Polymer Vol. 39 No. 24 pp. 6041–6048, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00057-3

Styrene–divinylbenzene copolymers post-crosslinked with tetrachloromethane

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(Received 17 October 1997; revised 22 December 1997; accepted 7 January 1998)

This paper describes a method of preparation of permanently porous functionalized styrene copolymers by the chemical transformation of gel or macroporous styrene–divinylbenzene copolymers. As a crosslinker, tetrachloromethane was used in the presence of a Friedel–Crafts catalyst (aluminium or ferric chloride). By the modification of the macroporous copolymers, very high surface area resins, equivalent to Davankov's hypercrosslinked resins, have been obtained. The post-crosslinked polymers show high specific surface areas, a narrow distribution of small pores, and good mechanical stability and thermal resistance. The modification of the gel-like copolymers, because of the slow reaction rate and restricted reagent diffusion, produced copolymers with only very modest surface areas. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: post-crosslinking; macronetwork; styrene–divinylbenzene copolymers)

INTRODUCTION

At present, permanently porous copolymers, *i.e.* copolymers that retain porosity also in the dry state, are prepared by suspension radical copolymerization, post-crosslinking of the copolymer, or, possibly, by a combination of both methods.

In 1963, Millar *et al.*[1] described the preparation of porous materials by suspension copolymerization of styrene with divinylbenzene in the presence of an inert solvent. The porous structure, characterized by the specific surface area and pore volume, varies over a wide range with the amount of crosslinker used and the type of inert solvent. By suspension copolymerization, polymer sorbents with a maximum specific surface area of $750\,m^2\,g^{-1}$ can be prepared. High surface area macroporous resins are produced by many manufacturers worldwide and are finding increased application as sorbents for separation or analytical purposes. Macroporous copolymers were mainly used in processes in the form of a fixed or fluidized bed, because these resins are adversely affected by mechanical attrition when stirred. Their mechanical properties worsen with increasing porosity.

Polymers in which linear polymer chains are linked by alkylation following polymerization are termed post-crosslinked, or macronetworks[2], isoporous[3] or hypercrosslinked[4]. Hypercrosslinked polymers were obtained by crosslinking linear polystyrene or its macroporous copolymers in the swollen state with a bifunctional reagent. Typical crosslinkers[5–8] are chloromethyl methyl ether, α,α'-dichloro-*p*-xylene[9–11], 4,4′-bis(4-chloromethyl)-biphenyl, dimethylformal, tris(chloromethyl)mesitylene, and 1,4-bis(4-chloromethylphenyl)butane. Due to their lower volatility[13] and their being less hazardous compared with chloromethyl methyl ether, chloromethyl ethyl ether and polyfunctional alkylation agents such as chloromethyl polyethers[12], polyfunctional acylation agents and sulfur halogenides were used for the crosslinking of polystyrene. Styrene–vinylbenzyl chloride[14–16] copolymers react in the presence of a Friedel–Crafts catalyst to give permanently porous structures with a specific surface area of $691\,m^2\,g^{-1}$. Of the Friedel–Crafts catalysts, stannic and ferric chlorides as well as titanium tetrachloride were used. Ando *et al.*[17] described a method of preparation of porous polymers by treating free double bonds of styrene–divinylbenzene copolymer with a small amount of a Friedel–Crafts catalyst in a solvent. The polymers prepared by the post-crosslinking of linear polymers form flexible, three-dimensional networks capable of absorbing substantial amounts of solvents[18].

The aim of the polymer post-crosslinking method described in the present paper was to prepare more regular networks in the whole of the polymer bulk compared to a non-even crosslink distribution in polymers obtained by the copolymerization of monomers with crosslinkers. Using a post-crosslinking reaction, phase separation occurs under the formation of a permanently porous structure with specific surface areas greater than $1000\,m^2\,g^{-1}$. Commercially available are hypercrosslinked polymers with the trademarks Lewatit EP63, Purolite MN100, MN150, MN200, Diaion HP 10, HP 20, HP 40, and HP 50, which are used exclusively as sorbents.

In this paper, the post-crosslinking of styrene–divinylbenzene copolymers is described using tetrachloromethane as crosslinking agent.

EXPERIMENTAL

Materials

A gel copolymer was prepared as follows. A reaction mixture of styrene (200 ml) with technical-grade divinylbenzene (0.84 ml) and dibenzoyl peroxide (2 g) in the reaction vessel of a Buchi reactor (Switzerland) was flushed with nitrogen. The reactor was then filled with 1600 ml of an

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aqueous solution of NaCl (10 wt%) and starch (4 wt%), and nitrogen was introduced for another 10 min. A suitable stirring rate was selected (530 rev min^{-1}) and the polymerization process was performed under laboratory conditions for 10 min and at 90°C for 20 h. After the completion of the reaction, the mixture was allowed to cool for about 2 h with stirring, soluble components were removed from the polymer by repeated decantation with water and alcohol, and the residue was dried in a vacuum dry-box at 60°C for 24 h. The fractions 0–0.09 mm, 0.40–0.50 mm and 0.5–1.00 mm were obtained by sieving.

A macroporous copolymer was prepared by the suspension copolymerization of technical-grade divinylbenzene in toluene as an inert solvent. Technical-grade divinylbenzene (120 ml) was mixed with benzoylperoxide (1 wt%) and toluene (732 ml) as the inert phase. The reactor vessel was filled with this mixture and an aqueous phase containing 10 wt% of NaCl and 4 wt% of starch was also added. Nitrogen was bubbled through the mixture for 10 min. After selecting the required stirring rate (624 rev min^{-1}), the mixture was polymerized at 85°C for 9 h. After completion of the polymerization, the mixture was cooled for 2 h and the polymer was decanted three times, with water, methanol and water, respectively. After drying under vacuum, the product was fractionated on sieves. The particles of size 0.50–0.80 mm had a specific surface area of 690 $m^2\ g^{-1}$, a pore volume of 1.252 ml g^{-1}, and a 25 mol% double bond content.

Toluene, tetrachloromethane and 1,2-dichloroethane, both of analytical grade, were distilled before use. The anhydrous aluminium and ferric chlorides were pure chemicals.

Post-crosslinking of polymers

A mixture of 0.256, 0.64 or 1.28 g of anhydrous $AlCl_3$ or $FeCl_3$, and 0.83, 0.93, 1.02, 1.11, 1.30 or 1.85 ml of freshly distilled tetrachloromethane was cooled to 0–5°C. After 1 h of stirring, the temperature rose to 10–15°C and 2.09 g of the gel or macroporous copolymer pre-swollen in 15 ml of 1,2-dichlorethane for 25 h were added. During stirring, the mixture was cooled to −20°C and was stirred for another 4 h at that temperature. After increasing the temperature to 10–15°C, the mixture was stirred for another 3, 6, 24, or 72 h. The polymer was filtered off and washed successively with 75 parts of 1,2-dichloroethane, ethanol and distilled water, and decanted with water. The remainder of the reactive chlorine-containing groups were hydrolyzed by heating with water at 100°C for 4 h, if not stated otherwise. The modified polymer was washed with water and dried under vacuum at 1.3 kPa and 80°C.

Characterization of polymers

The composition of the synthesized polymers was determined by elemental analysis and i.r. spectroscopy using the KBr technique on a FT-i.r. Perkin-Elmer 1000 PC

Table 1 Effect of the catalyst/monomer unit ratio on the crosslinking reaction and the phase separation

$AlCl_3$/monomer unit ratio	Cl (%)	S_g^a ($m^2\ g^{-1}$)	Solvent regain (ml g^{-1})		Porosity[b] (%)	
			H_2O	EtOH	H_2O	EtOH
0.50	2.56	49.7	0.13	1.54	12.5	62.9
0.25	2.34	29.0	0.15	0.84	14.2	48.0
0.10	1.91	5.1	0.12	0.33	11.7	26.6

Conditions: gel-like polymer, 0.3% DVB; reaction time, 24 h; molar ratio of CCl_4/monomer unit, 0.6

[a] Specific surface area

[b] By solvent regain measurement, Porosity $= V_g/(V_g + (1/d))$, where V_g is the solvent regain and d is the true density of the polymer

Table 2 Effect of the grain size of the gel-like polymer on the crosslinking reaction and the phase separation

Grain size (μm)	Cl (%)	S_g^a ($m^2\ g^{-1}$)	Solvent regain (ml g^{-1})		Porosity[b] (%)	
			H_2O	EtOH	H_2O	EtOH
0–90	1.40	258	0.42	2.14	31.7	70.2
400–500	1.15	138.2	0.35	1.94	27.6	68.1
500–1000	1.67	126.9	0.26	2.18	22.0	70.5

Conditions: gel-like polymer, 0.3% DVB; reaction time, 24 h; molar ratio of CCl_4/monomer unit, 0.5; molar ratio of catalyst ($AlCl_3$)/monomer unit, 0.6

[a] Specific surface area

[b] By solvent regain measurement, Porosity $= V_g/V_g + (1/d)$, where V_g is the solvent regain and d is the true density of the polymer

Table 3 Content of reactive groups in the post-crosslinked polymer

DVB (wt%)	CCl_4/monomer unit	$AlCl_3$/monomer unit	Reaction time (h)	Total Cl (mmol g^{-1})	Hydrolyzable Cl	
					(mmol g^{-1})	(%)[a]
60	0.5	0.5	6	0.71	0.12	17
	0.5	0.5	6	0.77	0.13	16
0.3	0.6	0.5	24	0.74	0.26	28
	0.6	0.5	24	0.76	0.21	28
60	0.6	0.5	3	0.80	0.26	32
	0.6	0.5	3	0.78	0.26	33

[a] Of total chlorine

Table 4 Mechanical and thermal properties of copolymers

Adsorbent	Structure	Penetration modulus (MPa)	Maximum depolymerization rate temperature (°C)
Sample 193[a]	Post-crosslinked PST	1050	451
Sample 301[b]	Post-crosslinked PST	1289	470
Sample 271[c]	Post-crosslinked PST	1350	457
Starting polymer	Macroporous ST-DVB	748	350
Sample G-5[d]	Macroporous GMA-EDMA	61	250

[a] Gel-like copolymer crosslinked with chloromethyl methyl ether
[b] Macroporous copolymer crosslinked with carbon tetrachloride
[c] Gel-like copolymer crosslinked with carbon tetrachloride
[d] Macroporous copolymer of 2,3-epoxypropyl methacrylate and ethylene dimethacrylate (95 wt%)

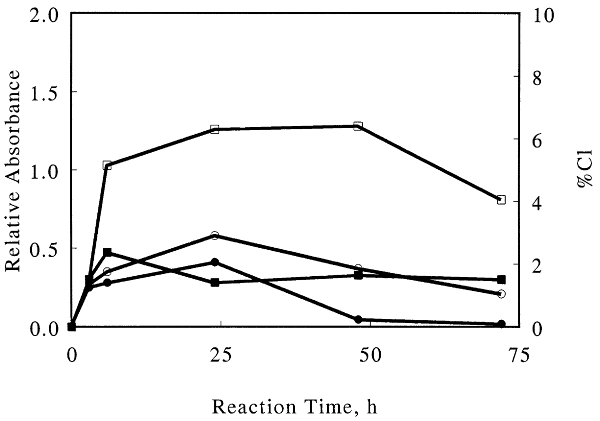


Figure 1 Effect of reaction time in the reaction of the gel-like polymer on the relative i.r. absorbances (○) A_{para}/A_{CH_2}, (●) A_{meta}/A_{CH_2}, (□) A_{pCO}/A_{CH_2}, and (■) the chlorine content. (Polymer, 0.3% DVB; $AlCl_3$/monomer unit ratio, 0.5; molar ratio of CCl_4/monomer unit, 0.6)

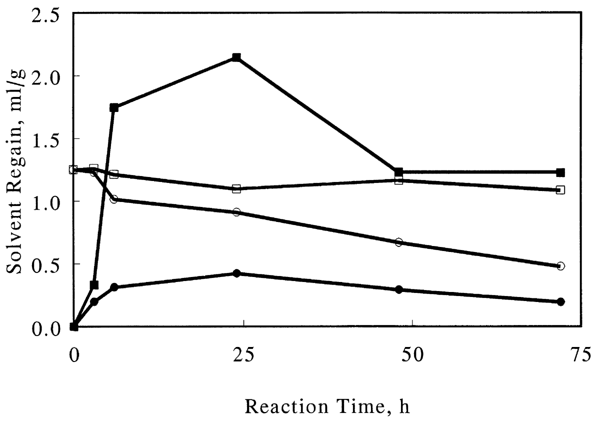


Figure 3 Effect of reaction time on (○,●) water and (□,■) ethanol regain of the (●,■) gel-like and (○,□) macroporous copolymers. (Gel-like polymer, 0.3% DVB; macroporous polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5; molar ratio of CCl_4/monomer unit, 0.6)

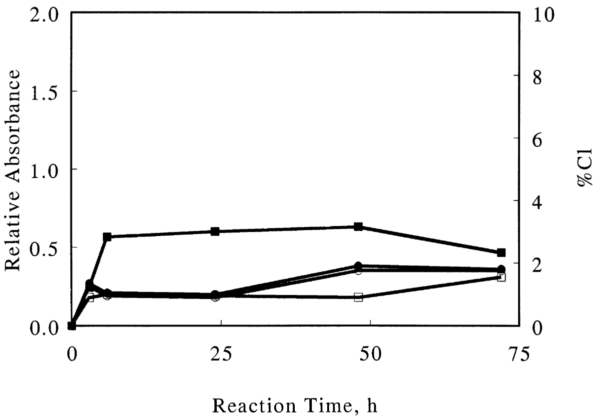


Figure 2 Effect of reaction time in the reaction of the macroporous polymer on the relative i.r. absorbances (○) $Apara/A_{CH_2}$, (●) A_{meta}/A_{CH_2}, (□) A_{CO}/A_{CH_2}, and (■) the chlorine content. (Polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5; molar ratio of CCl_4/monomer unit, 0.6)

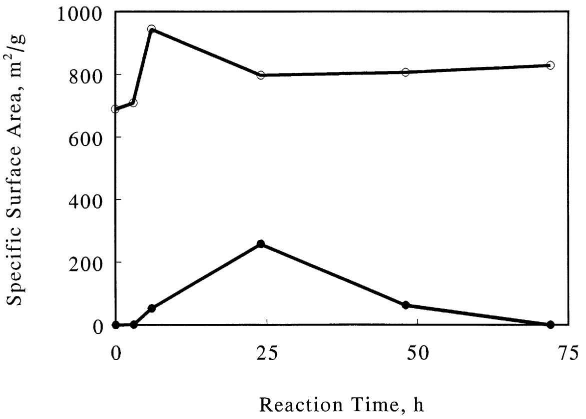


Figure 4 Effect of reaction time on the specific surface area of the (●) gel-like and (○) macroporous copolymers. For conditions, see *Figure 3*

spectrometer. The product was characterized by the bands of para- and meta-disubstituted aromatic rings and C=O groups at 790 cm^{-1}, 840 cm^{-1}, and 1660 cm^{-1}, respectively. The band intensities were related to the intensity of the CH_2 band at 2940 cm^{-1} used as an internal standard. The content of hydrolyzable chlorine was determined argentometrically in samples hydrolyzed by boiling with 1 M NaOH for 1 h.

The water and ethanol regains[19] were determined by the centrifugation technique. The specific surface area was calculated by use of the three-point BET equation from the dynamic sorption and desorption of nitrogen measured on the Quantasorb apparatus (Quantachrom Co., USA). The thermal stability of the samples was followed by d.t.g. on a Du Pont instrument with a heating rate of 10°C min^{-1}.

The total content of pendant vinyl groups in the network was estimated from high-resolution solid-state ^{13}C n.m.r. spectra[20].

The dependence of the mechanical stress on pressure was measured with dry individual particles on an Instron TM instrument at the laboratory temperature. From that, the penetration moduli of samples were evaluated.

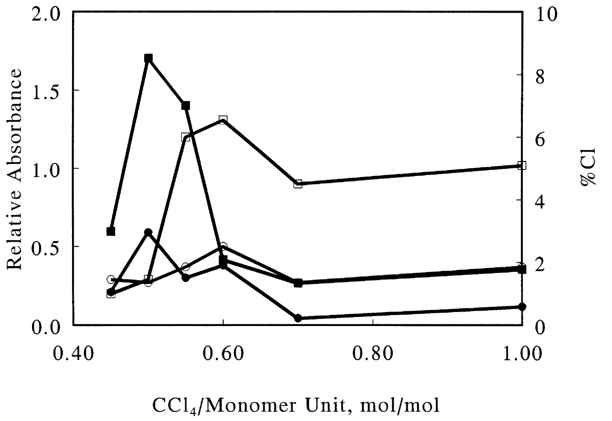


Figure 5 Effect of the CCl_4/monomer unit molar ratio for the gel-like polymer on the relative i.r. absorbances (○) A_{para}/A_{CH_2}, (●) A_{meta}/A_{CH_2}, (□) A_{CO}/A_{CH_2} and (■) the chlorine content. (Polymer, 0.3% DVB; $AlCl_3$/monomer unit ratio, 0.5)

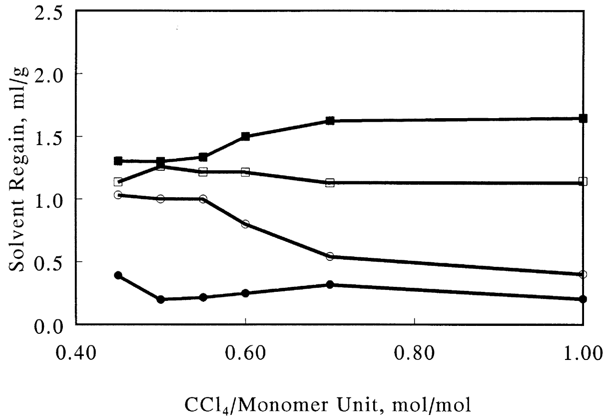


Figure 6 Effect of the CCl_4/monomer unit ratio on the (○,●) water and (○,●) ethanol regain of the (●,■) gel-like and (○,□) macroporous copolymers. (Gel-like polymer, 0.3% DVB; macroporous polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5)

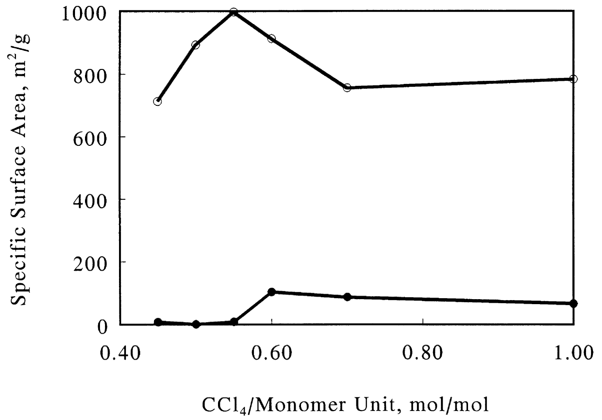


Figure 7 Effect of the CCl_4/monomer unit molar ratio on the specific surface area of the (●) gel-like and (○) macroporous copolymers. (Gel-like polymer, 0.3% DVB; macroporous polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5)

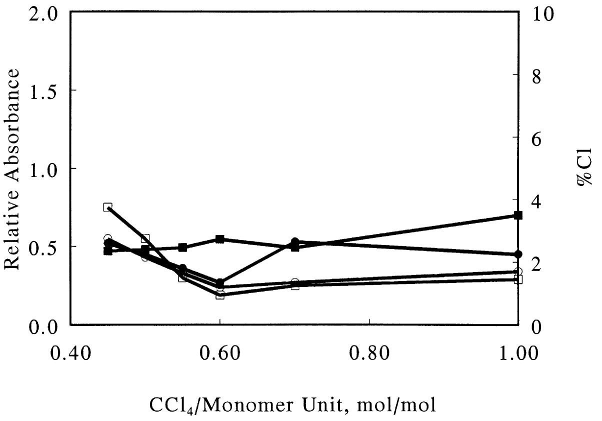


Figure 8 Effect of the CCl_4/monomer unit molar ratio of the macroporous polymer on the relative i.r. absorbances (○) A_{para}/A_{CH_2}, (●) A_{meta}/A_{CH_2}, (□) A_{CO}/A_{CH_2}, and (■) the chlorine content. (Polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5)

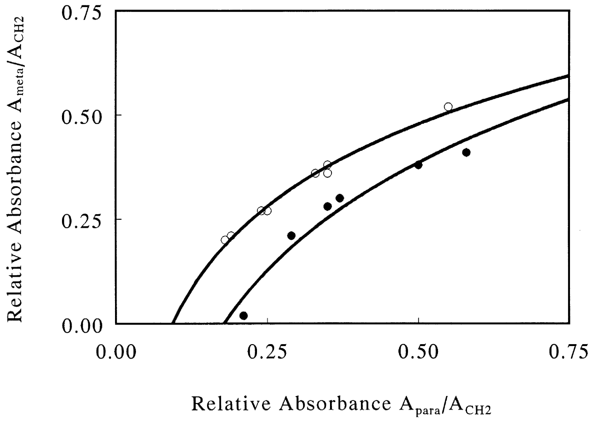


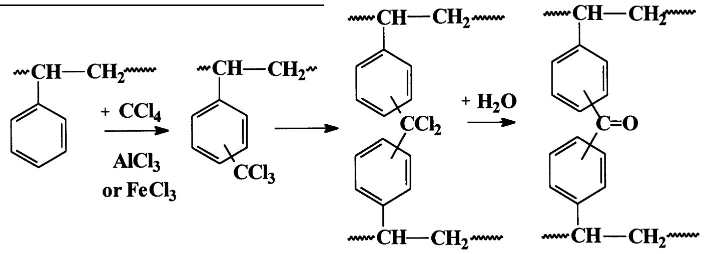
Figure 9 Comparison of the relative i.r. absorbances A_{para}/A_{CH_2} and A_{meta}/A_{CH_2} of the (●) gel-like and (○) macroporous copolymers. (Gel-like polymer, 0.3% DVB; macroporous polymer, 60% DVB; $AlCl_3$/monomer unit ratio, 0.5;, molar ratio of CCl_4/monomer unit, 0.6)

The results are summarized in *Tables 1–4* and *Figures 1–11.*

RESULTS AND DISCUSSION

Post-crosslinking of polymers

The method of preparation of permanently porous copolymers used is based on the reaction of styrene–divinylbenzene copolymers with tetrachloromethane (molar ratio of reagent to monomer unit, 0.45–1) in the presence of a Friedel–Crafts catalyst, according to the follwing reaction scheme.



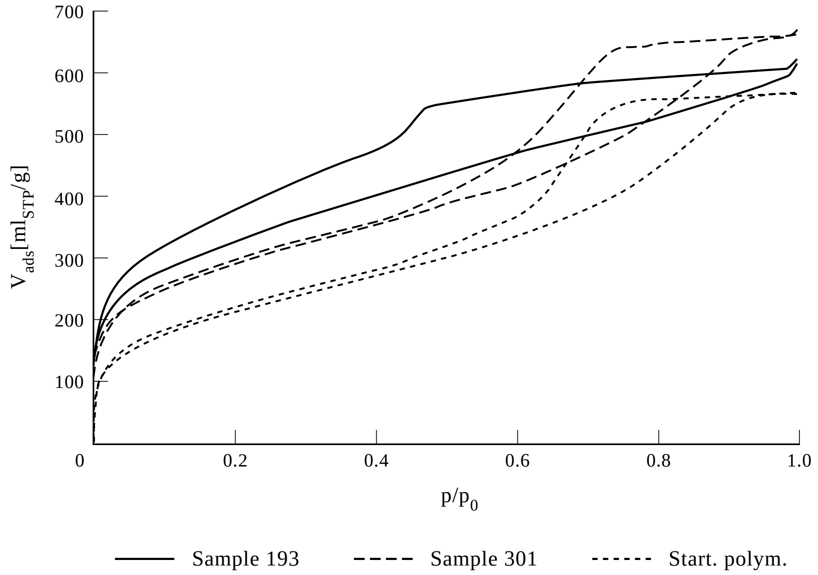


Figure 10 Nitrogen adsorption isotherm of (●) post-crosslinked copolymer (sample 301) and (○) starting macroporous copolymer

As starting materials for subsequent transformations, gel and macroporous styrene–divinylbenzene copolymers with 0.1–52 wt% of the crosslinker were used. Anhydrous aluminium or ferric chloride was used as the Friedel–Crafts catalyst in molar ratios of catalyst to monomer unit of 0.1–0.5. The reactions were performed in 1,2-dichloroethane at −20 to −30°C for 3–72 h. If desirable, the hydrolysis or aminolysis of dichloromethylene or trichloromethyl groups followed.

The course of the reaction proposed in the scheme was confirmed by elemental analysis and from i.r. spectra of the product; it is in accordance with the course of the reaction of corresponding low-molecular-weight compounds[21] (*Figures 1* and *2*). Also, the bands of the meta- and especially the para-disubstituted aromatic rings at 790–830 cm^{-1} are substantially more intense in the macroporous copolymer. The increase in relative absorbances amounts to 5–28%. In the macroporous polymer, in addition to a considerable content of carbonyl groups in the gel copolymer, only a low content of carbonyl groups was found, as determined from the i.r. band at 1560 cm^{-1} in the alkaline-hydrolyzed polymer. The crosslinking reaction is both intramolecular and intermolecular, *i.e.* it occurs on the same polymer chain or between two different chains. The intramolecular crosslinks do not restrict the swelling of the polymer, as follows from a relatively high degree of swelling in some solvents, such as 1,2-dichloroethane and ethanol (*Figure 3*).

The gel copolymer with a crosslinker content of 0.3 wt% and the macroporous copolymer were more appropriate starting polymers for post-crosslinking than the gel copolymer with 1 and 10 wt% of crosslinking agent, because the latter showed more substantial phase separation manifested by an increase in specific surface area values.

Macroporous styrene–divinylbenzene copolymers contain considerable amounts of free double bonds (from 25 to 45 mol%) which were used in crosslinking by the Friedel–Crafts reaction[17]. The starting gel-like copolymer, however, does not contain any free double bonds. Hence, the

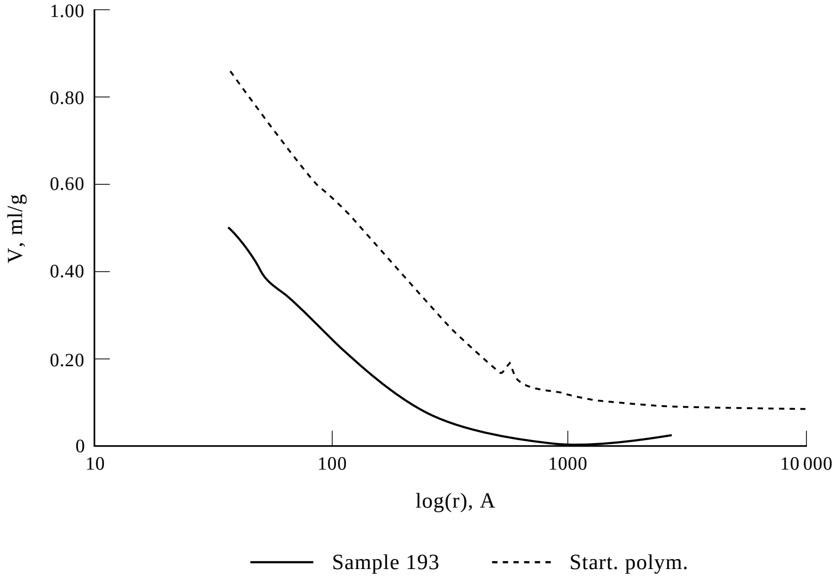


Figure 11 Mercury porosimetry of (●) post-crosslinked copolymer (sample 301) and (○) starting macroporous copolymer

crosslinking mechanism cannot be explained in this case by the reaction of free double bonds, but only in terms of the above scheme.

Effect of reaction conditions on polymer transformation

There exist certain differences in the courses of the reactions of gel and macroporous copolymers, depending on the effect of the conditions of the crosslinking reaction on the transformation. In the case of the gel copolymer, the reaction conversion increases, as measured by the relative content of para-disubstitution and C=O groups (*Figure 1*). The increasing regain of the solvent (*Figure 3*) and the specific surface area values (*Figure 4*) correspond to the separation of the polymer phase. As a consequence of the presence of intramolecular bonds, regain of ethanol, which swells the hypercrosslinked polymer, increases. In the case of the macroporous copolymer, there exist maxima in the dependences of the relative contents of both paradisubstitution and C=O groups on the reaction time (*Figure 2*). Also, the specific surface area (*Figure 4*) and the solvent regain values (*Figure 3*) display maxima after 6 h of reaction and thus confirm the assumption that the degree of crosslinking also reaches a maximum.

The maximum in the ethanol regain for the gel resin and the subsequent fall-off with time (*Figure 3*) could be associated with remote intermolecular crosslinking which would restrict the macroscopic swelling in contrast to local crosslinking. Another reason might be a reverse course of the alkylation reaction because the used catalyst also acts in this direction. A reverse reaction is more significant with the macroporous copolymer because of the high degree of the starting crosslinking which, among other things, hinders the diffusion of the reagent into the polymer bulk. Owing to the heterogeneity of the subsequent chemical conversion, the reverse reaction — dealkylation — can occur in the surface layers.

In the initial experiments, the molar ratio of reagent to monomer unit was kept at 0.5, because at this ratio the reaction with chloromethyl methyl ether[4], transalkylation of the polymer, cannot occur in the first step of the reaction, so that the residual reactive sites are then free for post-crosslinking. Tetrachloromethane, in contrast to chloromethyl methyl ether, reacts more slowly and shows a lower reaction conversion: para-disubstitution and also the content of C=O groups continue to increase even at molar ratios of reagent to monomer unit of above 0.5 (*Figure 5*). In the same direction, the ethanol regain (*Figure 6*) and the specific surface area values also continue to increase (*Figure 7*).

The degree of para-disubstitution and the C=O group content in the modified macroporous copolymer (*Figure 8*) reach maximum values at a molar ratio of reagent to monomer unit of 0.6. This indicates that a limiting value of the degree of crosslinking was reached. Beyond those maxima, para-disubstitution decreases, but the chlorine content continues to increase, which under these conditions can be accounted for by the reverse course of the reaction in which some crosslinks are cleaved in the surface layers of the particles. The catalyst used also catalyzes the reverse reaction with cleaving of the crosslinks. This is also confirmed by increasing water and ethanol regains.

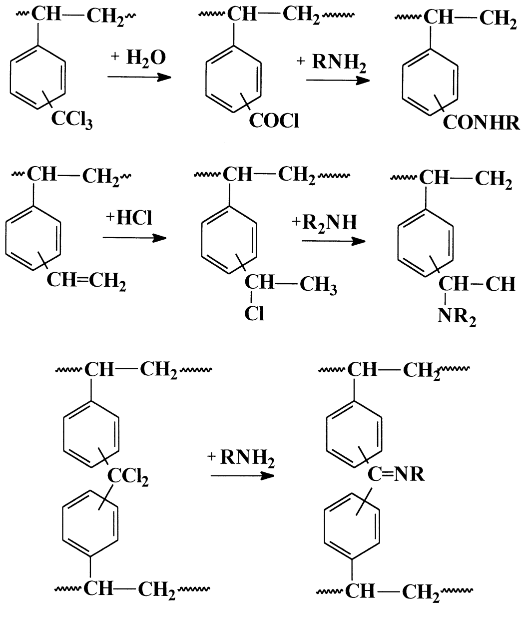
In the case of the gel and macroporous copolymers, two different dependences (*Figure 9*) of the relative C=O group content and the meta-disubstitution on the para-disubstitution were observed. This confirms that in macroporous highly crosslinked copolymers, meta-disubstitution is sterically hindered.

The crosslinking reaction is, to a great extent, affected by the concentration of the catalyst, $AlCl_3$ (*Table 1*), and the size of the polymer particles (*Table 2*). The size effect can be explained by the hindered diffusion of the reagent into the polymer bulk.

With dioxane as solvent and $FeCl_3$ as catalyst, or other potential crosslinking agents such as 1,2-dichloroethane, dibromomethane and dichloromethane, the reaction becomes very slow or does not occur at all.

Reactive groups

As confirmed by the analysis of total and hydrolyzable chlorine, the product after the Friedel–Crafts reaction contains, in addition to the chlorine firmly bonded to the aromatic rings, reactive aliphatic bonded chlorine also (*Table 3*). The larger part of the chlorine is bonded to the aromatic rings. In the transformation of the macroporous copolymer, the content of aliphatic bonded chlorine increases to up to 30% of the total chlorine. This can be explained by steric hindrance: for a more crosslinked starting copolymer, it may be difficult to adopt an aromatic conformation appropriate for the crosslinking reaction. In the copolymer crosslinked to a higher degree, the content of reactive groups increases only a little with reaction time. The amount of tetrachloromethane used in the reaction has also a small effect. The reactive, aliphatic bonded chlorine can be used for further transformation. The dichloromethylene, trichloromethyl or chloroethyl groups that are possibly present can be hydrolyzed or aminolyzed in the next step; at that, functional groups are introduced into the polymer, as follows from the reaction scheme.



Reactions of the hypercrosslinked unhydrolyzed polymer with primary, secondary and tertiary amines were attempted. The starting substances were derivatives of the macroporous copolymer, which had higher contents of hydrolyzable chlorine than gel polymer crosslinked to a lower degree. The reaction with diethylenetriamine proceeded with a conversion of 80% (relative to the chlorine content in the copolymer) and the reaction with triethanolamine only to 33%, apparently due to a higher steric hindrance.

The reaction of the copolymer with the amines was also followed by i.r. spectroscopy. The spectral bands due to the meta- and, in particular, the para-disubstituted benzene rings at 790 and 830 cm^{-1} were considerably more intense after the reaction of the macroporous copolymer. The increase in intensity was from 5 to 28%. The carbonyl group content increased analogously (by 28%) but the hydroxy group content was lower. By sulfonation of the hypercrosslinked copolymer with chlorosulfonic acid, a polymer with 2–7 mmol SO_3H groups per gram was synthesized.

Porous structure

In post-crosslinking, the short dichloromethylene bridges introduced reinforce the structure of the polymer, and separation of the polymer phase occurs. A heterogeneous, permanently porous structure is formed which is stable in the swollen state as well as in the dry state. As follows from the nitrogen adsorption isotherm (*Figure 10*) and mercury porosimetry measurements (*Figure 11*), such a permanently porous structure contains, besides macropores and mesopores, an increased amount of micropores, which are needed for the sorption of small organic molecules. By post-crosslinking, copolymers can be prepared with specific surface area values around 1000 $\mathrm{m}^2\,\mathrm{g}^{-1}$ and even higher. In consequence of such high specific surface values, phase separation in the polymer must occur at a molecular level, because the specific surface area is indirectly proportional to the size of the microparticles forming the porous structure

$$R = 3000/(S_g d)\ (\mathrm{nm})$$

where R is the radius of the microparticles, S_g is the specific surface area ($\mathrm{m}^2\,\mathrm{g}^{-1}$), and d is the true density of the polymer ($\mathrm{g\,ml}^{-1}$).

From the nitrogen adsorption isotherm measurement under static conditions (*Figure 10*) the micropore content in this type of copolymer was evaluated. The micropore content in the post-crosslinked macroporous copolymer is 0.6 $\mathrm{ml\,g}^{-1}$, which is twice that of the starting macroporous copolymer. It also follows from *Figure 10* that the hysteresis loop (which confirms some restriction during the nitrogen desorption process), is more important in the samples obtained by transformation of the gel-like polymer (sample 193) than by transformation of the macroporous copolymer (sample 301). The mercury porosimetry (*Figure 11*) data show the shifting of pore distributions to the smaller pores during the crosslinking reaction.

As follows from *Figures 4* and *7*, it is possible to prepare, by modification of the gel copolymers, products with specific surface areas up to 258 $\mathrm{m}^2\,\mathrm{g}^{-1}$. The modification reaction of the gel-like copolymer with tetrachloromethane in comparison with the chloromethyl methyl ether[4] reaction proceeds more slowly and with a side reaction; therefore only copolymers with very modest surface areas have resulted.

By modification of the macroporous copolymer, a product with specific surface area (*Figure 8*) up to 998 $\mathrm{m}^2\,\mathrm{g}^{-1}$ was obtained. The higher specific surface area values were reached after 6–24 h of reaction and at reagent/monomer unit ratios of 0.55–0.6.

From the viewpoint of the application of hypercrosslinked copolymers as sorbents, the specific surface area represented by the micropore content is a parameter that should be enhanced. Therefore, for the sorption of small molecules, polymers with high specific surface area values are required.

Other properties of hypercrosslinked copolymers

Hypercrosslinked copolymers show a high thermal stability. The weight loss at 300°C amounts to only 2%, and at 400°C it amounts to 6%. Their thermal stability, characterized by the temperature of the maximum rate of decomposition, in particular depolymerization[22], decreases in the order (*Table 4*)

$$\text{sample 301} > \text{sample 271} > \text{sample 193}$$
$$\gg \text{starting polymer} \gg \text{sample G} - 5$$

Good mechanical properties of hypercrosslinked copolymers permit their use in stirred reactors with fluidized beds. The penetration modulus (*Table 4*) measured with individual particles is 1000 MPa, *i.e.* about four orders higher than for the macroporous copolymer prepared by suspension copolymerization. Methacrylate copolymers (G-5) generally have a lower mechanical stability compared to styrene–divinylbenzene copolymers.

In comparison with macroporous copolymers, the hypercrosslinked copolymers prepared in this work have better mechanical properties and, in particular, abrasion stability, higher values of the specific surface area and a higher content of micropores and, as a consequence, higher sorption activity. When compared with active carbon, the advantage of using hypercrosslinked copolymers primarily lies in their mechanical properties and, in particular, in the low pressure drop obtained in columns. This is a consequence of the regular spherical shape of their particles, without powdery admixtures, and undiminished sorption activity.

The hypercrosslinked copolymers are characterized by a narrow distribution of small pores and by high values of the specific surface areas. This is why sorbents with a permanently porous structure are suited for sorption from the gas or liquid phase[23]. A relatively high micropore content in comparison with macroporous copolymers predestines the polymers for the sorption and separation of small molecules.

CONCLUSION

The method of preparation of porous sorbents described in the present work consists primarily of using tetrachloromethane, a less carcinogenic reagent, in the Friedel–Crafts-type reaction, leading to sorbents with the same properties as those using the carcinogenic chloromethyl methyl ether. In crosslinking, reactive groups are also introduced into the polymer, which can be used for subsequent transformations.

The described hypercrosslinked polymers with high specific surface areas can be used as sorbents, especially sorbents of organic substances from the gas and liquid phase. Due to their better mechanical properties, the polymers can be used in new types of absorbers with moving beds. They are particularly suitable for the sorption of organic substances from air, for example in paint shops, or for the sorption of organic substances from water, such as aromatic compounds, dyes, and surface-active substances. Their advantage also lies in possible regeneration by heating or by extraction with solvents.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge support for this work by grant no. 203/96/1388 from the Grant Agency of the Czech Republic.

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