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以聚硫醚和聚氧醚为主链的低聚物对贵金属离子的萃取性能

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摘　要

溶剂萃取目前已广泛应用于贵金属的分离和富集[1]，但目前多限于使用小分子硫化物、胺类及醚类等作萃取剂。近年来，用低聚物作为过渡金属的萃取剂以及液态分离膜的流动载体已有报导。[2]最近，作者首次报导了用低分子量的聚硫醚及其衍生物作为贵金属离子的萃取剂，[3]与小分子萃取剂相比，它们具有无毒、无臭味，S、N含量高、萃取容量大等特点。本工作进一步研究了一系列以聚硫醚和聚氧醚为主链的低聚物对贵金属的萃取性能，比较了这两类低聚物对二元混合离子体系的萃取分离效果，并通过两类萃取剂的联合使用，成功地实现了Au(Ⅲ)-Pd(Ⅱ)-Pt(Ⅳ)三元混合体系的萃取分离。此外，还研究了一些低聚物与贵金属离子的络合物的紫外光谱。

低聚物萃取剂（$\bar{M}$ = 700~2000）的结构如下：

$$-\left(CH_2-\underset{\underset{CH_2R}{|}}{CH}-S\right)_n-$$

R=H，	OC_2H_5，	OC_4H_9，	$N(C_2H_5)_2$，	$N(C_4H_9)_2$，
PS	PSO1	PSO2	PSN1	PSN2

$$-\left(CH_2-\underset{\underset{CH_2R}{|}}{CH}-O\right)_n-$$

R=OC_2H_5，	OC_4H_9，	$N(C_2H_5)_2$，
PO1	PO2	PON1

实验结果表明：

1．低聚物的硫含量越高，其萃取容量（C）也越大。PS的硫含量最高，其对Ag(Ⅰ)、Pd(Ⅱ)、和Au(Ⅲ)的（C）也最大，分别为0.78克银／克PS，0.64克钯／克PS和1.32克金／克PS。当硫含量相近时，则氮含量较高者，其（C）也较大。所以PSN1>PSN2，PSN1>PSO1，PSN2>PSO2不含硫的萃取剂PO1-2和PON1的（C）最低。

2，PS对Au(Ⅲ)的萃取率（R）虽然可达100%，但用它对Ag(Ⅰ)、Pd(Ⅱ)进行萃取时，由于它与Ag(Ⅰ)和Pd(Ⅱ)的络合物在有机相中不能全部溶解，故有不同程度的第三相（沉淀）生成。PSN1-2在萃取Ag(Ⅰ)、Pd(Ⅱ)、Au(Ⅲ)等时生成第三相的现象更为明显。但当在PS侧链引入OR基团后，则可大大提高萃取剂与金属离子络合物在有机相（二氯乙烷）中的溶解度，故PSO1-2在萃取时均无第三相生成，因而对Pd(Ⅱ)、Au(Ⅲ)的（R）可达99%以上。可以认为，它们是Ag(Ⅰ)、Pd(Ⅱ)和Au(Ⅲ)的良好萃取剂。

3．含有叔胺结构的PSN1-2是Pt(Ⅳ)的有效萃取剂，（R）~99%，（C）=0.47-0.11克铂／克PSN1-2，而其它低聚物则几乎不能萃取Pt(Ⅳ)。PO1-2对Au(Ⅲ)的（R）较高（~98%）而对其他离子的（R）则很低（~4%），且萃取时均无第三相生成，这说明它们对Au(Ⅲ)具有较高的选择性。

4．用PS和PO2能在Au(Ⅲ)——Pt(Ⅳ)和Au(Ⅲ)——Pd(Ⅱ)体系中优先萃取Au(Ⅲ)，但PO2的分离效果更佳，用它萃取一次，有机相中的Au(Ⅲ)含量则可达99%以上。用PSO2萃取一次则可将Pd(Ⅱ)从Pd(Ⅱ)——Pt(Ⅳ)体系中完全萃取出来而不萃取Pt(Ⅳ)。Au(Ⅲ)——Pd(Ⅱ)——Pt(Ⅳ)三元体系可通过PO2和PSO2的联合使用将它们完全分离，即先用PO2萃取Au(Ⅲ)，再用PSO2将Pd(Ⅱ)从剩余的Pd(Ⅱ)——Pt(Ⅳ)中萃取出来。

EXTRACTION PROPERTIES OF POLYTHIOETHERS AND POLYETHERS FOR NOBLE METALS

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Solvent extraction has been widely used in the separation and concentration of noble metals(1), the commonly used extractants are small molecular organic compounds containing sulfur, oxygen and nitrogen. In recent years, some linear oligomers were found to be used as extractants for transition as well as noble metal ions(2,3).

The present paper deals with the synthesis of the oligomer extractants having polythioethers and polyethers as their main chains and their extraction properties for noble metal ions, and makes a comparative study on the polythioethers and polyethers in the selective extraction of binary and trinary metal-ion systems.

The structures of the oligomer-extractants (M=700-2000) are listed below:

$-\!\!\left(CH_2-\underset{\underset{CH_2R}{|}}{CH}-S\right)\!\!-_n$ R=H, OC_2H_5, OC_4H_9, $N(C_2H_5)_2$, $N(C_4H_9)_2$

PS PSO1 PSO2 PSN1 PSN2

$-\!\!\left(CH_2-\underset{\underset{CH_2R}{|}}{CH}-O\right)\!\!-_n$ R=OC_2H_5, OC_4H_9, $N(C_2H_5)_2$

PO1 PO2 PON1

The experimental results manifest the following points:

1. The higher S-content an oligomer has, the higher extraction capacity (C) it has for Ag(1), Pd(II), Au(III). The (C) of PS for these three metal ions, the highest among the eight oligomers, are 0.78g Ag/gPS, 0.64gPd/gPS, and 1.32gAu/gPS respectively. And its extraction percentage(R) for Au(III) is close to 100%. But the third phase (precipitates) will be formed when PS is used to extract Ag(1) and Pd(II). The extractants PSO1 and PSO2, whose complexes with noble metal ions can dissolve well in organic phase (1,2-dichloroethane) owing to their OR groups which are suggested responsible for the increasing of the solubility of the complexes in organic phase, have high(R) for Pd(II), Au(III) ($>99\%$), and are considered as the effective extractants for Ag(I), Pd(II), Au(III), although their (C) are lower than that of PS. (0.57-0.33 gPd/g PSO1-2, 0.95-0.57gAu/gPSO1-2)

2. PSN1 and PSN2 are good extractants for Pt(IV), (R)$\sim$99%, and (C)=0.47-0.11g Pt/g PSN1-2, while other oligomers can hardly extract Pt (IV). Comparing with the other oligomers, PO1 and PO2 have the lowest(C) for all four ions. But they have high (R) for Au(III) ($>98\%$) and low (R) for other ions ($\sim$4%). It means that PO1-2 have high selectivity for Au (III).

3. Au(III) can be dominantly extracted from Au(III)-Pt(IV) mixture by both PS and PO2, but the latter is more effective and can leave Pd(II) intact when used in the extraction of Au(III)-Pd(II) mixture. Pd(II) can be completely extracted and separated from Pd(II)-Pt(IV) mixture by PSO2. The separation of Au(III)-Pd(II)-Pt (IV) can be achieved by the first use of PO2 to extract Au(III) from the mixture and then the use of PSO2 to extract Pd(II) from the rest Pd(II)-Pt(IV) mixture.

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C-2

一类新的氨基二硫代羧酸型螯合树脂的合成及吸附性能

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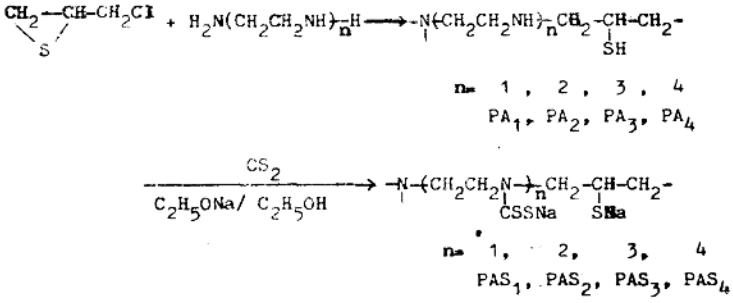
氨基二硫代羧酸型螯合树脂是一类对金属离子具有优良吸附性能的螯合树脂[1—5]。本工作按下列方法制得了四种新的氨基二硫代羧酸型螯合树脂，其合成路线及主要结构如下：



Scheme 1

这四种树脂均未见文献报导。树脂结构经元素分析（Table 1）和红外光谱表征。

Table 1 Preparation of PAS Resin

Resin	PA Resin		CS_2	PAS Resin		
	n	(g)	(ml)	Yield (%)	Elemental Analysis N(%)	S(%)
PAS_1	1	4.00	9.6	64.3	9.06	30.61
PAS_2	2	3.00	8.4	59.2	10.70	30.34
PAS_3	3	5.00	16.4	53.9	11.00	27.62
PAS_4	4	5.00	20.5	48.3	12.60	28.41

采用静态法测定了PH对树脂吸附性能的影响。结果表明，PH=4—6时，树脂对Au(Ⅲ)和Pt(Ⅳ)的吸附率最大，分别为99.6%和97.0%，但对Pd(Ⅱ)吸附甚少。并测定了树脂对Au(Ⅲ)、Pt(Ⅳ)等六种金属离子的吸附容量（Table 2），并与相应的PA树脂的吸附容量作比较。结果表明，PAS树脂对金属离子的吸附能力大小次序：Au(Ⅲ)＞Ag(Ⅰ)＞Pt(Ⅳ)＞Hg(Ⅱ)＞Cu(Ⅱ)＞Pb(Ⅱ)＞Zn(Ⅱ)。PAS树脂对Au(Ⅲ)的吸附容量为1.7—2.6gAu/g树脂；对Ag(Ⅰ)的吸附容量为7—9.7mmolAg/g树脂，均超过了相应的PA树脂[6]对Au(Ⅲ)、Ag(Ⅰ)的吸附容量1.1gAu/g树脂和6—6mmolAg/g树脂，树脂对Cu(Ⅱ)、Hg(Ⅱ)的吸附容量分别为：0.65—1.1mmolCu/g树脂和1.2—3.1mmolHg/g树脂，比相应的PA树脂对Cu(Ⅱ)和Hg(Ⅱ)的吸附容量2.7—3.6mmolCu/g树脂和5mmolHg/g树脂为低。PAS树脂对贵金属具有较高的吸附选择性，其中PAS_4树脂在PH=4的Au(Ⅲ)、Cr(Ⅲ)、Co(Ⅱ)、Ni(Ⅱ)、Cu(Ⅱ)、Zn(Ⅱ)、Mn(Ⅱ)的混合溶液中，室温24小时后，对Au(Ⅲ)可100%吸附，对Cu(Ⅱ)有少量吸附外，对其它离子几乎不吸附；在PH=7的Ag(Ⅰ)、Cu(Ⅱ)、Cd(Ⅱ)和Pb(Ⅱ)的混合溶液中，室温24小时后，只吸附Ag(Ⅰ)而不吸附其它离子。

Table 2 The Adsorption Capacities of PAS for Metal Ions (mmol M/g-Resin)

Resin	Au(III) (pH=4)	Pt(IV) (pH=4)	Ag(I) (pH=7)	Cu(II) (pH=5.6)	Hg(II) (pH=5.6)	Pb(II) (pH=5.6)	Zn(II) (pH=5.6)
PAS_1	1680.8*	172.8*	7.16	0.765	2.922	0.281	0.187
PAS_2	1833.3*	279.8*	7.29	1.129	3.088	0.374	0.235
PAS_3	2011.9*	145.7*	8.15	0.826	1.237	0.729	0.384
PAS_4	2649.7*	518.2*	9.71	0.664	1.418	0.940	0.538

"*": mg M/g-resin

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SYNTHESIS AND ADSORPTION PROPERTIES OF A NEW TYPE OF CHELATING RESIN BEARING DITHIOCARBAMATE GROUPS

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Abstract

A series of new type of chelating resins bearing dithiocarbamate groups are synthesized by the reactions shown in Scheme 1. The resins PA are prepared according to the method described proviously with certain modification to improve yield. All these resins are indentified by elemental analysis and IR spectra. The IR spectra of PAS resins showed new adsorption peaks at 1129 cm^{-1}(C=S group) and at 1454, 974 cm^{-1}(N-C=S group).

The effects of pH on the adsorption efficiency of PAS resin for Au^{3+}, Pt^{4+},and Pd^{2+} have been investigated. The experiment results showed that the adsorption efficiency of PAS for Au^{3+} and Pt^{4+} gives a higher value at pH=4-5 range. At this optimum pH the adsorption efficiency of PAS_4 for Au^{3+} and Pt^{4+} is 99.6% and 97.0% , respectively. The adsorption capacities and selectivities of PAS resins for the metal ions such as Au^{3+}, Pt^{4+}, Ag^{+}, Cu^{2+}, Zn^{2+}, Hg^{2+} and Pb^{2+} are also determined and compared with the corresponding PA resin containing mercapto groups only (see Table 2). It is found that the adsorption capacities of PAS for Au^{3+} and Ag^{+} are greater than that of PA resin. It is obvious that the dithiocarbamate groups introduced in to the PA resin play an important role in the adsorption of noble metal ions. PAS resin exhibits excellent selectivities. Au^{3+} can be absorbed by PAS_4 with high selection in the presence of Au^{3+}, Cu^{2+}, Cr^{3+} , Ni^{2+}, Zn^{2+}, Co^{2+} and Mn^{2+}. In addition, $Ag^{+}$is absorbed only by PAS_4 resin in the mixture of Ag^{+}, Cu^{2+}, Cd^{2+} and Pb^{2+}.

此为试读,需要完整PDF请访问: www.ertongbook.com

C-3　　大孔螯合树脂 PSB--钴(II)、铁(III)--SCN^- 协同吸附体系的研究

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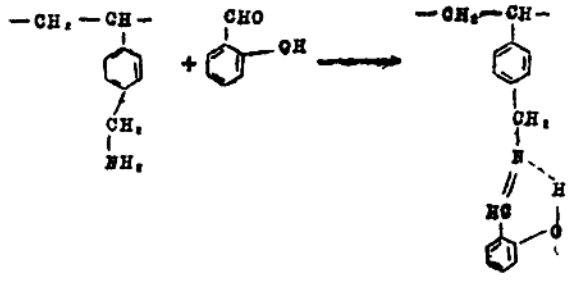
本文研究了大孔螯合树脂 PSB的合成及其对金属离子的吸附特性。结果表明：低分子络合剂 SCN^-能提高 PSB树脂对金属离子 Co^{2+}、Fe^{3+}的吸附容量及分配系数。利用协同效应解释了上述现象。

一、PSB 树脂的合成与结构



PSB树脂

（Poly-N-Salicylidenevinylbenzylamine）

红外光谱证实了上述功能基转换与 PSB树脂结构。

二、PSB树脂对金属离子的吸附特性

PSB 树脂的功能基含量虽高，但它对金属离子Co^{2+}、Fe^{3+}的吸附容量却不高。加入低分子络合剂 SCN^- 后，因协同效应的产生，PSB 树脂对钴(II)、铁(III)的吸附容量显著增加。

Table 1. Properties of Adsorption System PSB-C$_o$(II)、Fe(III)—SCN^-

Adsorption / System	PSB—C$_o$(II)	PSB-C$_o$(II)—SCN^-	PSB—Fe(III)	PSB—Fe(III)—SCN^-
Adsorption Capacity (mmol/g)	0.24	2.15	0.20	2.22
Distribution Coefficient	16.23	1.53×10^4	10.80	1.31×10^3
Synergistic adsorption Coefficient	/	9.43	/	12.13
Adsorption Rate $T_{1/2}$	/	<10min.	/	<10min.

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STUDIES ON THE SYNERGISTIC ADSORPTION SYSTEM OF MACRO-POROUS CHELATE RESIN PSB-METAL ION-SCN^-

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In this paper, the synthesis and chelating properties of macro-porous chelate resin poly-N-salicylidenevinylbenzylamine (PSB) were studied. It was shown that the adsorption capacity can be increased by thiocyanate (SCN^-), but can't be increased by orgainic solvents such as acetone. It is explained by synergistic adsorption effect and described by synergistic adsorption coefficient. The adsorption mechanism can be described as following:

$$Fe^{3+} + SCN^- \rightleftharpoons (Fe(SCN))^{2+} \xrightleftharpoons{SCN^-} (Fe(SCN)_2)^{+} \xrightleftharpoons{SCN^-} (Fe(SCN)_3)$$

$$\xrightleftharpoons{SCN^-} (Fe(SCN)_4)^- \xrightleftharpoons{SCN^-} (Fe(SCN)_5)^{2-} \xrightleftharpoons{SCN^-} (Fe(SCN)_6)^{3-}$$

$$Co^{2+} + SCN^- \rightleftharpoons (Co(SCN))^{+} \xrightarrow{SCN^-} (Co(SCN)_4)^{2-}$$

$$PSB + Fe(SCN)_n \xrightleftharpoons{SCN^-} PSB(Fe(SCN)_x) \qquad n = 0 \sim 6,\ x \leq 4$$

$$PSB + Co(SCN)_m \xrightleftharpoons{SCN^-} PSB(Co(SCN)_y) \qquad m = 0, 1, 4,\ y \leq 4$$

C-4

含杂环功能基树脂的合成及其对贵金属离子的吸附性*

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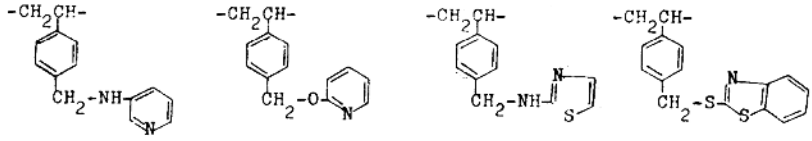
本文报道了下列四种含有杂环侧基的功能性树脂：



3-APR　　2-HPR　　2-ATR　　2-TBTR

研究了树脂的合成方法，树脂的功能基含量，树脂的功能基转化率，树脂对 Au(III) 的吸附容量。

在树脂2—HPR树脂2—TBTR合成时，必需使2—羟基吡啶、2—巯基苯骈噻唑先转变成钠盐，这样才能制得高功能基含量的树脂。树脂 3-APR、2-HPR、2-ATR、2-TBTR 的功能基转化率依次分别为 64.8%、84.5%、0.06%、69.3%。2—氨基噻唑中的氨基其碱性甚弱，因而反应困难。

3—APR、2—HPR、2—TBTR 的功能基含量依次分别为 3.22、2.09、3.01 毫摩尔功能基／克树脂。3—APR对 Au(III) 的吸附容量为 511.9 毫克 Au(III) ／克树脂。2—HPR对贵金属的吸附参数，列于下表1中。

图1是2—HPR对Au(III)、Pt(IV)、Pd(II)的吸附速率曲线。图2是2—HPR对十种金属离子的选择吸附性。由图2知在1～4 N酸度范围内，2—HPR对 Au(III)、Ni^{2+}、Co^{2+}、Pt(IV)的吸附率在92±5%之间。

2—TBTR在1～6 N HCl 中对Au(III)的吸附率较低，低于20%。在这三种树脂中对Au(III)的吸附容量按下列顺序递降：3—APR>>2—HPR>>2—TBTR。

1～6 N HCl 酸度范围内，2—HPR，2—TBTR对 Cu^{2+} 的吸附率很低，仅4.5%。因此，采用2—HPR树脂可一定程度上分离Au(III)—Cu^{2+}。

在温度20～50 °C范围内，酸度为4N HCl或 0.1N HCl 时，2—HPR对Au(III)的吸附容量，皆随温度提高而增大。例如：4N HCl场合下，50°C，2—HPR对Au(III)的吸附容量可以提高到800毫克Au(III)／克。

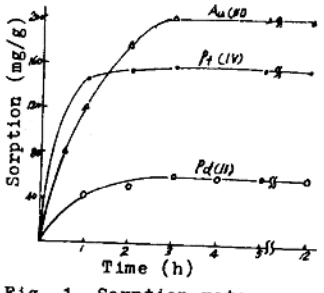


Fig. 1. Sorption rate curves of 2-HPR for Au(III), Pt(IV) and Pd(II)

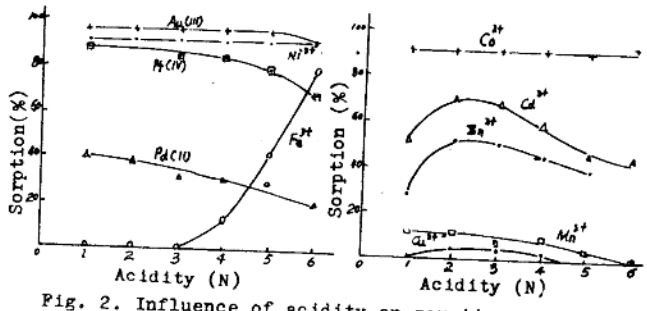


Fig. 2. Influence of acidity on sorption percentage of 2-HPR for different ions

* 国家自然科学基金资助课题

Table 1. The adsorption parameters of 2-HPR for Pt(IV), Pd(II), Au(III)

	1N HCl		4N HCl
	Pt(IV)	Pd(II)	Au(III)
Adsorption capacity (mg ion/g)	154	58	196
Distribution coefficient Kd(ml/g)	596	116	681
$T_{1/2}$ (h)	0.3	0.6	0.8

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SYNTHESES OF FUNCTIONAL RESINS BEARING HETEROCYCLIC RING AND THEIR ADSORPTION PROPERTIES FOR NOBLE METAL IONS*

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The synthetic methods of four kinds of functional resins bearing heterocyclic ring were examined, The percentage of functional group conversion of resins, the content of functional group of resins, and the adsorption capacity of resins were determined.

In the processes of syntheses of 2-HPR and 2-TBTR, 2-hydroxy pyridine, 2-thiolbenzothiazole must be converted into sodium salt, otherwise the percentage of conversion of functional group of the resins will be very low.

The percentages of conversion of functional group of 3-APR, 2-HPR, 2-ATR, 2-TBTR are 64.8%, 84.5%, 0.06%, 69.3% respectively. Because of the basicity of 2-aminothioazole (2-AT) is very low, so, the reaction between 2-AT and chloromethylated polystyrene beads is very difficultly.

The contents of functional group of 3-APR, 2-HPR, 2-TBTR are 3.22, 2.09, 3.01 mmol functional group/g resin, individually. The adsorption capacity of 3-APR for Au(III) is 511.9 mg Au(III)/g resin. The adsorption capacity of 2-HPR for Au(III), Pt(IV), Pd(II) are in Table 1.

The adsorption rates of 2-HPR for Au(III), Pt(IV), Pd(II) are in Figure 1. In the range of 1～4N HCl, the adsorption percentages of 2-HPR for Au(III), Ni^{2+}, Co^{2+}, Pt(IV) are in the range of 92±5% as shown in Figure 2.

In the range of 1～6N HCl, the adsorption percentages of 2-TBTR for Au(III) are lower than 20%. The order of the adsorption capacity of the resin for Au(III) is shown in the following:

3-APR≫2-HPR≫2-TBTR

In the 1～6N HCl range, the adsorption percentages of both 2-HPR and 2-TBTR resins for Cu^{2+} are only 4.5%. So, Au(III)-Cu^{2+} maybe separated by using 2-HPR.

At 4N HCl or 0.1N HCl solution, in the temperature range of 20～50°C, the adsorption capacities of 4-HPR are increasing with temperature. For an example, at 4N HCl, at 50°C, the adsorption capacity of 2-HPR for Au(III) increases to 300 mg Au(III)/g.

* The Project Supported by National Natural Science Foundation of China

C-5　　功能高分子微球研究　　标准聚苯乙烯微球的合成

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（中国科学院成都有机化学研究所）

标准聚苯乙烯微球广泛用于临床分析，胶体研究、生物医学等领域，可作为电子显微镜、光散射、沉降法等测定微小物体绝对长度的基准物。但是，用经典乳液聚合法难于得到大小均匀、单分散性好的标准聚苯乙烯微球。本文报导采用在分散剂存在下，将乳化剂用量控制在CMC以下的“无乳化剂”乳液聚合法合成各种粒径的单分散聚苯乙烯微球。在乳化剂浓度远低于临界胶束浓度的体系中，随着乳化剂十二烷基磺酸钠（SDS）用量的增加，胶乳粒径变小，但单分散性变好且转化率增加（图1，表1）。在该体系中加入适量的聚乙烯醇（PVA）作为分散剂，经5～6小时，聚合转化率可达90%以上，所得胶乳粒径随PVA用量增大而减小（图2）。在聚合体系的水相中添加能与水混溶的有机溶剂，可明显影响聚合行为，图3表出了分散介质中乙醇含量对胶乳粒径的影响，表2是其对粒径分布及转化率的影响。

本研究得到中国科学院科学基金资助。

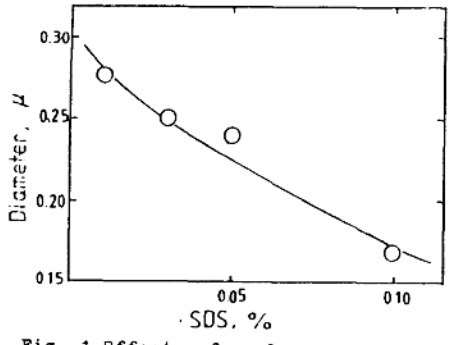

Fig. 1 Effects of emulsifier on the particle size

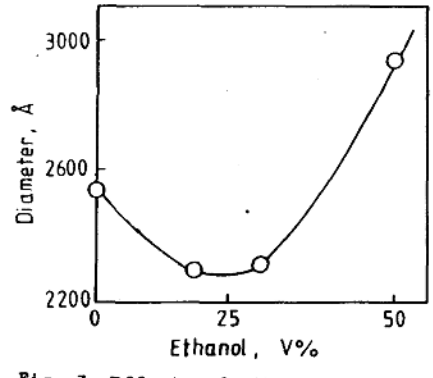

Fig. 3 Effects of ethanol amount on the particle size

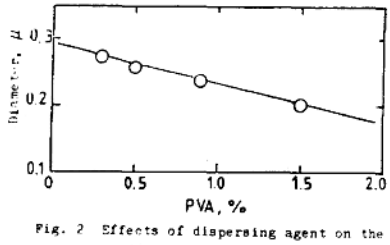

Fig. 2 Effects of dispersing agent on the particle size

Table 1. The effects of emulsifier amounts on the polymerization behaviors

SDS, %	Dispersion parameter	conversion, %
0.01	0.067	47.7
0.03	0.078	83.0
0.05	0.062	96.0
0.10	0.012	95.0

Table II. The effects of various organic solvents on the polymeric behaviors

Solvent	Surface tension dynes/cm	Diameter $\overset{d}{\text{Å}}$	Dispersion parameter	Conversion %
Isopropyl alcohol	21.7	2600	0.142	95
Ethyl alcohol	22.3	2300	0.062	83
Methyl alcohol	22.6	2300	0.024	65
Acetone	23.7	1900	0.045	70

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STUDIES ON FUNCTIONAL POLYMERIC MICROSPHERES. SYNTHESIS OF STANDARD POLYSTYRENE MICROSPHERES

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Standard polystyrene microspheres are widely used in the fields of biology, medicine and colloidal science, for example, calibration standar, microscopy, particle size determination counter, blood cell counter, light scattering, turbidity, filtration studies and so on. A soap-free emulsion polymerization of monodispersive polystyrene microspheres in the presence of dispersing agent is reported in this paper. The effects of the amounts of dispersing agent, emulsifier (concentration < CMC) and organic solvents in water phase on the polymerization behaviors and particle diameter are examined.

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C-6

PKT型光敏功能性胶束的催化作用

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在胶束催化的研究领域，一个重要的发展方向就是设计具有特殊功能作用新型结构的胶束。本文制备了一系列带有各种链长季铵盐的二苯酮衍生物（PKT）（$BP-OH_2-\overset{+}{N}R_2R'\cdot X^{-1}$）并同时用做光敏剂和表面活性剂。

图(1)表示了氮气下由各种二苯酮（BP）／三乙胺（TEA）水体系引发甲基丙烯酸甲酯（MMA）光聚合。结果表明，PKT型功能性胶束的催化效果比普通胶束好得多，聚合速度（R_p）比简单的BP水体系高10倍以上。

下面分别讨论各种结构因素

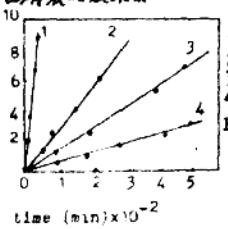
a，分子聚集的影响，随PKT—3'（$R=CH_3$，$R'=C_{12}H_{25}$）浓度增加至临界胶束浓度，R_p随PKT—3浓度急剧增高。这说明，形成的胶束能显著地促进聚合速度。

b，活性头基的影响，图(1)表明PXT的正离子BP基团（$BP-OH_2-\overset{+}{N}\equiv$）的引发能力比BP在均相和胶束中都高得多，并且在相同条件下，PKT—3（胶束体系）比较PKT—1（$R=R'=C_2H_5$）（非胶束体系）的结果说明，胶束的催化效果明显优于活性头基。

C，链长的影响，PKT化合物引发的R_p明显地分成两类，链较长的一类（$C>8$）的R_p都比较高，另一类（$C<8$）则较低。这与它们形成胶束的能力有关，一般$C>8$才能形成胶束（图(2)）。

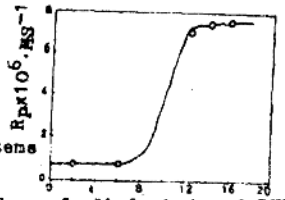
d，抗衡离子的影响，抗衡离子对R_p影响的研究表明，R_p的顺序为$Cl^->Ac^->Br^-$。由于Br^-对三线态BP的淬灭而导致BP光还原反应速度的降低。

综合上述，同普通胶束相比较，PKT功能性胶束高效的催化效果可以归为(1)光敏剂局部浓度很高；(2)有效的胶束静电效应；(3)增溶的反应物在胶束表面的顺序排列。



1 (PKT-3) 2×10^{-3}M (>CMC) (TEA) 2×10^{-2}M,
2 (PKT-3) 3×10^{-4}M (<CMC) (MMA) 1.4×10^{-1}M
3 (BP) 3.4×10^{-4}M/OTAB 1.9×10^{-3}M (CMC)
4 (BP) 3.4×10^{-4}M

Fig.1 Polymerisation in various systems



The number of alkyl chain of PKT

Fig.2. Relationship between R_p and chain length of PKT

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THE CATALYSIS OF PKT TYPE PHOTOSENSITIVE FUNCTIONAL MICELLE

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A significant development in the field of micellar catalysis is the design of novel structural micelles with specific functional role[1]. A series of benzophenone (BP) cationic derivatives having tetraalkylammonium in the para-position and with various length alkyl chain (PKT) ($BP-CH_2\overset{\oplus}{N}R_2R'\overset{\ominus}{X}$) were prepared and used as photosensitizers and surfactants in this paper.

The comparison studies of photopolymerization of MMA using various benzophenone(BP)/triethylamine(TEA) systems as photoinitiators were carried out in the aqueous solution under N_2. The results obtained (Fig.1) indicate that catalytic effects of PKT type functional micelles are far higher than that of common micelles with enhancement of polymerization rate over 10 times compared with simple BP in water solution.[2]

The structural influence are discussed as following.

a. Molecule aggregation effect. The relationship between polymerization rate and concentration of PKT-3($R=CH_3$ $R'=n-C_{12}H_{25}$) indicates that a sharp rate-enhancement was observed at the CMC of PKT-3, after that the polymerization rate increases gradually. It demonstrates that the micelles formed play an important role in promoting the polymerization.

b. Effect of active head group . The photoinitiation ability of cationic BP group ($BP-CH_2-\overset{\oplus}{N}\zeta$) in PKT is much higher than that of simple neutral BP in both homologeneous (<CMC) and micellar (>CMC) systems as shown in Fig.1 .

However the rate-promoting efficiency by micellar catalysis is obviously greater than that of active head group in PKT, which has been proved by comparison study of PKT-1($R=R'=C_2H_5$) (non micellar system) with PKT-3(micellar system) under the same condition.

c. The chain length effect. These PKT compounds may be divided into two classes. One (C>8) exhibits high polymerization rate and other lower R_p. These differences in reactivity are markedly related to their ability to form micelle. In general, it requires C>8 (Fig.2).

d. Effect of counter ions. The influences of negative ions of PKT on the photopolymerization have been examined. The R_p is in order $Cl^->Ac^->Br^-$. Obviously, the quenching of BP(T_1) by Br^- leads to decrease in primary photoreduction of BP.

Based on the mention above, the much higher rate- ehancement of PKT functional micelles may be attributed to following factors compared with common micelles: (1) very high local concentration of photosensitizer, (2) more effective electrostatic effects, (3) orientation of reactant molecules in the micellar interface.

取代苯胺的化学氧化聚合*

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新型导电聚合物—聚苯胺（PA_n），由于具有较高的电导及良好的环境稳定性，被认为是目前最有希望在实际中得到应用的导电聚合物[1,2]。但聚苯胺由于本身结构的复杂性和不溶不熔，使结构表征受到了较大的限制。在此基础上，我们选取了取代苯胺作为研究对象，通过考察取代基和取代基位置对聚合物结构与性能的影响，来研究苯胺类聚合物的结构与性能关系[3,4]。我们的结果表明[4]取代苯胺聚合物有较好的溶解性，在一系列有机溶剂中可以完全溶解，因而，为结构研究创造了有利条件。本文详细研究了甲苯胺（o—，m—，p—）在盐酸水溶液中的聚合反应；利用IR、^{1}H—NMR、元素分析等手段，表征了可溶聚合物。

一　取代苯胺的化学氧化聚合反应

研究了聚合条件（如聚合介质的PH值、氧化剂用量等）对甲苯胺（o—，m—，p—）聚合反应的影响，结果表明，甲苯胺（o—，m—）的聚合反应强烈依赖于聚合介质的PH值，它不仅影响聚合物的颜色、收率，而且也影响聚合物的结构和电性能。当氧化剂用量变化时，邻和间甲苯胺的聚合规律一致，且完全不同于对甲苯胺。

二　聚合物的IR光谱和^{1}H—NMR谱

IR光谱（图1）研究结果表明，本征型聚邻甲苯胺（POT）和聚间甲苯胺（PMT）的结构一致，主链中均含有1,2,4—取代苯（B），（B）—NH—（B）和醌环（Q）结构单元。

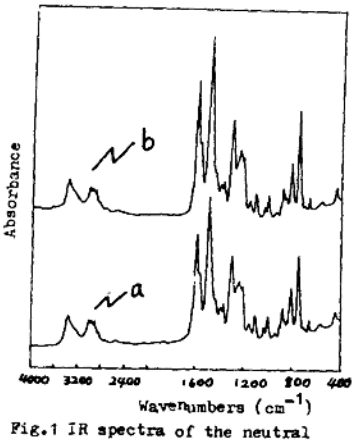


Fig.1 IR spectra of the neutral PoT and PmT
a-PoT, b-PmT

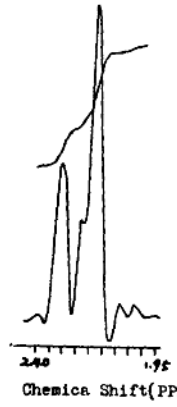
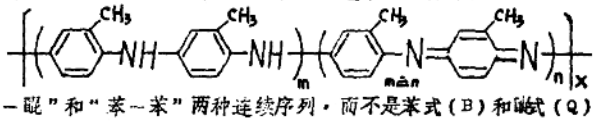


Fig.2 ^{1}H-NMR spectrum of the methyl group($-CH_3$) for the neutral PoT

本征型POT中甲基的^{1}H—NMR谱（图2）表明，聚合物主链中含有五类或六类甲基（$-CH_3$），它们可能分别位于不同环境的B、Q和端基上。由（B）$-CH_3$和（Q）$-CH_3$的相对含量可以推出，聚合物主链中B和Q的比例约为3：1，元素分析的结果（表1）也给出同样的结论，因而，本征型POT和PMT的可能结构为：



即结构中存在"苯—醌"和"苯—苯"两种连续序列，而不是苯式（B）和醌式（Q）交替存在。这与^{13}C—NMR的研究结果一致[5]。

* 国家自然科学基金资助项目

Table.1 The elemental composition of the neutral PoT and PmT

polymer	elemental analysis (%)				composition*	
	C	H	N	Cl	I	II
poly-o-toluidine (PoT)	78.19	6.01	12.20	1.11	$C_7H_{6.46}N_{0.94}Cl_{0.03}$ ($C_7H_{6.49}N_{0.94}$)	$C_7H_{6.50}N$
poly-m-toluidine (PmT)	77.74	5.96	12.30	1.45	$C_7H_{6.44}N_{0.94}Cl_{0.04}$ ($C_7H_{6.48}N_{0.94}$)	$C_7H_{6.50}N$

* 1) I: experimental composition; II: calculated composition, the mole ratio of B to Q is 3:1.
2) The hydrogen contents in the brackets are equal to the sum of the hydrogen and chlorine contents measured, because the hydrogen in the phenyl ring is replaced by the chlorine for the HCl 1,4-addition.

基于聚合反应和聚合物结构，提出了甲苯胺（O—，m—）在酸性（PH<1）和碱性（PH≒14）条件下的聚合机理。

1. 酸性条件（PH<1）

邻和间甲苯胺聚合时，偶合增长发生在N和C_4位置—“头—尾”偶合；对甲苯胺由于对位甲基的存在，聚合时偶合增长只能发生在N和C_2位置。

2. 碱性条件（PH≒14）

甲苯胺（O—，m—，P—）主要采取“头—头”偶合方式，形成取代偶氮苯作为主要产物。

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CHEMICAL OXIDATIVE POLYMERIZATION OF SUBSTITUTED ANILINE

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ABSTRACT

Chemical oxidative polymerization of toluidine(o-,m-,p-) in the acid solution has been studied, and the resulting polymers are characterized by IR, ^{1}H-NMR and elemental analysis. It is shown that the pH value of the polymerization solution affects not only the colour and yield, but also the structure and properties of polymers obtained. The o- and m-toluidine have similar polymerization behavior in terms of it dependence on oxidant concentration, but the p-toluidine does not. IR spectroscopy reveals the existence of biphenylamine strucyure (B)-NH-(B), 1,2,4-substituted benzene and quinone ring(Q) in the molecular chain of neutral poly-o-toluidine (PoT) and poly-m-toluidine(PmT). The mole ratio of B to Q is about 3:1 according to ^{1}H-NMR and elemental analysis. Based on the above results, a possible polymerization mechanism of toluidine(o-,m-,p-) in the acid solution is proposed.

C-8

苯胺的化学法聚合及所得产物的表征

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（中国科学院长春应用化学研究所）

近年来，聚苯胺（PAn）的合成，结构及性能的研究已成为导电高分子领域中热门的研究课题。通过化学和电化学方法均可得到PAn。对用化学法合成PAn的研究，大多限于追求高电导率的样品[1-3]，而没有详细研究诸因素对苯胺化学氧化聚合的影响。本文研究了氧化剂浓度、聚合溶液的酸浓度、苯胺浓度以及氧化剂种类对苯胺聚合的影响。

当氧化剂浓度$(NH_4)_2S_2O_8$与单体浓度的摩尔比小于2：1时，增加氧化剂浓度仅提高聚合物收率，而对聚合物电导率影响不大；当二者比例高于3：1时，过剩的氧化剂可继续氧化聚合物主链，使之断链形成小分子化合物，并在链端带有羰基，同时HCl的加成产物也增多（见表1）。

当聚合溶液的酸浓度由0.5升至8 M时，所得PAn的电导率、脱式含量及真实掺杂率同时下降，而由于HCl的加成产物的增多及脱式含量的降低，使本征态的可溶百分率增大（见表2）。

若苯胺浓度较低，其聚合行为及产物性能与高氧化剂浓度下的聚合行为是类似的；而当苯胺浓度较高时，则形成多取代亚胺脱类的小分子化合物。

如采用$KClO_3$、H_2O_2、$K_2Cr_2O_7$、$KMnO_4$、$FeCl_3$及PbO_2等作为氧化剂，所得产物与在相应条件下$(NH_4)_2S_2O_8$体系的性能差别不一，其中以$KClO_3$和H_2O_2作氧化剂时，产物电导率较高。

Table 1 Effect of oxidant concentration (Ox) on aniline (An) polymerization[1] and PAn properties

Ox/An molar ratio	polymer yield (%)	content of small[2] molecular (%)	conductivity S/cm	Cl content[3] in neutral PAn	true doping level (%)
4:1	20.1	74.84	2×10^{-12}		
3:1	66.5	25.00	1.1×10^{-1}	0.463	27.3
2:1	95.6	8.64	1.4	0.264	38.8
1:1	76.7	4.50	3.2	0.130	40.0
0.5:1	40.3	2.53	5.2	0.068	40.2
0.25:1	22.1	1.84	9.2	0.049	41.5
0.125:1	11.2	1.46	3.3		

1. polymerization conditions: [HCl] =3M; [An] = 0.5M
2. extracted with $CHCl_3$ from doped PAn
3. compared to C content 6

Table 2 Effect of acid concentration on aniline polymerization*and PAn properties

HCl (M)	polymer yield (%)	soluble part** (%)	conductivity S/cm	Cl content in neutral PAn	true doping level (%)
0.5	43.3	27.1	8.2	0.024	36.6
1	41.4	32.9	5.5	0.030	40.0
3	40.3	35.1	5.2	0.068	40.2
4	41.5	49.3	3.1		
5	33.7	60.4	5.8×10^{-1}	0.31	38.5
6	32.5	72.5	3.5×10^{-1}	0.41	31.3
7	28.7	100	1.3×10^{-2}	0.90	15.0
7.5	24.4	100	3.9×10^{-3}		
8	12.6	100	5.8×10^{-12}	1.36	3.3

* (Ox)/(An) = 1:2
**extracted with THF from neutral PAn

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THE CHEMICAL POLYMERIZATION OF ANILINE AND THE CHARACTERIZATION OF THE POLYMERS OBTAINED

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ABSTRACT

The effects of oxidants and their concentration,acid and monomer on aniline polymerization have been investigated by FTIR and elemental analysis. When the molar ratio of oxidant $(NH_4)_2S_2O_8$ to monomer is lower than 2:1,increasing concentration of oxidant increases polymer yield,but has litter effect on the conductivity and structure of the polymers. If the ratio is over 3:1,extra oxidant can continue to oxidize the backbone of polymer and results in breaking polymer chain. The conductivity,Q content and true doping level of PAn decrease with increasing acid concentration in the polymerization solution from 0.5-8 mol/l. Small molecular compounds are obtained with high aniline concentration. The products obtained with $KClO_3$, H_2O_2, $K_2Cr_2O_7$, $KMnO_4$, $FeCl_3$ and PbO_2 as oxidants are different. The conductivity of products obtained with $KClO_3$ and H_2O_2 is higher. The polymerization mechanism is deduced according to the above polymerization behaviours and the structure of polymer obtained in different conditions.

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