Chemistry for Sustainable Development **15** (2007) 319–324

Synthesis of Sulphur-Containing Ionites by Means of Living Radical Copolymerization

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(Received March 17, 2006; revised January 19, 2007)

Abstract

Moulded copolymers of styrene with divinylsulphide were synthesized by means of the living radical polymerisation with N,N′-bis(vinyloxyethyl)thiuramdisulphite as an initiator without any solvents. It was shown that the formation of a polymeric body proceeds without the formation of a macrogel. Individual particles of copolymers were discovered using scanning electron microscopy. These particles are monospheroids with a size about 1 μm; they determine further formation of the moulded polymeric body as granules. Copolymer modification was carried out, ionites were obtained. The effect of the nature and concentration of acids on the extraction of silver, gold and platinum ions was established. High distribution coefficients equal to (2.0–6.5) 10^4 were obtained for the chloride complexes of gold and platinum. The possibility to use sorbents for concentrating precious metals and for analytical purposes was demonstrated. A method of sorbent regeneration was developed.

INTRODUCTION

The possibilities of further improvement of the modern synthetic classes of sorbents having a framework of copolymers of styrene with divinylbenzene have already been exhausted with respect to the composition of the matrix and synthesis technology. Because of this, the main focus is concentrated during the recent years on the improvement of performance characteristics of sorbents by means of manufacturing ionites according to the monosphere technology; the use of monospheres allows one to decrease the hydrodynamic resistance of sorption columns by 10–20 % and to improve the integral kinetic parameters [1, 2]. Replacement of divinylbenzene with divinylsulphide (DVS) in copolymerisation with styrene has a number of advantages: flexibility, mechanical strength and osmotic stability of the matrix. The presence of sulphide sulphur renders additional complex-forming properties to the polymeric framework and increases thermal and radiation stability [3, 4].

The sorbents obtained by means of radical polymerisation are characterized by micro-inhomogeneous structure which is due to the chain mechanism of macromolecule formation [5]. Realization of a three-dimensional radical polymerisation in the mode of living chains (TRPL) may be considered as a potentially highly efficient instrument of macromolecular design. With such a mechanism of three-dimensional polymerisation, instead of a usual (chain) mode of macrochain growth, a stepwise mode is realized, which allows one to decrease the amount of defects in the spatial structure of the sorbents.

We proposed to use DVS as a cross-linking agent for the synthesis of ionites based on styrene by means of the living radical polymerisation; we proposed N,N′-bis(vinyloxyethyl)thiuramdisulphide (VTDS) synthesized for the first time in our laboratory to use as the initiator of polymerisation (iniferter).

The goal of the present work was synthesis of new sulphur-containing ionites by means of the living radical copolymerisation and investigation of their structural and sorption properties.

EXPERIMENTAL

Divinylsulphide and VTDS were synthesized according to the procedures described in [6, 7]. Styrene was purified from the inhibitor by vacuum distillation (34 °C at 11 mm Hg). Divinylsulphide with a purity of 99.8 % (according to the data of GLC) was distilled immediately before experiments (83 °C) to remove the inhibitor.

The copolymer for obtaining ionites was synthesized under the following conditions: DVS content in reaction 10 mol. %, reaction time 168 h, temperature 70 °C, in mass. The ampoule with the reaction mixture was degassed in vacuum by means of freezing/melting to the residual pressure of 10^{-2} mm Hg. The copolymer was washed with hexane, diethyl ether, and dried in vacuum to the constant mass. The yield was 95.0 %. The copolymer is a finely granulated insoluble powder of white colour. Additional polymerisation of the copolymer was carried out in the mode of stepwise temperature rise from 70 to 120 °C for 5 h. Chloromethylation and amination of the copolymer were carried out according to the procedures described in [8, 9].

The IR absorption spectra were measured with Bruker IFS 25 spectrometer in tablets with KBr. The sorption characteristics were determined at room temperature in the static mode with respect to the silver cation Ag^+, hexachloride complex of platinum Pt^{4+} and tetrachloride complex of gold Au^{3+} [10]. Residual concentrations of the metals were monitored by means of atomic absorption (AAS-1 spectrometer) and photometry [11].

RESULTS AND DISCUSSION

For synthetic sorbents with a polymeric framework (matrix), the formation of a three-dimensional cross-linked network is important because its structural features determine the area of sorbent application. We discovered that copolymerisation of styrene with DVS in the mode of living chains proceeds without the formation of macrogel and monolith formation stage [12]. Isolation of the copolymer does not require precipitation procedures because its particles are formed as grains with the high degree of conversion, similarly to crystallization from saturated solutions; they can easily be washed with solvents and do not stick together. A reaction under similar conditions but initiated by DAC is accompanied by the formation of monolith blocks of copolymers. Different mechanisms of macrochain growth: chain (under initiation with DAC) and stepwise (under initiation with the iniferter) affect the structure of the polymeric body which is formed as blocks in the first case and as granules in the second one. As a consequence, the polymers have different performance properties.

At the early stage of structure formation, the properties of the polymers are formed. The microstructure (size, character of surfaces) of the copolymer of styrene with DVS synthesized in the presence of VTDS was investigated by means of scanning electron microscopy (SEM). The SEM images of macromolecules is shown in Fig. 1, *a*. They are monodisperse spherical particles with a size of about 1 μm.

Copolymers of styrene with DVS synthesized in the presence of DAC do not possess highly organized structure (see Fig. 1, *b*), which is due to the manifestation of gel effect at early stages of the reaction [12] and due to the formation of macrogel.

A specific characteristic feature of the formation of supramolecular structures during the realization of TRPL of styrene with DVS is the formation of individual particles of the polymeric body in the form of regular spheroids (see Fig. 1, *a*) which are the nuclei of structural formations and predetermine further morphology of polymers.

According to the theory of microheterogeneity, the formation of microgel particles dur-

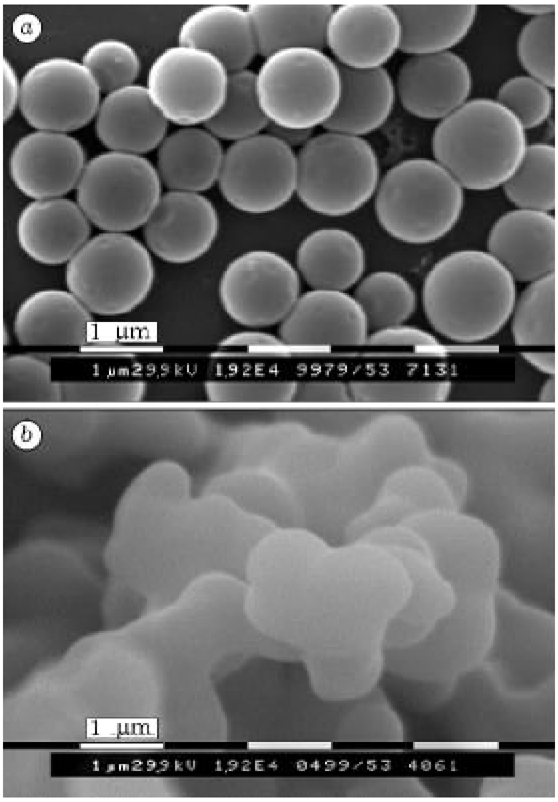

Fig. 1. SEM images of styrene copolymers with DVS at a ratio of 90 : 10 mol. % (degree of conversion was 3 %). *a* – VTDS, *b* – DAC. Magnification 19200.

ing three-dimensional polymerisation is first of al due to the chain character of macromolecular growth [13]. In TRPL of styrene with DVS initiated by iniferters, the chains grow synchronously. This excludes microphase layering because of the accumulation of long primary macromolecules in the medium of the initial oligomer; thus the reaction system remains uniform during the process (homogeneous gel formation) up to deep conversion [14].

The copolymers of styrene with DVS and their modified forms were analysed by means of IR spectroscopy. The IR spectra of the copolymers of styrene with DVS, we observe characteristic bands due to the vibrations of C_6H_5 groups (537, 697, 757, 1451, 1584, 1601 cm^{-1}) and CH_2=CH–S (875, 960, 1582 cm^{-1}). After the performed stepwise additional polymerization, the spectra of copolymers did not exhibit the characteristic bands of CH_2=CH–S groups.

The chloromethylated copolymer with the initial content of DVS links equal to 13.5 % (Table 1) (with the theoretically possible chlorine insertion at a level of 20.14 %) contains 11.49 % chlorine, which corresponds to 57.08 % modification of polystyrene units. The absorption bands at 839 and 1513 cm^{-1} appear in the IR spectra of chloromethylated copolymer; these bands point to the presence of *para*-derived benzene rings. The band appearing at 1264 cm^{-1} relates to the fan deformation vibrations of CH_2Cl group in the styrene ring [15]. The absorption bands at 537, 697, 757 cm^{-1} which are characteristic of non-substituted links of polystyrene are conserved, which is an evidence of incomplete chloromethylation of polystyrene links.

The second stage of ionite synthesis is amination, which is carried out at the chloromethylated links of polystyrene. According to the nitrogen content in the modified copolymer (see Table 1), amination has proceeded by 50.55 % (taking the nitrogen content 4.78 % for the complete amination of the copolymer) and accounts for 88.57 % of the chloromethylated polystyrene links.

Investigation of the sorption characteristics of the modified copolymer of styrene with DVS was carried out for metals in the cation form (Ag^+) and in the anion forms for gold and platinum ($[AuCl_4]^-$ and $[PtCl_6]^{2-}$, respectively).

Investigation of the dependence of the degree of gold, platinum and silver ion extrac-

TABLE 1

Characteristics of the initial and modified copolymers of styrene with divinylsulphide

Copolymer	Concentration, mass %				
	C	H	S	Cl	N
Initial copolymer	89.34	7.94	4.81	–	–
Chloromethylated copolymer	76.07	6.89	3.69	11.65	–
Aminated copolymer	80.25	7.93	2.54	4.23	2.52

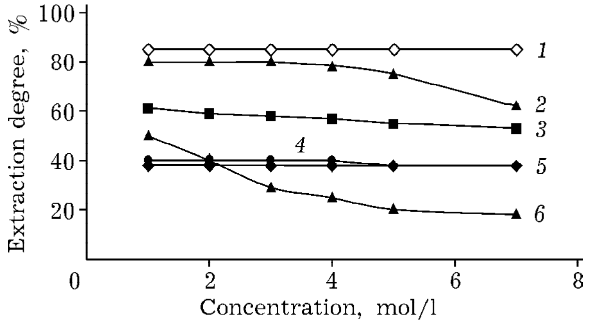

Fig. 2. Dependence of the extraction efficiency for the chlorocomplexes of Au (*1*, *2*), Pt (*3*, *6*) and Ag cation (*4*, *5*) on the concentration of sulphuric (*1*, *4*, *6*) and hydrochloric (*2*, *3*) acids. m_{sorp} = 10 mg, m_{Au} = 1.28 mg, m_{Pt} = 0.94 mg, m_{Ag} = 7.0 mg, t = 2 h, V_{sol} = 20 ml.

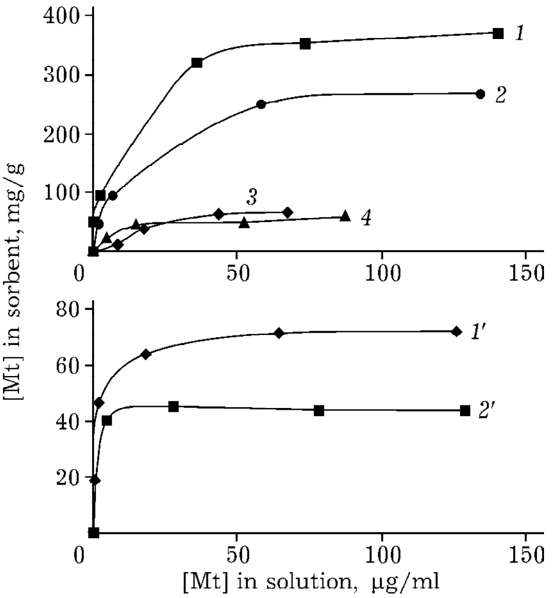

Fig. 3. Curves of the equilibrium distribution of Au (*1*, *2*), Ag (*3*, *4*), Pt (*1'*, *2'*) in the solutions of 1 M H_2SO_4 (*1*, *3*, *2'*), 1 M HNO_3 (*4*) and 1 M HCl (*2*, *1'*). m_{sorp} = 10 mg, V_{sol} = 20 ml, t = 2 h.

tion on the concentration of the acid within the range 1–7 mol/l showed the following. For the concentration of hydrochloric acid above 4 mol/l, a decrease in gold ion sorption is observed, while the concentration of sulphuric acid does not affect the degree of extraction (Fig. 2, curves *1*, *2*). For platinum ions, the degree of extraction decreases with an increase in acid concentration (see Fig. 2, curves *3*, *6*). Sorption of silver cations does not depend on the concentrations of nitric and sulphuric acids (see Fig. 2, curves *4*, *5*).

Investigation of the dependence of the degree of metal ion extraction on the time of contact between the solutions and the solid phase of the sorbent showed that the establishment of sorption equilibrium occurs with a high rate; for the anion forms of metals, it takes 30–60 min with $\tau_{1/2}$ equal to 15 and 9 min (see Fig. 3, curves *1*, *1'*, *2*, *2'*), respectively, while for the cation form it takes 15 min with semi-sorption time $\tau_{1/2}$ equal to 8 min (see Fig. 3, curves *3*, *4*). Under the conditions of sorption equilibrium, the dependence of the degree of metal ion extraction on their concentrations in solution was investigated; sorption capacities under the static conditions and metal distribution coefficients were calculated (Table 2).

The largest sorption capacity of the copolymer is exhibited towards gold ions for which also high distribution coefficients are observed (see Table 2). On the basis of the data on the sorption activity of modified copolymer of styrene with DVS, one may assume the mechanism of the interaction of the sorbent with metal ions. For nitrogen-, sulphur-containing sorbents and acidocomplexes of gold and platinum, both ion exchange and coordination interactions are possible, while only coordination ones are possible for silver. The appearance of the dependencies of ion metal extraction efficiency (see Fig. 2) provides evidence of their coordination interaction with the sorbent because for the case of ion exchange interaction one should observe the competitive

TABLE 2

Sorption capacity (SC) of modified copolymer of styrene with divinylsulphide and the coefficients of metal distribution (*D*) for solutions: 1 M HCl, 1 M H_2SO_4, 1 M HNO_3

Metal form	HCl		H_2SO_4		HNO_3	
	SC, mg/g	*D*	SC, mg/g	*D*	SC, mg/g	*D*
$[AuCl_4]^-$	270	$4.6 \cdot 10^4$	370	$5.0 \cdot 10^4$		
$[PtCl_6]^{2-}$	59	$2.0 \cdot 10^3$	65	$3.0 \cdot 10^4$		
Ag^+			44	$5.0 \cdot 10^4$	73	$1.0 \cdot 10^4$

effect of acid ions and a more sharp decrease in the sorption activity with an increase in the anion concentration.

Investigation of the IR spectra of sorbent samples treated with acids and the samples after metal sorption (concentrate) showed that they coincide in the positions of IR bands and their intensities. Since the gold content of the sorbent is high (270 mg per 1 g), the coordination of gold-containing ions with respect to the structural fragments of the copolymer should cause changes in the parameters of IR bands. The main mechanism of gold sorption is ion exchange, when the chloride anion Cl^- in the $-N^+(C_2H_5)_3Cl^-$ group is exchanged for the anion $[AuCl_4]^-$. The vibrations of the anion $[AuCl_4]^-$ manifest themselves in the region 320–350 cm^{-1}. It is impossible to detect the corresponding IR band in our experiments because we recorded the IR spectra within the range 400–4000 cm^{-1}.

Taking into account the sorption capacity values (see Table 2), only coordination sorption interaction is to be assumed for silver cation; both coordination and ion exchange sorption interaction may be assumed for the tetrachloride complexes of gold and platinum.

The specific feature of the application of this sorbent is its easily regeneration and the possibility of repeated use in sorption cycles. It was established that at room temperature 3 % thiocarbamide solution may be used as an eluent. Desorption is carried out by almost 100 % within 1 h under static conditions.

From the solutions of acids with the concentration of 1 mol/l, the sorbent extracts copper ions by 70 % (for copper content equal to 1 mg/20 ml) and is selective to iron, nickel, cobalt, zinc, aluminium ions. Using synthetic solutions, we demonstrated the possibility of quantitative extraction of gold in the presence of a 1000-fold excess if nonferrous metals with the possibility of their further elution with thiocarbamide, followed by atomic absorption detection for the concentrations 0.2–0.1 μg/ml. The determination was carried out on the basis of the calibration dependence built up to thiocarbamide solutions of the chloride complex of gold. The modified copolymer was used for sorption – atomic absorption determination of gold in the samples of products from raw materials processing and in the standard ore sample (VKO-2) (Table 3) with the preliminary decomposition [11]. The standard deviation characterizing the error of determination does not exceed 15 %.

CONCLUSION

By means of the living radical polymerisation with N,N′-bis(vinyloxyethyl)thiuramdisulphide as an initiator, a copolymer of styrene with divinylsulphide was obtained. The structure of the copolymer was investigated by means of IR spectroscopy and electron microscopy. It was shown that the copolymer does not contain unreacted $S-CH=CH_2$ groups; the individual particles of the polymer phase are monospheroids. Unlike for the classical polymerisation of these monomers using DAC, the living radical polymerisation allows one to obtain the moulded polymer of styrene with DVS in the form of granules without using solvents.

Modification of the copolymer was carried out; an ionite was obtained which is stable in acid solutions and within the acid concentration in solution 1–7 mol/l extracts silver, gold and platinum ions with the time of equilibrium establishment 15–40 min. On the basis of the curves of equilibrium distribution, the sorption capacity and distribution coefficients were calculated. High distribution coefficients

TABLE 3

Atomic absorption determination of gold content in ore samples and in processing products, g/t

Sample	True, g/t	Determined, g/t	S_r, %
Convector dust (n = 8)	7.70	7.45 ± 0.19	3.2
Cyclone dust (n = 3)	3.24	2.96 ± 1.09	14.9
Standard sample VKO-2 (n = 3)	4.75	4.60 ± 0.60	8.7

Note. n is the number of determinations.

$(2.0-6.5) \cdot 10^4$ were obtained for the chloride complexes of gold and platinum. The conditions of sorbent regeneration were determined. It was shown that desorption proceeds by almost 100 % within 1 h under static conditions.

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