Synthesis and chromium complexation properties of a ionic polynorbornene

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Abstract

New ionic polynorbornenes for the selective adsorption of Cr(VI), Cr(III) and Ni(II) ions are synthesized and characterized. The metal ions complexing capacity of obtained polynorbornene resins (**1–3**) is dependent on the structure of the cross-linking diamines. The highest capacities were found for resin **3**. At pH = 1 Cr(VI) and Cr(III) were sorbed above 94% from an aqueous solution. The desorption of chromium ions from the loaded resins was also studied.   © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

In the past several years much attention has been focused on the preparation of ionic polymers which can be used as antistatic agents, biomedical devices, high selective membranes, etc. The ability of ionic polymers to form polymer–metal complexes may be applied to recover different metals from lean ores and wastes [1]. Thus, compounds of chromium are widely used in the plating industry and resulting

wastes may contain Cr(VI) in the range 15–70 parts per million (ppm) [2]. As these compounds are known to be detrimental to human health [3], it is important to remove them from wastes [4,5].

Many studies have reported on the synthesis and characterization of a large number of coordinating resins with sorption properties for heavy metal ions [6–9]. The polymer membranes are very attractive for metal extraction due to its selectivity, high ion-exchange rate and high chemical and mechanical stability.

There are many investigations on the preparation of functionalized polymers by the ring-opening metathesis polymerization (ROMP) of norbornene derivatives [10–12]. The norbornene monomers are attractive due to their facile

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functionalization, high reactivity in ROMP and in the ring-preserving polymerization [13,14]. The high molecular weight functionalized polynorbornene with good mechanical properties can be obtained by ROMP using appropriate catalysts tolerating functional groups.

High tolerence of heteroatoms and protic functionalities makes Ru containing compounds very attractive catalysts for the metathesis of various polar monomers. Earlier it has been demonstrated that the simple ruthenium complexes can be activated for the olefin metathesis by addition of diazoesters as carbene source [15]. Authors in Refs. [16,17] used diphenyl cyclopropene and diazoalkanes as carbene source for the preparation of novel alkylidene ruthenium complexes that are highly efficient catalysts in the olefin metathesis reaction and tolerate a large number of polar functional groups.

Recently the efficiency of the new vinylidene ruthenium(II) complexes for ROMP of norbornene derivatives has been reported [18].

The goal of the present study is to synthesize a precursor polynorbornene from available monomer using accessible Ru-containing metathesis catalysts and to characterize this completely soluble polymer prior to cross-linking and to study the binding ability of cross-linked ionic polynorbornene (IPN) to Cr(VI), Cr(III) and Ni(II) by batch method.

2. Experimental

2.1. Materials

Polymerization solvents, chlorobenzene and toluene, were distilled over calcium hydride. Pyridine, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutylenediamine, N,N,N',N'-tetramethylhexamethylenediamine, phenylacetylene and trimethylsilylacetylene were distilled before use. $RuCl_2(PR_3)_3$ and $Cl_2(PR_3)_2Ru=C=CH(t\text{-}Bu)$ $(R = PPh_3, PCy_3)$ were prepared according to the literature [18–20]. The metal salts were of analytical reagent grade. Other reagents (Aldrich) were used as received. 2-(Tosylamethyl)norborn-5-ene (TNB) was prepared as described previously [14].

2.2. Polymerization of TNB and preparation of cross-linked IPN

The metathesis polymerization of TNB was carried out using ruthenium catalysts (Table 1) under dry nitrogen atmosphere. A typical poly-

Table 1
Polymerization of TNB by ruthenium catalysts in chlorobenzene

Entry	Catalyst	Mon./Catal. (mol. ratio)	$[M]_0$ (mol/l)	T (°C)	Time (h)	Yield (%)	$M_n{}^f$ (10^5)	$M_w/M_n{}^f$
1	A[a]	100	1.0	70	24	48	1.2	2.21
2	A + 5CH≡CPh[b]	100	0.8	45	18	72	0.9	3.25
3	A + 5CH≡CPh	200	1.0	45	24	45	1.6	3.12
4	A + 5CH≡CPh	80	1.0	60	18	81	0.7	3.67
5	A + 5CH≡CSi(CH₃)₃[b]	100	0.8	45	24	78	1.1	3.09
6	A + 5CH ≡ CSi(CH₃)₃	80	1.0	60	18	85	0.6	2.87
7	B[c]	100	0.8	45	24	79	1.1	2.45
8	B	80	1.0	45	12	85	1.8	2.21
9[d]	C[e]	100	1.0	25	48	58	2.2	1.97
10[d]	C	100	1.0	40	12	89	3.1	2.11

[a] A = $RuCl_2(PPh_3)_3$.

[b] Generated in situ.

[c] B = $Cl_2(PPh_3)_2Ru=C=CH(t\text{-}Bu)$.

[d] Solvent CH_2Cl_2.

[e] C= $Cl_2(PCy_3)_2Ru=C=CH(t\text{-}Bu)$.

[f] Determined by GPC in chlorofom with polystyrene calibration standards.

merization experiment is as follows: 3 g of TNB was dissolved in 21 ml of chlorobenzene under dry nitrogen. Then, 30 mg of $RuCl_2(PPh_3)_3$ and 150 mg of phenylacetylene in chlorobenzene were added. The reaction mixture was heated at 45°C for 24 h. The polymer was precipitated into methanol and purified by precipitation from chloroform into methanol. The polymer was dried in a vacuum oven at 40°C for 24 h.

The preparation of cross-linked IPN was accomplished by adding *N,N,N',N'*-tetra-methylhexamethylenediamine (3.1 g, 0.018 mol) to 5.0 g (0.016 mol) of polymer in 200 ml of dry THF, followed by refluxing for 12 h. The obtained IPN was filtered off and dried under vacuum. Yield was 85%. Analysis (%): C 64.56, H 8.94, N 8.05, S 8.95 ($C_{25}H_{42}N_2SO_3$). The IPN with a particle size of 50 mesh was washed several times with porogenic solvents such as toluene and methylene chloride before use.

2.3. Sorption and desorption of Cr(VI), Cr(III) and Ni(II)

A batch type equilibration procedure was used to determine the metal ion uptake from aqueous solution using polynorbornene resin. A 100 mg sample of the resin was added to 10 ml of 1 g/l solution of the metal ion. pH was adjusted with NaOH or H_2SO_4 until the desired constant value was achieved. The pH value of the aqueous solution varies from 1 to 5. The two phases were shaken in a mechanical shaker for 3 h at 25°C. After the equilibration period, the two phases were separated and the solutions were analyzed for Cr(VI), Cr(III) and Ni(II). Desorption was carried out with Cr(VI), Cr(III) and Ni(II) loaded resins at maximum capacity. The ions eluted by shaking 0.1 g of the resin with 10 ml of 1 M HCl and 1 M NaOH, respectively, for 1 h. The resin was separated by filtration and metal ions were analyzed as mentioned above.

2.4. Measurements

Cr(VI), Cr(III) and Ni(II) were analyzed by an atomic absorption spectrometer (AAS) and UV-spectrophotometer (UV-320). FT-IR-spectra were recorded using a Nicolet 510 p spectrometer. Measurements of pH values were performed with a digital Extech Microcomputer pH-meter. ^{1}H NMR and ^{13}C NMR were taken with TMS (tetramethylsilane) as the internal standard using a Varian at 300 and 75.5 MHz, respectively. Molecular weights and molecular weight distributions of precursor polynorbornene were estimated relative to polystyrene standards using a Varian GPC (gel permeation chromatograph) apparatus with THF (tetrahydrofuran) solvent.

3. Results and discussion

Monomer TNB was polymerized using ruthenium vinylidene catalysts and ruthenium complexes generated in situ from $RuCl_2(Ph_3)_3$ and phenylacetylene (trimethyl-silylvinylacetylene). Table 1 summarized the typical results from ROMP of TNB. It is seen that generally in situ ruthenium complexes were effective and show activity comparable with that of ruthenium vinylidene catalysts in ROMP of TNB. On the other hand, ruthenium vinylidene catalysts (Table 1) gave polymers with narrower molecular weight distributions (MWD). The polymerization of TNB by ruthenium catalysts proceeds with high yields to produce polymers with the preferential trans configuration of double bonds. It is seen from the table that the polymer yield is sensitive to the monomer/catalyst ratio and an increase of this ratio to more than 100 decreased the polymer yield. The results of GPC analysis show that the number average molecular weights (M_n) and MWD are of $0.6–2.2 \times 10^5$ and 1.97–3.25, respectively (Table 1). The ^{1}H-NMR spectra of both the monomer and the polymer show that the olefinic monomer signals between 5.65 and 6.1 have disappeared and a new signal with a maximum of 5.30 ppm has occurred, corresponding to the linear olefinic protons of the predominant trans double bonds of the polymer [11]. The ^{13}C NMR spectrum also suggests that the polymer contains pre-

dominantly trans double bonds. The spectrum consists of aromatic and olefinic peaks at 128–130 and 131.4–135.7 ppm., respectively. The olefinic resonances were assigned to head-to-tail and tail-to-head enchaiments along the chain [11].

It is important to note that the polymerization of quaternary ammonium containing norbornenes is troubled by the poor solubility and its high hydrophylicity. The preparation of a ionic polynorbornene via the modification of precursor polymer is much more feasible. The cross-linked ionic polynorbornene (IPN) was prepared from tosylate containing polynorbornene using N,N,N',N'-tetramethyldiamines (Fig. 1). The FT-IR spectrum of IPN shows strong absorption of the N–CH$_3$ group at 3426 cm^{-1}, aliphatic C–H stretching in the region 2860–2968 cm^{-1},
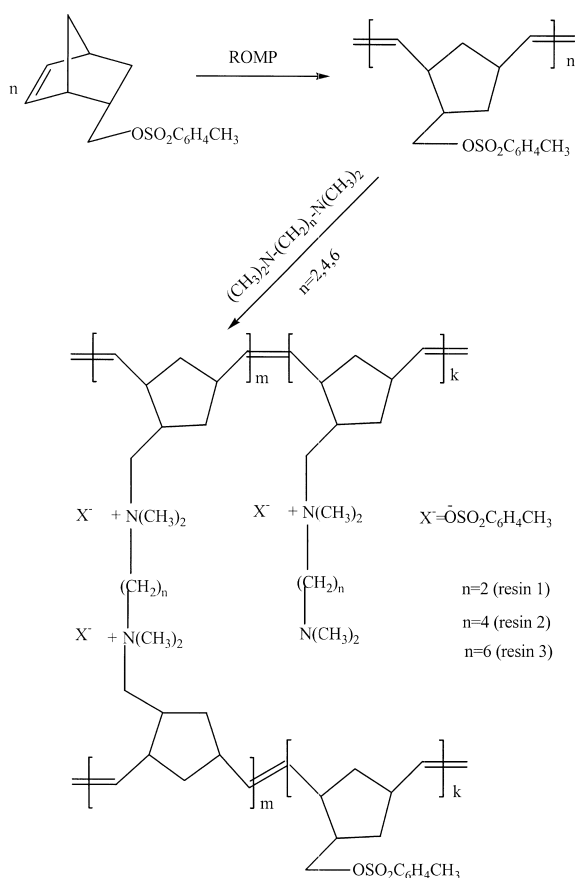
aromatic C–H bonds near 3059 cm^{-1} and the characteristic bands at 954 cm^{-1} corresponding to the trans double bonds of the polymer [11,12].

It is well known that the activity of resins in adsorbing metals is dependent on the diffusion of the metals into the polymer. For example, steric hindrance caused by polymeric matrix limits the coordinating ability of resins. It has been found that the capacity of IPN in adsorption of metals depended on the structure of cross-linking diamines. The ionic polymers prepared using N,N,N',N'-tetramethylethylenediamine (resin **1**) and N,N,N',N'-tetramethylbutylenediamine (resin **2**) demonstrate poorer adsorbing capacity compared to these obtained using N,N,N',N'-tetramethylhexamethylenediamine (resin **3**). The adsorption capacity of resins for Cr(VI), Cr(III) and Ni(II) at pH 1 are presented in Table 2. The retention percentages of the metal ions by the resin **3** as a function of shaking time at room temperature for the different pH are reported in Table 3 (pH = 1) and in Table 4 (pH = 3). It is seen that the time needed for completely saturation of the binding capacity of the resin for the Cr(VI) and

Fig. 1. Synthesis of cross-linked ionic polynorbornene.

Table 2
Maximum sorption capacity of resins for chromium and nickel ions at pH 1

Resin	mmol/g resin		
	Cr(VI)	Cr(III)	Ni(II)
1	1.5±0.1 (76%)	1.4±0.1 (72%)	1.0±0.1 (58%)
2	1.7±0.1 (87%)	1.7±0.1 (86%)	1.1±0.1(67%)
3	1.8±0.1 (95%)	1.8±0.1 (97%)	1.3±0.1 (78%)

In parenthesis, the sorption percentage of resins for the metal ions.

Table 3
Percent chromium (VI), chromium (III) and nickel (II) adsorbed as a function of contact time for resin **3** at pH 1.0

Metallic ion	Time (min)				
	20	40	60	90	180
Cr(III)	91.9	95.3	96.5	96.8	97.2
Cr(VI)	89.5	94.6	95.2	95.4	95.1
Ni(II)	60.3	71.1	76.2	78.4	–

Table 4
Percent chromium (VI), chromium (III) and nickel (II) adsorbed as a function of contact time for resin **3** at pH 3.0

Metallic ion	Time (min)				
	20	40	60	90	180
Cr(III)	45.9	55.7	60.3	64.7	64.8
Cr(VI)	38.2	50.5	57.4	58.4	–
Ni(II)	62.7	79.1	85.8	89.9	91.2

Cr(III) was about 20 min. As seen from Tables 3 and 4, the increase of pH decreased the coordinating ability of resin for the chromium ions. This behavior can be explained by considering the mechanism of retention as an anionic exchange where $Cr_2O_7^{2-}$ and CrO_3^{3-} species are involved. The sorption of Ni(II) on resins increases with increasing pH (Tables 3 and 4). This results suggest that the increase in pH promotes easy complexation of Ni(II) with $N(CH_3)_3$ amine groups of polynorbornene resins. The FT-IR spectrum of loaded with Ni(II) resin **3** shows a new band at 567 cm^{-1}. This band indicates that amine groups participate in coordinating with Ni(II) [21].

Attempts were made to desorb Cr(III) and Ni(II) from the resins using hydrochloric acid of various concentrations. It is observed that 1 M of HCl was very effective to desorb Cr(III) and Ni(II) from the resins. Analysis of the elution percentages of Cr(VI) from loaded resins in acid media shows that chromium could be recovered to the extent of 60%. When alkali (1 M NaOH) was used for the desorption, the elution percentages were found to be 85%. It is important to note that the desorption of Cr(VI) with alkali followed by acid is very high and the total desorbed chromium was found to be 95% from resin **3**, 84% from resin **2** and 76% from

resin **1**. There was no change in capacity even after three cycles of adsorption and desorption operations for the resin **3**. The particle size degradation was found to an extent of 1.5–2% (Table 5).

4. Conclusions

Three new ionic polynorbornene resins are synthesized and characterized for the selective adsorption of Cr(VI), Cr(III) and Ni(II) ions. The metal ions complexation properties of resins (**1**–**3**) are dependent on the pH and the structure of the cross-linking diamines. Thus, ionic polymers prepared using *N,N,N′,N′*-tetramethylethylenediamine (resin **1**) and *N,N,N′,N′*-tetramethylbutylenediamine (resin **2**) as cross-linking agents demonstrate poorer ability in adsorbing metals than these obtained with *N,N,N′,N′*-tetramethylhexamethylenediamine (resin **3**). Resin **3** is highly selective for Cr(VI) and Cr(III) at pH = 1 and this resin shows no change in capacity even after three cycles of adsorption and desorption operations.

Table 5
Percentage of chromium (III) recovery in acid and basic media

Resin	HCl		NaOH	
	1 M	4 M	0.25 M	1 M
1	76.8	78.9	65.7	76.2
2	78.2	80.3	72.7	78.9
3	94.8	88.4	86.9	92.7

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