Chlorinated Crosslinked Adsorbents

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ABSTRACT: High crosslinked copolymers based on poly(ethylstyrene-*co*-divinylbenzene), bead shaped, have chlorinated, resulting in adsorbents with a high content of chlorine (45.0% Cl). The chlorination process of the copolymer beads (0.40-0.80 mm in diameter) was carried out in 1,2-dichloroethane in the presence of a Friedel–Crafts catalyst (AlCl₃, FeCl₃), at 5–40°C, yielding yellow beads without any cracks and good mechanical strength. The chlorination degree of the samples is high because each vinyl aromatic unit contains 1.8–2.2 chlorine atoms. The chlorinated copolymer samples were used to retain Cephalosporine C from standard solutions comparatively with commercial adsorbents (Amberlite XAD-4 Rohm, Haas Co.; SP-206/7, Mitsubishi Kasai Corp., Japan). © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1579–1587, 1998

Key words: poly(ethylstyrene-divinylbenzene) copolymers; polar adsorbents; macroporous adsorbents; chlorinated macroporous adsorbents

INTRODUCTION

During the last two decades, numerous macroreticular adsorbents based on crosslinked *co*(polystyrene) type, without any functional groups, were marketed by many manufacturers of ionexchangers.

Generally, the network adsorbents are characterized by pore volume, specific surface area, pore diameter, and bead size distributions. The success of the adsorbent applications in the pharmaceutical technology depends on the porous network structure, its polarity, and many other parameters.¹⁻⁸

The adsorbent structure is influenced most by the amount of diluent (porogen) used in the copolymerization process as well as the quantity of divinylbenzene. It is well known that a good solvent leads to adsorbents with narrower pores, that is, networks suitable as packing materials for the chromatographic columns.

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The pore formation mechanism was explained by Kuhn and Kunin.^{4,9} A macroreticular bead consists of an agglomerated microsphere, forming particles separated by void volumes.⁹ The chlorination (bromination) of poly(ethylstyrene-*co*-divinylbenzene) beads P(EtSt-DVB), results in polar adsorbents, improving their selectivity and capacity to adsorb water-soluble organic compounds, particularly, antibiotics from the broth media.³

This article reports the results of the chlorination reaction study performed on poly(ethylstyrene-*co*-divinylbenzene) beads and the investigation of the adsorbent features via microscopic analyses, as well as the ability to remove Cephalosporine C from the broth medium.

EXPERIMENTAL

Materials and Preparation of the Network Beads

Divinylbenzene (DVB) of technical grade, was freed of inhibitors and distilled before use. The concentration of fresh distilled divinylbenzene was determined via gas chromatography (GC)

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analysis; it was 56.32% DVB; 32.03% ethylstyrene, and 11.05% nonpolymerizable compounds (inert compounds). The inert–porogen media were toluene and xylene, used as received. Benzoyl peroxide was purified by recrystallization from a mixture of chloroform–methanol 1/1 (v/v) and dried in vacuum at room temperature. Gelatine (0.15% vs–H₂O), NaCl (3.5% vs–H₂O) and ammonium salt of poly(maleic anhydride-*co*-styrene) (0.70% vs–H₂O) were used to stabilize the organic droplet suspension.

The porogen-diluent quantity (f_g) used throughout the experiments is expressed by the following relationship: f_g = weight of monomers/weight of monomers + weight of porogen (g/g). Hence, the monomer concentration (C_m) in the organic phase (copolymerization mixture) can be calculated from the relationship $%C_m = 100 \times f_g$. The aqueous suspension polymerization process was carried out with an organic : water phase ration of 1:3 to 1:5.

Beads (0.40-0.80 mm in diameter) of copolymers washed on filter, leached and extracted with methanol (acetone) were dried in a vacuum oven at 50°C for 50 h. They were then analyzed according to methods described elsewhere.¹⁰

The chlorination process of dried beads was performed in a 1-L flask fitted with a thermometer, cooler, and stirrer at various values of temperature. A weighted quantity of dried beads (1 mol) was introduced into the flask, which contained anhydrous 1,3-dichloroethane (500 g) and let to swell for 5 h at room temperature. After that, 5 g of anhydrous FeCl_3 was added at 150–200 rpm, and finally a dry chlorine flow was passed. Chlorine content was determined potentiometrically accordingly to Schöniger's method.¹¹

High values of the chlorination degree were recorded. Each aromatic unit contains 1.8–2.2 chlorine atoms/structural unit.

Methods of Pore Structure Determination

All sample were characterized by measuring and calculating the following characteristics: the skeletal (ρ) and apparent densities (ρ_{ap}), porosity (%*P*), solvent-uptake coefficient, pore volume (*PV*), surface area (*S*), thermal stability, infrared (IR) spectrum, and transmission and scanning microscopy.

The regain of Cephalosporine C was measured in dynamic conditions (on packed columns with chlorinated poly(ethylstyrene-*co*-divinylbenzene).

The skeletal density (ρ) and the apparent density (ρ_{ap}) of copolymers were determined by picnometric methods with *n*-heptane and mercury as the confining fluids. For determination of ρ_{ap} , first, the beads were outgassed in a picnometer and then were filled under vacuum with mercury at 20°C. The specific surface areas were measured by the N₂ adsorption method¹² on a Ströhlein AREA meter.

A few samples were characterized by thermogravimetric analysis (TGA). The measurements were performed on a 20-mg powder sample at a

Number	DVB (%) ^b	Apparent Density (g/mL)	Porosity (%)	Cyclohexane Regain (mL/g)	Pore Volume (mL/g)	Specific Surface (m²/g)	Mean Pore Diameter (nm)
Toluene							
1	40.0	0.8577	20.58	0.27	0.240	275.0	3.49
2	45.0	0.7220	33.13	0.57	0.459	371.2	4.95
3	55.0	0.6240	42.22	1.47	0.677	461.6	5.08
4	61.3	0.5427	49.75	1.70	0.917	652.5	5.62
Xylene							
5	40.0	0.6681	38.14	1.77	0.575	198.1	7.72
6	45.0	0.6095	43.83	1.62	0.719	335.8	8.56
7	50.0	0.6118	43.62	1.65	0.713	376.25	7.58
8	55.0	0.6100	43.78	1.55	0.718	453.8	6.33
9	61.3	0.5821	46.35	1.44	0.796	525.2	6.06

Table I Main Characteristics of Macroporous Samples Synthesized in the Presence of Porogens^a

^a Toluene; xylene; 65.0% porogen/organic phase; skeletal density, 1.085 g/mL.

^b Divinylbenzene; 56.32% DVB; 32.03% ethylstyrene; and 11.05% nonpolymerizable compounds.

Number	DVB (%)	Apparent Density (g/mL)	Porosity (%)	Cyclohexane Regain (mL/g)	Pore Volume (mL/g)	Chlorine Content (%)	Specific Surface (m²/g)	Mean Pore Diameter (nm)
Toluene								
1	40.0	0.8690	19.53	1.00	0.225	42.56	333.6	2.698
2	45.0	0.6809	36.95	1.10	0.543	37.13	376.8	5.760
3	55.0	0.6130	43.24	1.19	0.705	45.53	445.5	6.333
4	61.3	0.5881	45.54	1.10	0.775	45.20	513.4	6.034
Xylene								
5	40.0	0.7638	29.60	0.87	0.387	51.32	347.3	4.457
6	45.0	0.7263	33.06	1.06	0.455	51.05	439.2	4.144
7	50.0	0.7087	34.68	1.00	0.489	45.12	442.3	4.422
8	55.0	0.6606	39.11	1.17	0.592	42.33	453.2	5.225
9	61.3	0.6205	42.80	0.97	0.690	45.55	472.1	5.846

Table II Main Characteristics of Chlorinated Porous Copolymer Samples^a

^a $M_{\text{copolymer}}$ - M_{AlCl_3} : 1.0 : 0.03 mol; temperature, 40°C; time, 8 h.

heating rate of 12°C/min up to 900°C in air on an Erdey–Paulik Budapest Derivatograph; α - Al₂O₃ was used as the reference material. The values of the pore volume (*PV*), and the so-called macroporosity (*Q*) were calculated using the following equation^{13,14}:

$$PV(Q) = 1/\rho_{ap} - 1/\rho \text{ (mL/g)}$$
 (1)

where ρ_{ap} is the apparent density (g/mL), and ρ is the skeletal density (g/mL) determined by the picnometric method in *n*-heptane.

The porosity (% P), the so-called void volume was calculated according to equation (2), as follows:

$$\%P = 100 \times (1 - \rho_{ap}/\rho) \tag{2}$$

and it represents the percentage of the empty pores (void volume) contained by the beads.

The average pore diameter (\overline{D}) was calculated according to following relationship:

$$\bar{D} = \frac{4PV}{S_{\rm BET}} \times 10^3 (\rm nm) \tag{3}$$

	Com	position (4	%)		Chlorine			
Number	Styrene	Ethyl- styrene	DVB	Average Molecular Weight	Network Moles/100 g Copolymer	Weight of Chlorinated (g/mol)	of Sample (Monosubstituted) (%)	Experimental Content (Atom/ Structural Unit)
Toluene								
1	49.19	10.81	40.0	116.14	0.8610	151.64	23.41	1.82
2	42.83	12.16	45.0	117.78	0.8490	153.28	23.16	1.88
3	30.13	14.87	55.0	121.30	0.8244	156.80	22.64	2.02
4	22.13	16.57	61.3	125.63	0.7960	161.13	22.03	2.05
Xylene								
5	49.19	10.81	40.0	116.14	0.8610	152.64	23.41	2.19
6	42.83	12.16	45.0	117.78	0.8490	153.28	23.16	2.20
7	36.48	13.15	50.0	119.54	0.8367	155.04	22.82	1.98
8	30.13	14.87	55.0	121.30	0.8244	156.80	22.64	1.87
9	22.13	16.57	61.3	125.63	0.7960	161.13	22.03	2.07

Table III Structural Composition of the Chlorinated Sample

where $S_{\rm BET}$ is the specific surface area (BET method, cylindrical model, was assumed for the pore shape).

The scanning electron microscopy (SEM) studies were performed on the fractured bead, which was fixed on a copper support and covered with a thin layer of gold. The investigations were carried out using a Leitz SEM 1600T type scanning electron microscope.

RESULTS AND DISCUSSION

The chlorination reaction of poly(ethylstyrene-codivinylbenzene), P(EtSt-DVB), in the presence of anhydrous FeCl₃ takes place accordingly to a Friedel–Crafts mechanism, (that is, an aromatic electrophilic substitution reaction), where FeCl₃ favors the formation of chlorine cation /Cl⁺/, as follows:

$$R_1R_2 - C_6H_4 + |Cl^- - Cl^+| \rightarrow$$

 $R_1R_2C_6H_3 - Cl + HCl$

Macroporous samples based on P(EtSt-DVB) were prepared by a suspension copolymerization technique in the presence of various ratio of toluene and xylene (65.0% porogen of the whole organic phase). In order to obtain high-porosity networks, large quantities of porogens and DVB were needed. Therefore, samples with DVB percentages between 40.0 and 65.0% DVB were synthetized. Beads of 0.40-0.80 mm in diameter were analyzed, and their features are listed in Table I.

Table I shows that most of samples possess large specific surface areas, $(275-652 \text{ m}^2/\text{g})$, which depend on the DVB percentage (mixture dilution was kept constant throughout the experiments), while the mean pore diameter varies conversely with the quantity of DVB.

The use of xylene as porogen led to porous beads with larger mean pore diameter and less-specific surfaces comparatively with toluene. For instance, a copolymer with 61.3% DVB prepared in the presence of toluene has 652.5 m²/g, while one performed in the presence of xylene only 525.2 m²/g (a difference of 127.3 m²/g; see Table I). This difference between the specific surface values of the two networks cannot be only explained by the solvent-polymer solubility parameters, which are quite close (Table I).

The chlorination of samples whose characteristics were listed in Table I led to yellowish copoly-



Figure 1 Influence of temperature and time on chlorination process of P(EtSt-DVB) (61.3% DVB): (\bigcirc) 40°C; (\times) 20°C; (\bigcirc) 5°C.

mers containing 37.13–51.22% Cl, that is, 1.82–2.19 chlorine atoms/structural unit (Tables II and III).

It was noticed that the chlorination process is also influenced by temperature and time. Hence, the highest output of the conversion degree was recorded after 3 h at 40°C; 4 h at 20°C; and the lowest value, at 5°C for 15–27 h (Fig. 1).

The chlorination reaction of the networks leads to the important modifications of the bead morphologic structure as it results from the values of the main features listed in Table II. Generally, the specific surface and the mean pore diameter vary significantly.

It should be mentioned that the changes of the morphological structure within the beads were observed during the chemical reaction carried out on poly(styrene-*co*-divinylbenzene) in order to prepare ion exchangers. The thermal stability of halogenated copolymers, which contained 43.2% Cl, was compared with a nontransformed P(EtSt-DVB) via TG and DTG (Fig. 2).

Results given in Figure 2 show the behavior of the copolymers. The thermal stability of the chlorinated copolymer is less than the initial sample, particularly after 400°C. Both samples are stable up to 300°C; after that, the degradation process starts and ends at 575°C (curve 2) and 640°C (curve 1). It is also seen that the degradation mechanism of the network consists in exothermal and endothermal reactions (Fig. 2). The study of the thermal behavior of the chlorinated P(StEt-DVB) is useful when such networks are used as packing materials in gas chromatography.



Figure 2 TGA of P(EtSt-DVB) (curve 1) and chlorinated copolymer (curve 2) (both samples contain 61.3% DVB).

Infrared spectra of polymeric adsorbents were used to established their chemical and molecular structure. Commercial divinylbenzene used to prepare the adsorbents consists of a mixture of mand p-divinylbenzene and a large percentage content of ethylstyrene isomers (particularly meta and para). The tetrafunctionally bound of DVB is not prone to substitution, and a correlation might be expected to exist between DVB content and the intensity peaks. The values are listed in Table IV.

The chlorinated copolymer structure as results from Table IV is very complex because each aromatic ring is tri- and tetra-substituted; schematically, it can be represented by the following scheme:



The inner microscopic structure of the chlorinated networks reveals the morphology of the beads (nonchlorinated and chlorinated samples) in Figure 3(a-d).

The mechanism of pore formation, according to Kuhn and Kunin,⁹ is a three-stage process. During the first stage, polymer microgels soluble in the monomer-toluene system are formed. As the polymerization reaction proceeds, the polymer chains become less and less swollen and then become entangled. This stage ends by forming of nuclei. In the second stage of the pore structure

Table IV The Vibrational Spectra of Poly(ethylstyrene-co-divinylbenzene)^a

Vibration (cm ⁻¹)	Assignment
810-815	
910	
1070	1,3-Disubstituted components
1090	
850	1,4-Disubstituted components
2970	Divinylbenzene
1000	Adsorbtion of 1,3- and 1,4-disubstituted
700	Phenyl ring adsorbtion
1500; 1590–1630	c==c
2860; 2920–2940	Methylene groups of main chain
835; 825; 885	Trisubstituted aromatic ring
1040; 1065	Chlorine bound to the aromatic ring

 $^{\rm a}\,61.3\%$ DVB and 47.12% Cl.







formation, the entanglements between the polymer chains increase, and nuclei aggregate into microspheres. In the third stage, the microspheres aggregate, yielding particles separated by channels of varying sizes. The morphology of our copolymers prepared in the presence of toluene was characterized by SEM. For comparison, Amberlite XAD-4, an adsorbent whose structure is similar to our samples, was chosen.

One can observe that the standard sample Amberlite XAD-4 consists in a uniform distribution of particles and microspheres [Fig. 3(a)]. A similar structure can be observed for P(EtSt-DVB), where microspheres are better emphasized in Figure 3(b). The bead external aspect does not show any cracks of chlorinated sample, as shown by Figure 3(c). Also, the SEM of P(EtSt-DVB) proves the existence of larger channels in Amberlite XAD-4, that is, a structure with large pores. The chlorination process of P(EtSt-DVB) changes the inner structure of the bead, as shown in Figure 3(c) and (d). The pore distribution becomes more uniform with smaller void volumes.

The structure changes might be better understood calculating other features according to the Hrădil assumptions.^{14,15}

In the present study, the pore shape arises as a space limited by microscopic particles. Under the above assumptions, the mean pore size was defined as the radius of a spherical bead, which can still pass through the space between microscopic particles of the polymer, forming its macroporous structure. Pores in the individual lattices form infinite pores, which, however, need not be straight at all. The idea of an infinite cylindrical pore is best fulfilled in a primitive cubic lattice, where pores having dimensions of microscopic particles are really straight in the direction of the main lattice axes. The assumption of an infinite cylindrical pore is not incorrect; it is only a limiting case on the wide scale of ordering of microscopic particles in a macroporous copolymer.

But, a real macroporous structure may differ from an ideal model system because of a number of factors, as follows, (1) nonuniformity of the particle size distribution of microscopic spherical particles; and (2) various geometry of the particles (nonspherical and intergrown par-

Figure 3 Scanning electron microscopy photos of (a) Amberlite XAD-4 (magnification $5000\times$) and (b) P(EtSt-DVB) (sample 4; 45.2% Cl; magnification $4200\times$); (c) external and (d) internal structure.

Number	Temperature (°C)	Specific Density (g/mL)	Apparent Density (g/mL)	Porosity (%)	Pore Volume (mL/g)	Surface Area (m²/g)	Mean Pore Diameter (nm)	Chlorine (%)	Chlorine Atoms/Structural Unit
1	0	1.2200	0.7220	40.81	0.565	544.60	4.15	25.11	1.13
2	15	1.3820	0.6030	56.37	0.935	573.47	6.52	31.55	1.41
3	30	1.3880	0.5865	57.75	0.985	542.70	7.26	35.20	1.58
4	40	1.4080	0.6019	57.25	0.951	588.50	6.46	42.00	1.88
5	50	1.4924	0.6509	56.38	0.866	534.30	6.48	49.60	2.22
6	60	1.6725	0.6143	63.27	1.030	574.20	7.17	44.10	1.98

Table V Influence of Temperature on the Main Features of Poly(ethylstyrene-co-divinylbenzene)^a

^a % DVB, 61.3%; sample 4; Table I.

ticles), which may close some porous domain. Such defects are shown by the microscopic photos.

Hence, several features were calculated and listed in Table V for nonchlorinated and chlorinated samples 61.3% DVB prepared in the presence of toluene, or xylene (Table VI).

The chlorination process acts on the P(EtSt-DVB) matrix, changing the inner structure of the beads a little (Table V).

One can notice that strongly crosslinked copolymers having an average pore radius $\bar{r} = 3.0$ nm possess pores, which predominantly consist of narrow space between spherical particles (according to the \bar{a} value) situated at an average distance $\bar{a} = 0.302 - 0.395$ nm. This statement becomes

particularly important if one imagines the effect of pore distribution on the average distance, when a few large pores may greatly affect the average radius of the pore.

The aim of this study was to prepare an adsorbent able to adsorb Cephalosporine C from the culture filtrates.

Therefore, several chlorinated samples were tested on standard solutions (70.0 and 90.0% purity degree) in dynamic conditions (columns with 16.0 mm i.d.) at 2.8-3.0 pH value. The influent solution concentration was 500 ppm. All tests were performed on 50-mL adsorbent at a flow rate of 1 bed volume/h (1 BV/h). Both influent and elution were carried out with an aqueous solutions of acetone (20.0% acetone).

Chlorine Content (%)	Network Density (g/mL)	Pore Volume (mL/g) ^a	Specific Surface (m²/g)	Porosity (%) ^b	Mean Pore Radius [r(nm)] ^c	Mean Particle Radius $[\bar{R}(\mathrm{nm})]^{\mathrm{d}}$	Mean Pore Radius [$ar{r}(nm)]^e$	$\begin{array}{c} \text{Mean} \\ \text{Distance} \\ \text{of} \\ \text{Particle} \\ [\bar{a}(\text{nm})]^{\text{f}} \end{array}$	$egin{array}{c} { m Corrected} \ { m Mean} \ { m Pore} \ { m Radius} \ (ar r_{ m cor})^{ m g} \end{array}$
Toluene (Inert Medi	um)							
45.20	$1.0850 \\ 1.4520$	$0.917 \\ 0.775$	$652.5 \\ 513.4$	$49.75 \\ 45.57$	$2.811 \\ 3.019$	$4.237 \\ 4.024$	$\begin{array}{c} 1.897 \\ 2.038 \end{array}$	$\begin{array}{c} 0.318\\ 0.302 \end{array}$	$1.579 \\ 1.736$
Xylene (I	nert Mediu	m)							
45.60	$1.0850 \\ 1.4531$	0.796 0.690	$525.2 \\ 472.1$	$\begin{array}{c} 46.35\\ 42.80\end{array}$	$3.031 \\ 2.923$	$5.265 \\ 4.373$	2.046 1.973	0.395 0.328	$\begin{array}{c} 1.651 \\ 1.645 \end{array}$

Table VI Some Relationships Derived for Calculation of the Mean Pore and Particle Radius of Poly(ethylstyrene-co-divinylbenzene) Networks, Which Contain 61.3% DVB

^a Pore volume (PV) = $1/d_{ap} - 1/d_{sp}$. ^b Percentage of porosity = $100(1 - d_{ap}/d_{sp})$.

^d $R = 3 \times 10^{3}/d_{sp} \cdot S.$ ^e $\bar{r} = C \cdot 10^{3}$ PV/S (C = 1.35).

 ${}^{\rm f}\bar{a} = 0.255 \times 10^{3} / d_{
m sp} \cdot {
m S}.$

$$r_{\rm cor} = r - a.$$

 $^{^{\}rm c}r = 2.10^{3}$ PV/S.



Table VII Main Known Constituents Filtrates

Cephalosporine C belongs to the cephalosporine family, whose structure is given in Table VII.

The experiments, whose curves are plotted in Figure 4, present a large range of the adsorption capacities for Cephalosporine C.

The maximum amount of Cephalosporine C (curve 2) is given by a chlorinated sample, which contains 47.13% Cl, an average pore diameter of 6.63 nm, and 61.3% DVB.

Generally, the chlorination degree and its average pore diameter determine the adsorption capacity of the adsorbent, for the same crosslinking percentage. The experimental results concerning the adsorption capacity of Cephalosporine C prove the relationships that exists between the synthesis parameters of adsorbents (Fig. 4; Table VI).

The synthesized sample, which was tested, retained a large amount of Cephalosporine C (16.00-32.00 g/L), and the elution of CC was complete after a few hours (98.0-99.0% output).

The elution curves showed a quite narrow distribution without tails, but the recovering of CC depends on the adsorbent features (crosslinking and chlorination percentages).

Samples of adsorbent kindly supplied by Rohm and Haas Co. of USA (Amberlite XAD-4) and Mitsubishi Kasai Corp. of Japan (adsorbents type SP-206 and SP-207) were used as standard adsorbents for Cephalosporine C, applying the same conditions. Similar values of the adsorption capacity for the SP-206/207 sample (27–39 g CC/L were recorded, while the Amberlite XAD-4 sample adsorbed only 7.0–8.0 g CC/L. The chlorinated samples exhibit a good mechanical strength because, after 100 cycles (adsorption–desorption), the beads do not present any cracks.



Figure 4 Elution curves of Cephalosporine C from the chlorinated P(EtSt-co-DVB) sample with various chlorination degrees (curves: 1–43.5, 2–47.12, 3–41.05, 4–39.15, and 5–32.0% Cl).

CONCLUSIONS

The chlorination reaction of poly(ethylstyrene-codivinylbenzene) in the presence of anhydrous $FeCl_3$ led to polar adsorbents, which contained about 45.0% chlorine, that is, almost two chlorine atom/structural unit. The reaction rate depended on temperature and time.

The synthesized adsorbents exhibit a high rate of the adsorbtion capacity of CC (36 g/L), similar to the adsorbents, SP-206/207, made by Mitsubishi Kasai Corp. of Japan.

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