Postcrosslinking of Macroporous Styrene–Divinylbenzene Copolymers via Pendant Vinyl Groups: Effect of the Starting Copolymers on the Pore Structure of the Postcrosslinked Products

CHUNCAI ZHOU, JUN YAN, ZHINONG CAO

Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, People's Republic of China

ABSTRACT: In the presence of anhydrous ferric chloride as a Friedel–Crafts catalyst, the postcrosslinking reaction of macroporous styrene–divinylbenzene (St–DVB) copolymers synthesized under different conditions was carried out with 1,2-dichloroethane as a solvent. Without an externally added crosslinking agent, the specific surface area and pore volume, for copolymers with different DVB isomers or different DVB contents after reaction, in most cases increased significantly, and the increase was found to be heavily dependent upon the amount of the pendant vinyl groups in the starting copolymers. These results further confirm the role of the pendant vinyl groups in creating new crosslinking bonds in addition to those created by a free-radical crosslinking reaction in the starting copolymers, and an alkylation reaction of the vinyl groups with neighboring aromatic rings is believed to dominate the course of the postcrosslinking at a relatively high level of the vinyl group contents. The synthesis conditions, including the *n*-heptane content in a mixed diluent and the amount of the diluent, under which the starting copolymers were synthesized, play an important role in the increase of the surface area and pore volume of the copolymers after postcrosslinking. The effect of these conditions is attributed mainly to the swelling ability of the starting copolymers thus obtained in the solvent used for reaction. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 1668–1677, 2002

Key words: styrene–divinylbenzene copolymers; postcrosslinking; pendant vinyl groups; specific surface area; pore volume

INTRODUCTION

Macroporous styrene–divinylbenzene (St–DVB) copolymers are prepared by suspension polymerization of St with DVB in the presence of an inert diluent which is monomer-miscible and essentially insoluble in water.[1] Relationships between the synthesis conditions and the pore structure of the copolymers have been extensively studied.[1–5] The amount of DVB and the type of the diluent were found to play an important role in the design of the pore structure, which is characterized by the specific surface area and porosity of the copolymers. Commercially available St–DVB copolymer adsorbents usually have a high surface area, sometimes up to 800 m²/g, as is the case with Amberlite XAD-4, which is synthesized with about 80% DVB as a crosslinking agent.[6]

It is known that the macroporous St–DVB copolymers can be used as a starting material for preparing "hypercrosssslinked" or "macronetted" adsorbents by postcrosslinking.[7,8] The procedure generally consists of a chloromethylation of the macroporous copolymer and a following heating of the swollen chloromethylated copolymer in the presence of a Friedel–Craft catalyst. In this way, methylene bridges between polymer chains form, so creating a new crosslinking in addition to that due to the DVB part of the starting copolymers. The postcrosslinked copolymer shows a greatly increased surface area and micropores. Besides chloromethyl methyl ether, tetrachloromethane was also used as a crosslinking agent recently for the postcrosslinking of macroporous St–DVB copolymers.[9] Products with a high surface area around 1000 m^2/g were obtained.

Different from the postcrosslinking procedure mentioned above, an approach for the postcrosslinking of macroporous St–DVB copolymers without an externally added crosslinking agent was also reported in recent years. Ando et al.[10,11] and Takayanagi and Teshima[12] reported a method to increase the surface area and the porosity of the macroporous St–DVB copolymers by treating the swollen copolymer with a Friedel–Crafts catalyst. As starting materials, the copolymers had a high degree of crosslinking, including those with up to 80% DVB. The postcrosslinked products with a surface area of 1000 m^2/g (ref. 11) or 1200 m^2/g (ref. 12) were used as adsorbents for the purification of cephalosporin C (ref. 11) or for removing the bitter component in fruit juice.[12] Meteyer[13] reported a method of treating macroporous St–DVB copolymers also using Lewis acid as a catalyst. But instead of a swelling solvent, the postcrosslinking reaction was performed in the presence of water or another nonswelling liquid. The surface area and porosity for a highly crosslinked St–DVB copolymer (80% DVB) increased apparently by this method. The postcrosslinking process disclosed by Lundquist and Langenmyr[14] involves the use of organic sulfonic acids as a catalyst; the starting copolymers based on 80% DVB contain at least 1.0 mmol/g pendant vinyl groups. The postcrosslinked products, called a "superlink (SL) macroporous adsorbent," have a high surface area and porosity and low levels of residual vinyl groups and are free of residual contaminants from a conventional Friedel–Crafts reaction.

Without an externally added crosslinking agent, the enhancement of the surface area and the porosity after reaction was believed to be caused by the postcrosslinking of pendant vinyl groups in the copolymers. Nyhus et al. studied the reaction between aluminum chloride and pendant vinyl groups recently, and a postcrosslinking of pendant vinyl groups by cationic polymerization was suggested to have taken place.[15,16]

In our experiments, the effect of the pendant vinyl groups in the postcrosslinking reaction was further confirmed. Since the synthesis conditions of the macroporous St–DVB copolymers play an important role in their structure and property, such as the content of the pendant vinyl groups, the swelling ability of the network, the stability of the pore structure, and so on, which must, in turn, strongly influence the postcrosslinking reaction, we investigated, in this article, the effect of the starting St–DVB copolymers synthesized under different conditions on the pore structure of these copolymers postcrosslinked using anhydrous ferric chloride as a catalyst and 1,2-dichloroethane as a solvent.

EXPERIMENTAL

Materials

Technical DVB, consisting of 59.4% DVB isomers with the rest being mostly ethyl vinyl benzene (EVB), and styrene (St) were treated with an anion-exchange resin to remove inhibitors before use. DVB (51.7 p-DVB and 46.3% m-DVB), p-DVB (100%), and m-DVB (98.4%) were obtained by the purification of technical DVB according to the method proposed by Popov and Schwachula.[17] Reagent-grade toluene, n-heptane, anhydrous ferric chloride, and so on were used as received.

Synthesis of Starting Copolymers

The macroporous St–DVB copolymers used subsequently for the postcrosslinking were synthesized by the suspension polymerization method with toluene or the mixtures of toluene and n-heptane as an inert diluent.[18] The monomers St and DVB were mixed together with the inert diluent to form an organic phase, in which the initiator, benzoyl peroxide, was added to the amount of 1 wt % of the monomers. The organic-phase mixture was then added in a 1:3 volume ratio to the aqueous phase containing 0.2 wt % hydroxyethyl cellulose. The polymerization with stirring was allowed to proceed at 80°C for 16 h. The

copolymers obtained were washed with water and acetone and then extracted with acetone in a Soxhlet apparatus. After final washing with water to remove the acetone from the swollen copolymer beads, the beads were dried at 80°C, and those with 20–50 mesh in size were used for further experiments. In any case, the DVB content was expressed as the weight percent of the total weight of the monomers and the dilution degree was expressed as the volume ratio of the diluent to the monomers. When the mixed diluent of toluene and n-heptane was used, the n-heptane content was expressed as the volume percent of the total volume of the mixed diluent.

Postcrosslinking of Copolymers

In a typical experiment, 10 g of the macroporous St–DVB copolymer beads were fully swollen in 50 mL of 1,2-dichloroethane. After that, 1.5 g of anhydrous ferric chloride was added and the reaction, with stirring, was carried out at 80°C for 8 h. The copolymers after reaction were washed by acetone and water and dried at 80°C to obtain products with a light yellow color.

Characterization

The apparent density (d_a) of the copolymers in the dry state was determined by an improved mercury pycnometric method as described in our previous article, and the relative error of the measurement was less than 1%.[19] The true density (d_t) was assumed to be equal to the homogeneous St–DVB copolymers prepared beforehand from monomers containing various amounts of DVB.[20] The pore volume (V_p) was then calculated using the equation

$$V_p = 1/d_a - 1/d_t$$

The specific surface area (S) of the copolymers was determined by a conventional nitrogen adsorption BET technique using an ST-03 instrument. IR spectra of KBr pellets of the carefully ground copolymer beads were recorded on a Nicolet 670 spectrometer. The peaks at the following bonds: 1630, 1510, 990, and 795 cm^{-1} and so on, were used for calculation of the amount of the pendant vinyl groups in the copolymers, which will be detailed later.

RESULTS AND DISCUSSION

Pendant Vinyl Groups in Starting Copolymers

It has been known for many years that there is a large difference in the reactivity of the two DVB vinyl groups and a considerable amount of the second vinyl groups remains unreacted at the end of the copolymerization of St with DVB in some preparation conditions.[21] The level of residual (or pendant) vinyl groups could be quantified, for example, by using IR[22,23] or solid-state ^{13}C-NMR[24] spectroscopy and by bromination of the copolymers.[23] Hubbard et al. reported that Amberite XAD-4 had a vinyl content of 29–41% calculated from FTIR spectra[22]; Nyhus et al. mentioned that the vinyl content determined by the IR technique for polymers prepared by pure p-DVB and m-DVB with toluene as a diluent was 51.8 and 36.2%, respectively, and the vinyl content seemed to be independent of the diluent.[23]

We used FTIR spectra to quantify the relative amount of pendant vinyl groups in the St–DVB copolymers prepared under different conditions. On the basis of the technique developed by Bartholin et al.,[25] and referring to the method of Hubbard et al.,[22] the content of vinyl groups (X_{vb}, mol % of double bonds) is calculated by

$$X_{vb} = \frac{(A + B)}{2(C + D + E)} \times 100\%$$

where $E = (E_1 + E_2 + E_3)/3$, and peak heights at various bands multiplied by their extinction coefficients give A, B, C, D, E_1, E_2, and E_3. The vinyl peaks are at 1630 cm^{-1} (A) and 990 cm^{-1} (B); the $para$- and $meta$-disubstituted phenyl ring peaks at 1510 cm^{-1} (C) and 795 cm^{-1} (D), respectively; and the monosubstituted phenyl ring peaks at 1493 cm^{-1} (E_1), 1028 cm^{-1} (E_2), and 760 cm^{-1} (E_3). C, D, and E account for all the repeat units in the St–DVB copolymers.

The vinyl group content in mmol/g is then calculated from the X_{vb} and the average molecular weight per repeat unit (avg. MW)[22]:

$$\text{mmol } VB/g = (X_{vb}/\text{avg. } MW) \times 10$$

and the degree of crosslinking (X_{Cl}) is calculated by

$$X_{Cl} = \% \, DVB - X'_{vb}$$

where $X_{vb}{}'$ is the vinyl content in weight percent and can be obtained by converting the value of the vinyl content in mmol/g.

Table I shows the vinyl group content of St–DVB copolymers (60% DVB) synthesized with different DVB isomers, and toluene was used as an

Table I   Vinyl Group Content of St–DVB Copolymers (60% DVB) with Different DVB Isomers

| DVB Isomers | Vinyl Group Content | | Conversion[a] (%) |
	X_{vb} (%)	mmol/g	
p-DVB	26.4	2.21	52.0
p-, *m*-DVB	18.4	1.40	69.6
m-DVB	13.8	1.15	75.0

The copolymers were synthesized in the presence of toluene as an inert diluent at a fixed dilution degree of 2.0.

[a] Conversion of second double bonds.

inert diluent at a dilution degree of 2.0. It is clear that the vinyl content is much higher in the *p*-DVB-based copolymer than in the *m*-DVB based copolymer. The theoretical content of pendant vinyl groups in a linear St–DVB copolymer with 60% DVB is 4.6 mmol/g; therefore, the conversion of the second vinyl groups is only 52% for the *p*-DVB-based copolymer and 75% for the *m*-DVB-based copolymer. The lower conversion of the *p*-DVB-based copolymer compared to the *m*-DVB-based copolymer is thought due to the lower reactivity of the second vinyl groups for *p*-DVB than for *m*-DVB.

Table II shows the vinyl group content of St–DVB copolymers synthesized with different amounts of DVB. Toluene was also used as an inert diluent with a dilution degree of 2.0. We can see that the vinyl group content increases with increasing DVB content of the copolymers and the degree of crosslinking is significantly lower than the feed percent of DVB in the comonomers, except for the copolymer with 20% DVB. The increase in the vinyl contents with an increase in the feed percents of DVB is rationally considered as a result of an increase in the total vinyl groups introduced into the copolymers. But besides this, the reduced mobility of the polymer networks must be another important cause. The rigid networks of the copolymers at a higher DVB content severely restrict the reaction of second vinyl groups, therefore reducing the conversion.

Starting Copolymers with Different DVB Isomers

Table I shows that the amount of the pendant vinyl groups is different for copolymers synthesized with different DVB isomers. Accordingly, we are interested in knowing what is the result if

these three copolymers are used as starting copolymers for a postcrosslinking reaction without an externally added crosslinking agent. Table III shows a comparison of the pore-structure parameters for these three copolymers prior and after reaction. 1,2-Dichloroethane is used as a solvent, and anhydrous ferric chloride, as a catalyst, as detailed in the Experimental section.

As presented in this table, both the surface area and the pore volume for the *p*-DVB-based copolymer prior to reaction are much smaller compared with the *m*-DVB-based one, which correlated well with the conversion of the second vinyl group of 52 and 75% (Table I) for *p*-DVB- and *m*-DVB-based copolymers, respectively. But with a vinyl group content of 2.21 mmol/g, both the surface area and pore volume of the *p*-DVB-based copolymer increase profoundly after reaction and the increment of the specific surface area $(S_a - S_p)$ and the pore volume $(V_a - V_p)$ reached the values of 720 m^2/g and 1.33 mL/g, respectively, significantly greater than the corresponding values of 226 m^2/g and 0.616 mL/g for the *m*-DVB-based copolymer after reaction and for which the starting copolymer has a vinyl content of only 1.15 mmol/g (Table I). Besides this, a substantially total elimination of the pendant vinyl groups was observed by comparing the IR spectra of different DVB isomer-based copolymers at the bonds of 1630, 1410, 1015, and 990 cm^{-1} prior to and after reaction. From the above results, it is clear that the change of pore structure of the copolymers after reaction depends heavily upon the amount of the pendant vinyl groups, and the role of these vinyl groups in the postcrosslinking reaction is further confirmed by this result.

In regard to the reaction mechanism of the postcrosslinking, Nyhus et al. proposed that a

Table II   Vinyl Group Content of St–DVB Copolymers with Different Amounts of DVB

| DVB (%) | Vinyl Group Content | | Degree of Crosslinking $(X_{Cl}$ %) |
	X_{vb} (%)	mmol/g	
20	2.1	0.19	17.5
40	8.2	0.67	31.3
60	18.4	1.40	41.8
80	26.4	2.02	53.7
98	30.9	2.37	67.2

The copolymers were synthesized in the presence of toluene as a diluent with a dilution degree of 2.0.

Table III   Specific Surface Area and Pore Volume of St–DVB Copolymers (60% DVB) with Different DVB Isomers Prior to and After Postcrosslinking Reaction

DVB Isomers	Specific Surface Area (m²/g)			Pore Volume (mL/g)		
	S_p	S_a	$S_a - S_p$	V_p	V_a	$V_a - V_p$
p-DVB	470	1190	720	0.616	1.749	1.133
p-, m-DVB	710	1157	447	0.963	1.592	0.629
m-DVB	712	938	226	0.856	1.472	0.616

The copolymers' prior reactions were synthesized in the presence of toluene as an inert diluent and at a fixed dilution degree of 2.0. S_p and S_a represent the specific surface areas and V_p and V_a represent the pore volumes, prior to and after reaction, respectively.

complex intermediate was formed by the reaction of pendant groups with aluminum chloride and the postcrosslinking reaction then proceeded via electrophilic attack of the intermediate on the neighboring vinyl groups in the polymer matrix.[15,16] As a result, a methyl- and chloro-substituted alkylene-type bridge structure was formed between aromatic rings, as represented by (**I**):

$\sim$ phenyl–CH(CH₃)CH₂CH(Cl)–phenyl $\sim$ (**I**)

With a reaction temperature of 22°C and only a part of the pendant vinyl group consumption after the reaction in their case, the formation of structure (**I**) is possible, but should be limited, depending upon the probability of the pendant vinyl groups reacting with other adjacent vinyl groups. Because the pendant vinyl groups, which are fixed on the rigid polymer networks, were left unreacted during free-radical copolymerization, they should also be difficult to contact with each other and to react by a cationic polymerization mechanism. In our case, the reaction was carried out at a temperature of 80°C with ferric chloride as a catalyst and 1,2-dichloroethane as a solvent. It is believed that a higher temperature will facilitate the reaction of vinyl groups with the neighboring aromatic rings; the aromatic rings, after free-radical copolymerization, should be available and could react with vinyl groups following a mechanism different from the free-radical copolymerization, in the presence of a Friedel–Crafts catalyst. Only in this way can we explain the total elimination of the vinyl groups after the postcrosslinking reaction, and in such a reaction fashion, the possible alkylene bridge structure might be represented by (**II**) as designed by Ando et al.[10]:

$\sim$ phenyl–CH(CH₃)–phenyl $\sim$ (**II**)
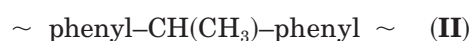
1,2-Dichloroethane is a commonly used solvent for preparing hypercrosslinked polystyrene with chloromethyl methyl ether as the crosslinking agent. As a bifunctional compound, it may be a crosslinker. To rule out this possibility in our case, chlorobenzene, a solvent with a monofunctional group, was used to take place of the 1,2-dichloroethane. Similarly, the surface area and pore volume increased significantly in this case after postcrosslinking; therefore, it is reasonable to think that 1,2-dichloroethane simply acts as a solvent, not as a crosslinker.
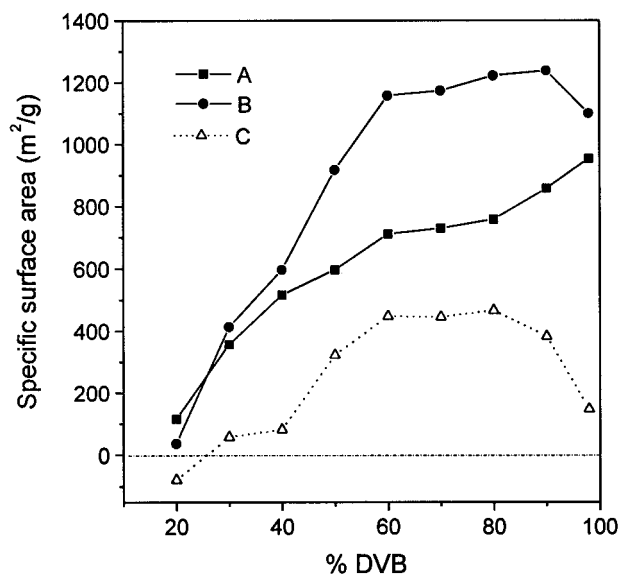
Starting Copolymers with Different DVB Contents

Figure 1 shows the dependence of the specific surface area of St–DVB copolymers prior and after the postcrosslinking reaction on the DVB content. The copolymers' prior reaction, that is, the starting copolymers, were synthesized in the presence of toluene as a diluent with a dilution degree of 2.0. As shown, the surface area of both copolymers prior to and after reaction increase with an increase in the DVB content on the whole, but the surface area (S_a) after reaction is much greater than is the surface area (S_p) prior to the reaction beyond the 40% DVB. A dotted line (curve C) in the same figure shows the relationship of the increment of the surface area, $S_a - S_p$, with the DVB content. As can be seen from this curve, the value of $S_a - S_p$ increases rapidly beyond the DVB content of 40%, almost remains unchanged in the range of 60–80% DVB, and decreases rapidly beyond 90% DVB.

It is interesting to note that a minus value of $S_a - S_p$ appears at 20% DVB. Since Friedel–Craft alkylation is a reversible reaction, a cleavage and

reformation of the crosslinking bonds assumed by Ando et al.[10] could proceed simultaneously during the postcrosslinking reaction. When a reverse reaction of alkylation dominates the course of the reaction, a substantial cleavage of crosslinks would happen, as manifested by a decrease in the surface-area value. The postcrosslinking of the 20% DVB copolymer, with a minus increment of surface area of -79 m^2/g, should be a case in point, and this is correlated well with the vinyl group content of the 20% DVB copolymer: It is only 2.1%, as shown in Table II. But in further correlating the values of $S_a - S_p$ in Figure 1 with the data of the vinyl content in Table II, we can find that with an increase in the vinyl content the value of $S_a - S_p$ in Figure 1 increases rapidly, up to 447 m^2/g at a DVB content of 60%, indicating that an alkylation reaction via pendant vinyl groups tends to dominate the course of the postcrosslinking with an increase in the vinyl content. From this result, we see again that the increase of the surface area after reaction is closely related to the amount of the pendant vinyl groups in the starting copolymers.

With a further increase in the amount of vinyl groups at a higher DVB content, although the surface area still increases profoundly after reac-

Table IV Pore Volume of St–DVB Copolymers with Different DVB Contents Prior to and After Postcrosslinking Reaction

| DVB (%)	Pore Volume (mL/g)		
	V_p	V_a	$V_a - V_p$
20	0.281	0.122	−0.159
30	0.597	0.494	−0.103
40	0.688	0.849	0.161
50	0.795	1.106	0.311
60	0.963	1.592	0.629

The copolymers are the same as those in Figure 1. V_p and V_a represent the pore volume prior to and after reaction, respectively.

tion, the value of $S_a - S_p$ tends to remain constant and even decreases beyond 90% DVB. This is understandable because more highly crosslinked polymers swell poorly in solvents, so the increase in the surface area achievable with these copolymers is severely limited. The effect of the swelling ability of the starting copolymers on the postcrosslinking reaction will be further discussed in the next part.

Table IV presents a comparison of the pore volumes of the same copolymers prior to and after the postcrosslinking reaction as that in Figure 1 with different DVB contents. As seen in this table, the pore volumes for copolymers with a DVB content of 20 and 30% after reaction are both lower than are those for the same copolymers prior to reaction. The same explanation as that for the minus increment of surface area in Figure 1 can be used to illustrate this phenomenon. Moreover, we can see that the increment of the pore volume ($V_a - V_p$) is also correlated well with the data of the vinyl content in the starting copolymers, in favor of our opinion that the alkylation reaction via pendant vinyl groups dominates the course of postcrosslinking at a relatively high level of the vinyl content.

Figure 1 Dependence of the specific surface area of St–DVB copolymers prior to and after postcrosslinking reaction on the DVB content. The copolymers' prior reactions were synthesized in the presence of toluene as a diluent with a fixed dilution degree of 2.0. Specific surface area: (curve A) prior reaction S_p; (curve B) after reaction S_a; (curve c) $S_a - S_p$.

Starting Copolymers Synthesized Using Mixed Solvents as the Diluent

Figures 2 and 3 show, respectively, the dependence of the specific surface area and pore volume of St–DVB copolymers prior to and after the postcrosslinking reaction on the n-heptane content in the mixed diluent of toluene and n-heptane. The copolymers' prior reactions were synthesized at a fixed DVB content of 60% and a dilution degree of
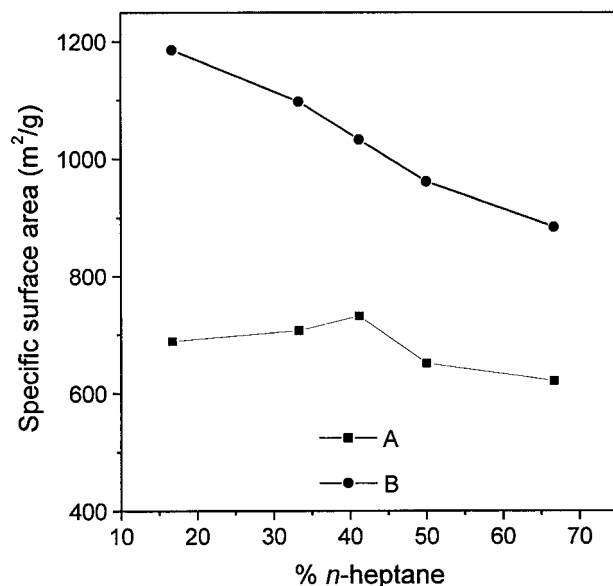
Figure 2 Dependence of the specific surface area of St–DVB copolymers prior to and after postcrosslinking reaction on the n-heptane content in the mixed diluent of toluene and n-heptane. The copolymers' prior reactions were synthesized at 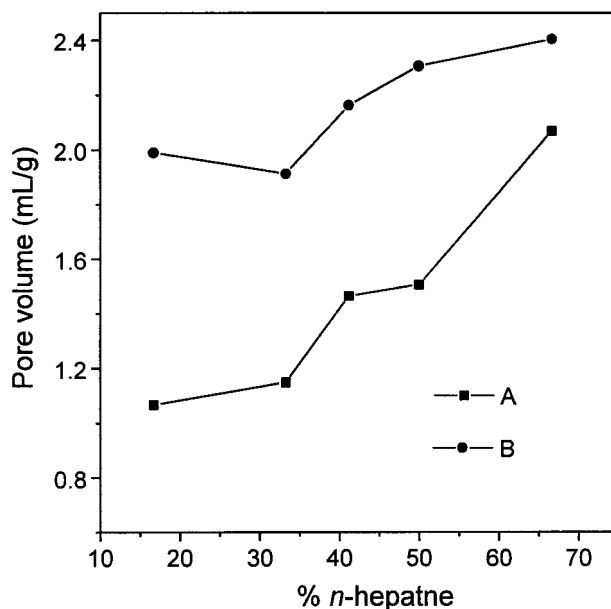a fixed DVB content of 60% and a dilution degree of 2.0. Specific surface area: (curve A) prior reaction S_p; (curve B) after reaction S_a.

2.0. From Figure 2, we can see that the surface area (S_p) for copolymers prior to reaction generally slowly decreases, with an increasing n-heptane content, but the surface area (S_a) for copolymers after reaction decreases rapidly. As a result, the increment of surface area ($S_a - S_p$) after reaction is much greater at a lower n-heptane content than at a higher n-heptane content. The change of the pore volume prior to (V_p) or after reaction (V_a) in Figure 3 shows a tendency opposite to that of the surface area in Figure 2 with a changing n-heptane content, but the increment of the pore volume ($V_a - V_p$) after reaction is also principally greater at a lower n-heptane content than at higher n-heptane content. The different increment, $S_a - S_p$ or $V_a - V_p$, at various n-heptane contents, may be explained mainly by a different swelling ability of these copolymers in the solvent used for the postcrosslinking reaction. In our reaction system, we used 1,2-dichloroethane, a solvent with a strongly solvating power for polystyrene. Since the alkylation reaction leading to the postcrosslinking of the St–DVB copolymer is performed in the swollen state, the postcrosslinking step "freezes" the swollen structure in place. The postcrosslinked product, then, is supported by the additional crosslinks, which pre-

vent this material from shrinking to its original, unswollen volume when the solvent is removed. Accordingly, the swelling ability of the starting copolymers in 1,2-dichloroethane should be very important for acquiring a substantial increase in the surface area and porosity. As is well known, the swelling ability of copolymers synthesized in a diluent with different solvating power is different. For the copolymers in Figure 2 or 3, the swelling ratio (V/V) in toluene, for example, increases with a decrease of the content of n-heptane, a nonsolvent for polystyrene, in the mixed diluent. At the contents of 17, 33, and 50% of n-heptane, the swelling ratio in toluene is 1.68, 1.51, and 1.29, respectively. This is correlated well with the increment of the surface area and pore volume; the corresponding value of $S_a - S_p$ at these contents of n-heptane is 489, 372, and 276 m²/g, respectively, and the change of the value of $V_a - V_p$ is similar. Clearly, for the copolymers with different contents of n-heptane, the stronger the swelling ability of a copolymer in the solvent, the greater is the increase of the surface area and pore volume after the postcrosslinking reaction.

In addition to the above explanation, the difference in the vinyl content for these copolymers

Figure 3 Dependence of the pore volume of St–DVB copolymers prior to and after postcrosslinking reaction on the n-heptane content in the mixed diluent of toluene and n-heptane. The copolymers' prior reactions were synthesized at a fixed DVB content of 60% and a dilution degree of 2.0. Pore volume: (curve A) prior reaction V_p; (curve B) after reaction V_a.

may be another factor causing the different increments of the surface area and pore volume mentioned above. But because the diluent type does not affect the vinyl content significantly,[23] the postcrosslinking reaction for copolymers with the same content of DVB would not be influenced too much, in this case, by the small difference in the vinyl content.
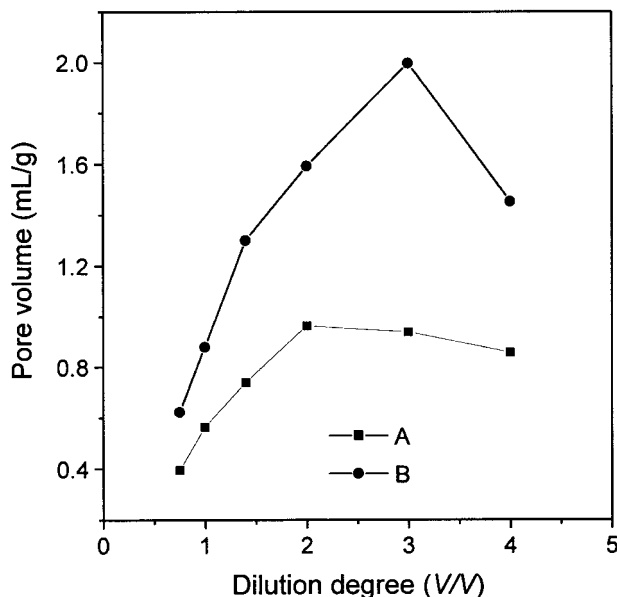
Starting Copolymers Synthesized Using Different Amounts of Diluent

The amount of the diluent used in the synthesis of the starting copolymers also shows an important influence on the postcrosslinking reaction of these copolymers. Figures 4 and 5 show, respectively, the dependence of the specific surface area and pore volume of the St–DVB copolymers prior to and after reaction on the dilution degree, expressed as a volume ratio of the diluent to the monomers. The copolymers' prior reactions were synthesized at a fixed DVB content of 60% and toluene was used as the diluent.

As can be seen in Figure 4, the surface area (S_p) for the copolymers' prior reactions does not change too much at different dilution degrees, but for copolymers after reaction, the change of the
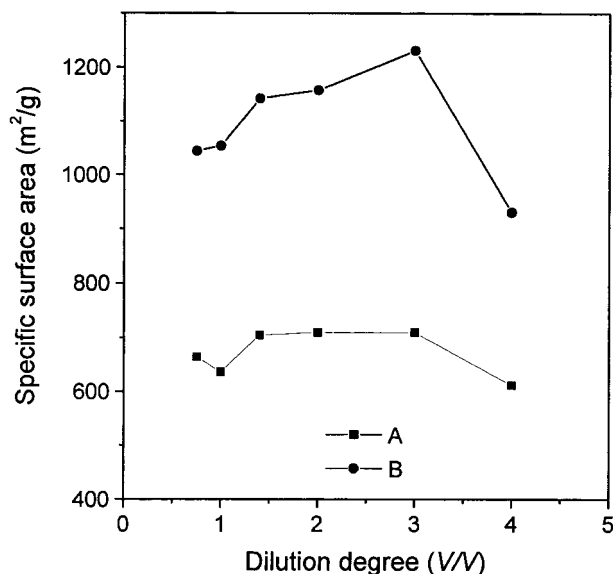
Figure 5 Dependence of the pore volume of St–DVB copolymers prior to and after postcrosslinking reaction on the dilution degree. The copolymers' prior reactions were synthesized at a fixed DVB content of 60% and toluene was used as a diluent. Pore volume: (curve A) prior reaction V_p; (curve B) after reaction V_a.

surface area (S_a) is more apparent; the surface area (S_a) increases with increase in the dilution degree, up to a value of 1231 m^2/g at a dilution degree of 3.0, and decreases sharply at a still higher dilution degree. The increment of the surface area ($S_a - S_p$) is thus 380, 418, 437, 447, 521, and 319 m^2/g at the dilution degrees of 0.75, 1.0, 1.4, 2.0, 3.0 and 4.0, respectively. Compared with the surface area in Figure 4, the pore volume in Figure 5 for both copolymers prior to (V_p) and after reaction (V_a) shows an increase with an increase in the dilution degree, but the pore volume after reaction (V_p) increases more, up to a point of a dilution degree of 3.0. The value of $V_a - V_p$ then also increases greatly, from 0.227 mL/g at a dilution degree of 0.75–1.060 mL/g at degree of 3.0, and decreases finally to 0.595 mL/g at degree of 4.0.

Previously, we attributed the different increments of the surface area ($S_a - S_p$) or the pore volume ($V_a - V_p$) in Figures 2 and 3 to the swelling ability of the starting copolymers synthesized using mixed diluents with different n-heptane contents. Here, probably, we can also ascribe the effect of the dilution degree in Figures 4 and 5 to the different swelling ability of the starting copolymers at different dilution degrees. With increase

Figure 4 Dependence of the specific surface area of St–DVB copolymers prior to and after postcrosslinking reaction on the dilution degree. The copolymers' prior reactions were synthesized at a fixed DVB content of 60% and toluene was used as a diluent. Specific surface area: (curve A) prior reaction S_p; (curve B) after reaction S_a.

Table V   Specific Surface Area and Pore Volume for St–DVB Copolymers (60% DVB) Prior to and After Postcrosslinking Reaction

Dilution Degree (V/V)	V_t (mL/g)	Specific Surface Area (m²/g)			Pore Volume (mL/g)		
		S_p	S_a	$S_a - S_p$	V_p	V_a	$V_a - V_p$
0.75	0.824	640	948	308	0.547	0.802	0.255
1.0	1.099	644	1035	391	0.757	1.088	0.331
1.4	1.538	713	1126	413	0.986	1.554	0.568
2.0	2.198	707	1079	372	1.148	1.913	0.765
3.0	3.297	697	1072	375	1.446	2.969	1.523

The copolymers prior reactions were synthesized in the presence of a mixed diluent of toluene and n-heptane at a fixed n-heptane contrast of 33%. V_t represents the volume of mixed diluent per unit weight of monomers (mL/g); S_p and S_a represent the specific surface areas and V_p and V_a represent the pore volumes, prior to and after reaction, respectively.

in the dilution degree, the volume of the copolymer in a solvating solvent increases. The swollen state may be partially fixed by the postcrosslinking, and the new pore structure will be supported by the additional crosslinks, in this way increasing the surface area and pore volume of the postcrosslinked products in the dry state. The increment of the surface area or the pore volume, on the one hand, depends upon the swelling of the starting copolymers in the solvent used for the reaction; therefore, the values of both $S_a - S_p$ and $V_a - V_p$ increase with increase of the dilution degree up to 3.0. On the other hand, the increment should depend upon the total crosslinks of the copolymer or the overall rigidity of the polymer network. It is known that, at a fixed DVB content, the crosslinking density of a copolymer network formed by copolymerization is very much dependent on the amount of the solvating diluent.[20] It should be also true for the postcrosslinking reaction that, with an increase in the amount of the solvent in the swollen copolymer, the crosslinking density decreases due to an enhanced intramolecular reaction. Therefore, at a too high dilution degree, for example, 4.0 in this case, both the copolymers prior to and after reaction reduce their ability to keep from shrinking when the solvent is removed. As a result, not only the surface areas or pore volumes prior to and after reaction, but also the increments of them at a dilution degree of 4.0 decrease as compared with those at a lower dilution degree, for example, 3.0.

Table V also presents the specific surface area and pore volume of the St–DVB copolymers prior and after reaction at different dilution degrees. But instead of a pure solvent toluene, the mixed diluent of toluene and n-heptane was used in the synthesis of the starting copolymers (60% DVB) in this table, at a fixed n-heptane content of 33%.

It is seen that with a mixed diluent being used in the synthesis of the starting copolymers the surface areas both prior to and after reaction just show a small change with changing the dilution degree as compared with those in Figure 4; only the pure solvent toluene was used as the diluent. Nevertheless, with only a small part of n-heptane in the mixed diluent, the increase in the pore volume for the copolymers prior to and after the reaction is greater compared with that in Figure 5. This is understandable because a solvating solvent as a diluent usually creates small pores, whereas a nonsolvent as a diluent produces materials with irregularly shaped large pores. For a starting copolymer with larger pores in the swollen state, the larger pores then would be preserved within the dried copolymer by postcrosslinking.

It is more interesting to note that the pore volumes (V_a), for copolymers after reaction at various dilution degrees in Table V, all approach the corresponding values of V_t, the volume of the diluent per unit weight of the monomers (mL/g) in the starting copolymerization system for the synthesis of the starting copolymers. This means that with the introduction of a small part of a nonsolvent into the diluent the enhanced rigidity of the starting copolymer networks allows the postcrosslinked products to maintain a total volume when the solvent is removed, approaching that of the copolymer in a swollen state.

CONCLUSIONS

Starting St–DVB copolymers synthesized under different conditions show a profound influence on the pore structure of these copolymers after the postcrosslinking reaction with anhydrous ferric

chloride as the Friedel–Crafts catalyst and 1,2-dichloroethane as a solvent. When the starting copolymers were synthesized with different DVB isomers, both the specific surface area and the pore volume increased much more for the *p*-DVB-based copolymer than for the *m*-DVB-based copolymer after reaction; this is correlated well with the amount of the pendant vinyl groups in these copolymers, therefore further confirming the role of the pendant vinyl groups in creating new crosslinking bonds in addition to those created by the free-radical crosslinking reaction in the starting copolymers. When the copolymers were synthesized with different amounts of DVB, the pore structure of the copolymers after the postcrosslinking reaction changes in different ways at different DVB contents. For the 20%DVB copolymer, in which the vinyl group content is only 2.1%, both the surface area and pore volume did not increase, but decreased, after the reaction. This phenomenon supports the assumption that a cleavage and reformation of crosslinking bonds could proceed simultaneously during postcrosslinking. With a very small amount of pendant vinyl groups, a reverse reaction of alkylation could dominate the course of postcrosslinking of the 20% DVB copolymer and a substantial cleavage of crosslinks would happen as manifested by a decrease in values of the surface area and pore volume. But, with an increase in the DVB content of the copolymers, the surface area and pore volume, after reaction, increase rapidly, and the increase is closely related to the amount of the pendant vinyl groups in the starting copolymers, indicating that an alkylation reaction using pendant vinyl groups tends to dominate the course of the postcrosslinking reaction with an increase in the vinyl content.

By changing the synthesis variables, the *n*-heptane content in a mixed diluent, and the amount of the diluent for the synthesis of the starting copolymers, the specific surface area of the postcrosslinked products could reach a value above 1100 m^2/g with ease, and the pore volume could be adjusted to a large extent. The effect of these two synthesis variables mentioned above, on the pore structure of the postcrosslinked products, could be attributed mainly to the swelling ability of the starting copolymers obtained under these different conditions in the solvent used for postcrosslinking reaction.

REFFERENCES

1. Abrams, I. M.; Millar, J. R. React Polym 1997, 35, 7.
2. Kun, K. A.; Kunin, R. J Polym Sci A-1 1968, 6, 2689.
3. Dusek, K. In Development in Polymerization; Haward, R. N., Ed.; Applied Science: London, 1982, Vol. 3; Chapter 4.
4. Guyot, A. In Syntheses and Separations Using Functional Polymers; Sherrington, D.C.; Hodge, P. Eds.; Wiley: New York, 1988; Chapter 1.
5. Okay, O. Prog Polym Sci 2000, 25, 711.
6. Hubbard, K. L.; Finch, J. A.; Darling, G. D. React Polym 1998, 36, 1.
7. Davankov, V. A.; Tsyurupa, M. P. React Polym 1990, 13, 27.
8. Davankov, V. A.; Pastukhov, A. V.; Tsyurupa, M. P. J Polym Sci Part B Polym Phys 2000, 38, 1553.
9. Hradil, J.; Králová, E. Polymer 1998, 39, 6041.
10. Ando, K.; Ito, T.; Teshima, H.; Kusano, H. In Ion Exchange for Industry, Streat, M., Ed.; E. Horwood: Chichester, U.K., 1988; pp 232–238.
11. Ando, K.; Ito, T.; Teshima, H. Jpn. Kokai 9 218 436, 1992.
12. Takayanagi, H.; Teshima, H. U.S. Patent 5 885 638, 1999.
13. Meteyer, T. E. U.S. Patent 5 218 004, 1993.
14. Lundquist, E. G. Langenmayr, E. J. U.S. Patent 6 147 127, 2000.
15. Nyhus, A. K.; Hagen, S.; Berge, A. J Polym Sci Part A Polm Chem 2000, 38, 1366.
16. Christy, A. A.; Nyhus, A. K.; Kvalheim, O. M.; Hagen, S.; Schanche, J. S. Talanta 1999, 48, 1111.
17. Popov, G.; Schwachula, G. Chem Technol 1978, 30, 144.
18. Yan, J.; Wang, X. H.; Chen, J. Q. J Appl Polym Sci 2000, 75, 536.
19. Yan, J.; Wan, J. Lizi Jiaohuan Yu Xifu, 1988, 4, 216; Chem Abstr 1989, 110, 174324p.
20. Yan, J.; Xu, R. N.; Yan, J. T. J Appl Polym Sci 1989, 38, 45.
21. Malinsky, J.; Klaban, J.; Duse K. J Macromol Sci Chem A 1971, 5, 1071.
22. Hubbard, K. L.; Finch, J. A.; Darling, G. D. React Polym 1998, 36, 17.
23. Nyhus, A. K.; Hagen, S.; Berge, A. J Appl Polym Sci 2000, 76, 152.
24. Robert, V. L.; Sherrington, D. C.; Snape, C. E. Macromolecules 1997, 30, 2868.
25. Bartholin, M.; Boissier, G.; Dubois, J. Makromol Chem 1981, 182, 2075.