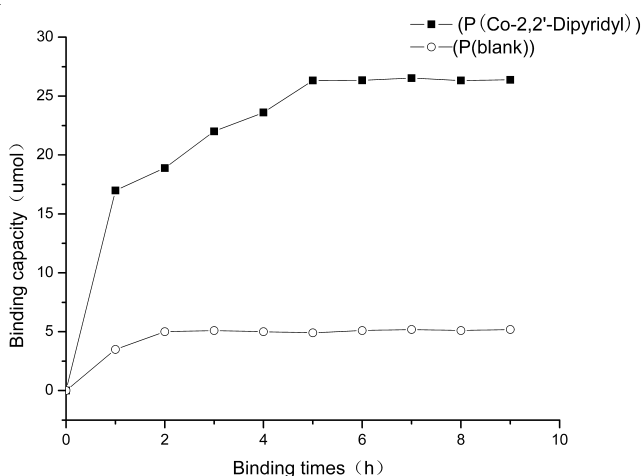


Fig. 2 Dynamic binding capacity of P(Co-2,2'-dipyridyl) and P(blank)

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