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Effects of post-crosslinking of macroreticular styrene–divinylbenzene copolymers on their morphology

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Abstract

We performed a detailed comparison of properties of two different styrenic polymers containing divinylbenzene as the crosslinker before and after the introduction of the additional crosslinks by Friedel–Craft's reaction of the residual double bonds. For the polymer characterization was used a wide selection of methods, including nitrogen adsorption/desorption, inverse steric exclusion chromatography, MAS NMR and AFM. The residual double bonds are quite probably located in the dense cores of the microgel domains where steric hindrances prevented them to react during the polymerization. Reinforcement of the cores of polymer microgel domains by transformation of the residual double bonds into additional crosslinks by the Friedel–Craft's reaction results then in greater stability of the already existing pores rather than in creation of new pores by incomplete collapse of swollen polymer gel.

Keywords: Post-crosslinking; Morphology; Macroreticular

1. Introduction

For separation of volatile molecules from liquids or gases porous polymer adsorbents represent quite competitive alternative to activated carbons. They are white or almost white, have good mechanical properties and their morphology and chemical nature, e.g. polarity can be controlled by copolymerization with suitable co-monomer or by post-polymerization functionalization. Conventionally they are prepared by suspension polymerization in the presence of liquids miscible with monomers but in which the produced polymer is insoluble ("porogenic solvents" or "porogenes"). Typical representative of this category of sorbents is, e.g. series of resins Amberlite XAD, manufactured by Rohm and Haas, Philadelphia. They exhibit very good separation properties in number of applications, but their apparent specific surface area (about 200–700 m^2/g) is significantly lower than the surfaces of active carbons. Consequently, their useful sorption capacity may be not as high as that of activated carbons. That is mainly due to limitations of the mechanism of the pore formation by phase separation of the crosslinked polymer from the porogenic solvent during polymerization process. Thus, created materials contain mainly macropores or mesopores and only small volume of micropores, which in the active carbons are chiefly responsible for their excellent adsorption properties. In micropores (pores having effective diameter < 2 nm) the sorbent–sorbate attractive forces attack sorbate molecules from a few directions simultaneously and hence, in micropores sorbate does not form a layer on the surface but fills the pore volume. Values of surface area of microporous materials determined from sorption data using e.g. BET equation in fact do

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not characterize the true extent of the surface but they should be interpreted as an indicator of the sorption capacity only. Such results give the size of a fictional area needed for spreading the sorbate filling micropores into a monolayer. Increase of the morphological dispersion behind the limits of polymerization technique producing more micropores is possible by post-polymerization crosslinking of swollen polymer. This way can be created materials exhibiting apparent BET surface area formally even higher than 2000 m^2/g. Such materials may replace conventional active carbon adsorbents in applications where mechanical properties or black color of carbons are objectionable.

First hypercrosslinked microporous polymers were prepared by Davankov and Tsyurupa using crosslinking by Friedel–Craft's reaction of chloromethyl groups [1]. The Purolite International Company currently produces polymer adsorbents based on this approach under the trade name Hypersol-Macronet™. Hypercrosslinked polymer adsorbents of undisclosed nature are produced also by other manufacturers (e.g. Dow, USA; Lanxess, Germany or Jiangsu N & G Environmental Technology Co. Ltd., China). Mechanisms of the morphological changes induced by the chloromethyl group transformation into additional crosslinks and specific properties of the resulting materials were investigated in a number of studies, like e.g. [2–6].

Unfortunately, the synthesis of polymer adsorbents by Friedel–Craft's post-crosslinking of chloromethylated polystyrene is connected with a number of problems; the most serious is the utilization of recognized carcinogen (chloromethyl methyl ether) as one of the reagents. It may present difficulties both in the manufacturing process and in the application of the resulting adsorbents. Also, the production cost of these resins is rather high.

Alternative possibility for post-crosslinking of polymeric materials is utilization of pendant vinyl groups remaining in the polymer mainly due to incomplete polymerization of the second double bonds of the crosslinking component. By Friedel-Craft catalyzed reaction of the vinyl groups with neighboring benzene rings can be created additional crosslinking modifying the morphology of the polymer. This approach was proposed for the first time by Ando and co-workers [7] as a method for increasing surface area of porous polymers beyond values achievable by polymerization in the presence of porogenic solvents. The effects of the starting styrene-*co*-divinylbenzene polymers (prepared using different divinylbenzene isomers, contents and porogenic solvents) on the post-crosslinking reaction using anhydrous ferric chloride as catalyst were recently thoroughly investigated by Zhou and coworkers [8]. However, in their paper the effects of the post-crosslinking on the pore structure are characterized only by changes in apparent surface area and pore volume. These global parameters tell very little about the changes in the polymer morphology introduced by the additional crosslinking. We performed a detailed comparison of properties of two different styrenic polymers containing divinylbenzene as the crosslinker before and after introduction of the additional crosslinks by Friedel–Craft's reaction of the residual double bonds. This information may help in understanding the mechanisms of polymer adsorbent morphology modifications and could be of assistance in tailoring their properties.

2. Experimental

2.1. Polymer adsorbents

Starting materials for this study were prepared by conventional suspension polymerization using divinylbenzene (DVB) (containing 80% DVB, Dongda Chemical Engineering Group Co., Shandong Province, PR China). No other comonomer was added, but for creation of porous structure, the monomers were diluted by the same volume of porogenic solvent. For this purpose were used two kinds of porogenic solvents: one was technical gasoline composed of aliphatic alkanes, which is precipitating agent for styrenic polymer and the other was 1,2-dichloroethane, which is a very good swelling solvent for the styrene-type polymers. After addition of 1% AIBN as initiator, the polymerization mixture was dispersed under stirring in water solution containing 1% of gelatin as suspension stabilizer. Temperature was gradually raised to 90 °C and in this temperature it was maintained for 8 h. The prepared polymer beads were then collected, washed and extracted in Soxhlet apparatus with acetone. Overall yield of the resulting beads with diameter 0.5–1 mm was about 90%. The polymer prepared using the precipitating porogene was designated as X-1A and the polymer prepared with the swelling porogene was designated as X-2A.

The post-crosslinking reaction was carried out in 1,2-dichloroethane as solvent using $FeCl_3$ as catalyst in amount corresponding to 20% of the polymer weight. The reaction temperature was 80 °C and the reaction time was 8 h. Apparently, the procedure did not change the shape or size of the polymer beads. The post-crosslinked samples were designated as X-1B and X-2B.

2.2. Texture characterizations

Pore size distribution of dry polymers was evaluated by conventional nitrogen adsorption/desorption measurements at liquid nitrogen temperature using computerized apparatus ASAP 2010 and associated software (Micromeritics, USA). Characterizations of swollen-state morphology were performed by inverse steric exclusion chromatography (ISEC) with tetrahydrofuran as the mobile phase using standard HPLC equipment connected to computer data acquisition system programmed for precise evaluation of the elution volumes. Detailed description of the experimental procedure and data evaluation is given elsewhere [9]. Evaluation of the pore size distribution in both the dry and swollen states was performed using the cylindrical pore model.

2.3. Determination of the residual double bond content

Bromination was performed by treatment with excess of bromine water at laboratory temperature for 24 h. The resultant polymer was exhaustively washed with distilled water and then with water–dioxane mixture (1:2). Bromine content analysis was performed by standard titration method after burning of a sample of the polymer in closed vessel filled with oxygen and absorption of hydrogen bromide into alkali solution. MAS NMR: solid state ^{13}C NMR characterization was performed using approach developed by Snape and others [10] on a Bruker AC200 spectrometer equipped for solid state analysis and operating at 50.26 MHz. Samples were spun in the range of 3000–7000 Hz in 7 mm diameter zirconia rotors with Kel-F caps. ^{13}C CP MAS NMR spectra were obtained using the standard Bruker cross polarization pulse sequence, with 3 ms Contact Time, 6 s Relaxing Delay, and processed with a 10 Hz exponential line broadening. The ^{13}C SPE MAS NMR (SPE = single pulse experiment) spectra were obtained with high power proton decoupling during acquisition, 30 s Relaxing Delay, and processed with a 10 Hz exponential line broadening. ^{13}C chemical shifts were externally referenced to solid sodium 3-(trimethyl-silyl)-1-propane sulfonate at 0 ppm. Cross polarization experiments were optimized using adamantane. Magic angle conditions were adjusted by observing ^{79}Br spinning side bands' pattern in a rotor containing 5% of KBr [11].

2.4. Atomic force microscopy

AFM pictures were generated using Multimode AFM Nanoscope IIIa (Digital Instruments, USA) in tapping mode. There were used silicone points OTESPA with diameter 5–10 nm oscillating at 358 kHz. There was observed no damage of the sample by the oscillating point.

3. Results and discussion

Content of the residual double bonds in the polymer samples before and after the post-crosslinking reaction was examined both by classical bromination method and by MAS NMR [10]. The analytically determined bromine concentration was significantly higher in the starting samples X1-A and X2-A than in the post-crosslinked ones (Table 1). It is clear evidence of consumption of the double bonds during the Friedel–Craft's reaction. However, in spite of exhaustive washing, quite substantial retention of bromine was found in X1-B and X2-B materials suggesting that the conversion of the residual double bonds in the post-crosslinking Friedel–Craft's reaction was not complete.

Table 1
Selected properties of the examined polymers

	Polymers			
	X1-A	X1-B	X2-A	X2-B
Br content in the polymers after bromination, mmol/g	2.9	2.4	3.7	2.1
Double bond content from ^{13}C SPE MAS NMR, mmol/g	3.7	0	3.4	0
Dry-state properties				
BET surface, m^2/g	383	670	590	1074
Pore volume, cm^3/g	0.88	0.72	0.46	0.77
Pore diameter, nm	24	37	3.9	3.9
Volume of polymer particles swollen in THF, cm^3/g	1.99	2.12	1.61	1.59

The ^{13}C CP MAS NMR spectra of samples X1-A and X2-A are shown in Fig. 1 (top traces). All resonances were assigned according to literature data [10]. In detail, aromatic rings are detected at about 144.5 ppm (quaternary carbons) and 127.5 ppm (CH carbons), and residual vinyl groups are quite clearly visible at about 137.2 ppm (CH=CH$_2$) and 112.0 ppm (CH=CH$_2$). The asymmetric signal about 40 ppm is due to overlapping of two peaks centered at 46.0 and 39.5 ppm that are assigned to methylene and methine carbon atoms of the polymer main chain, respectively [12]. Finally, the presence of ethylvinylbenzene impurity in DVB is well assessed by resonances at 29.3 and 13.5 ppm assigned to CH$_2$–CH$_3$ and –CH$_2$–CH$_3$, respectively.

The employed Cross Polarization Magic Angle Spinning experiments have been developed to enhance resolution and sensitivity in solid-state NMR spectra. Unfortunately, this experiment cannot be exploited for accurate quantitative analysis, due to the particular mechanism involved in magnetization building process [13]. Quantitative estimation of residual vinyl groups in samples X1-A and X2-A was made by performing SPE (Single Pulse Excitation) MAS NMR experiments that have been demonstrated to be a powerful tool for obtaining quantitative information in many type of solid samples [14–17]. Deconvolution of SPE MAS NMR spectra (not shown in figure) indicated that the polymer X1-A contained about 0.49 residual double bonds per monomer unit, while in the polymer X2-A there were about 0.44 residual double bonds per monomer unit. It corresponds to about 3.5 mmol of the residual double bonds per gram of the starting polymer (Table 1).

Even though SPE MAS NMR can be used to count carbon atoms in a highly quantitative manner, this technique is very time consuming with respect to Cross Polarization experiment and obtained spectra are generally much noisier, making SPE technique less sensitive than CP experiment. In fact signal intensity of proton bearing carbon atoms is largely increased by Cross Polarization mechanism [13]. Therefore, we recorded ^{13}C CP MAS NMR spectra of X1-B and X2-B samples with the aim of detecting even small quantity of residual vinyl groups. After the post-crosslinking treatment, signals at 137 and 112 ppm practically disappeared in the CP MAS spectrum (see Fig. 1, bottom trace), suggesting that all residual vinyl groups were reacted. As consequence, bromine determined in these samples had to be entrapped by different mechanisms than the reaction with vinyl groups. At the same time, the high amount of such non-specifically entrapped bromine suggests that during the bromination of the starting polymers X1-A and X2-A, a similar amount of bromine should be as well entrapped by the same mechanism, and only a fraction of the residual vinyl groups actually reacted with bromine. As a matter of fact, wet chemical methods do not detect vinyl groups in the most hindered parts of polymer, as previously reported in literature for styrene–divinylbenzene networks [18].

In conclusion, comparison of SPE MAS NMR and bromination methods shows that the bromination method is rather unreliable source of information on residual double bonds in the examined highly crosslinked polymers.

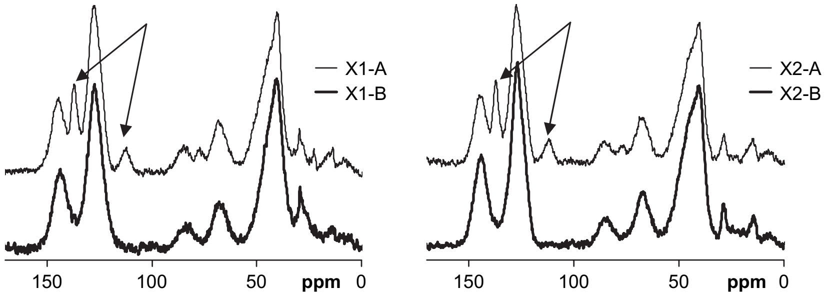

Fig. 1. ^{13}C CP MAS NMR spectra of the examined polymers before (X1-A, X2-A) and after (X1-B, X2-B) the post-crosslinking treatment. Arrows designate the peaks corresponding to the vinyl carbons.

Type of porogenic solvent used in the polymer synthesis influences the phase separation process in the course of the polymerization, character of the generated porosity [19] and its stability during drying. Pore distribution in dried samples of the starting polymers X1-A and X2-A as revealed by nitrogen adsorption porosimetry is shown in Fig. 2.

The character of the pore size distribution of the starting polymers corresponds to the known effects of the type of the porogenic solvent used in their preparations. Electron microscopy examinations of dried porous polymers prepared using precipitating porogene [20] show that polymer beads are composed of agglomerates of microspheres (100–200 nm) and each microsphere shows smaller nuclei (10–30 nm) partially fused together. Formation of the "microsphere" domains is result of phase separation due to the precipitation of the polymer from the non-solvent porogene [19]. In the polymer X1-A prepared using precipitating porogene the spaces between these domains appear as the bigger pores with diameter more than 10 nm. The smaller nuclei are formed by microsyneresis of the solvent and non-reacted monomer from DVB-rich microgels formed due to higher reactivity of DVB than styrene. In the presence of swelling porogenes, only the second mechanism operates and hence, the polymer X2-A contains only one class of very narrow pores with diameter in nanometer range. Mechanism of the influence of porogenic solvents on the character of pore size distribution was recently investigated and discussed by Macintyre and Sherrington [21]. Schematic depiction of the basic features of the morphology of the starting polymers X1-A and X2-A is shown in Fig. 3.

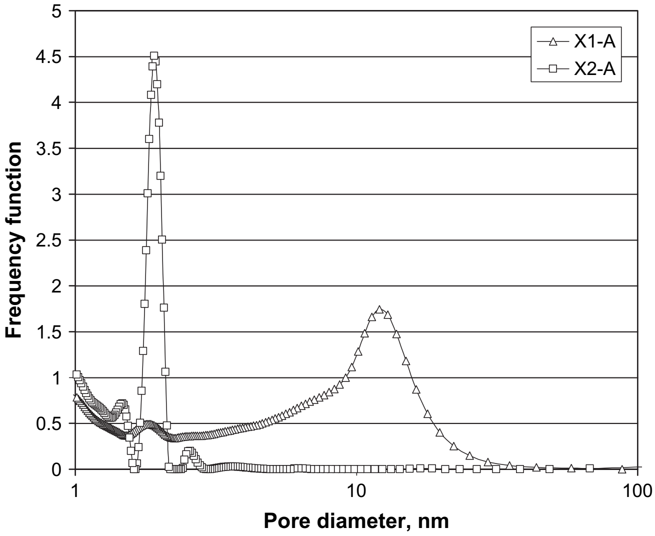

Fig. 2. Differential pore size distribution in the dried polymers X1-A and X2-A evaluated from the desorption isotherm of nitrogen.

Similar character of the pore size distribution, that is polydisperse distribution including wider pores with diameter $>$ 10 nm for the polymer X1-A and pore system composed of narrow pores only in the sample X2-A, was apparent also in the results of the characterization of the morphology of the polymers in tetrahydrofuran-swollen state by ISEC (Fig. 4).

Effect of the post-crosslinking modification on the morphology of the polymers in the dry state is most clearly visible in the changes of the apparent BET surface area (Table 1). The increase of the apparent BET surface in this case should be interpreted more as an increase of the micropore volume rather than as real increase of the pore wall area. Interpretation of the changes of overall pore volume and average pore diameter due to additional crosslinking is more complicated and will be discussed together with further analysis of the morphological properties of the examined polymers.

From ISEC chromatographic data it is possible to obtain without any preliminary suppositions the information on net volume of the swollen polymer particles. It can be determined as the difference between the volume of empty column and the "dead" volume that is the elution volume of a standard with sufficiently big molecules unable to enter pore system of the examined polymers (see Table 1). It shows that the additional crosslinking changes the overall volume of the investigated polymers little (X1) or not at all (X2).

In Figs. 5 and 8 are shown cumulative pore volume distributions both for dried polymers, as determined by conventional nitrogen adsorption/desorption porosimetry, and for swollen materials examined by inverse steric exclusion chromatography (ISEC). Data for the starting materials are shown using dotted lines and empty symbols, and for the post-crosslinked polymers are used black curves and filled symbols.

The observed differences in the dry and swollen-state morphologies of the same samples correspond very well to expectations. In the samples of the X1 series the bimodal pore character is apparent both in dry and swollen-state distributions. The post-polymerization crosslinking influenced in this series more significantly the bigger pores than the narrow

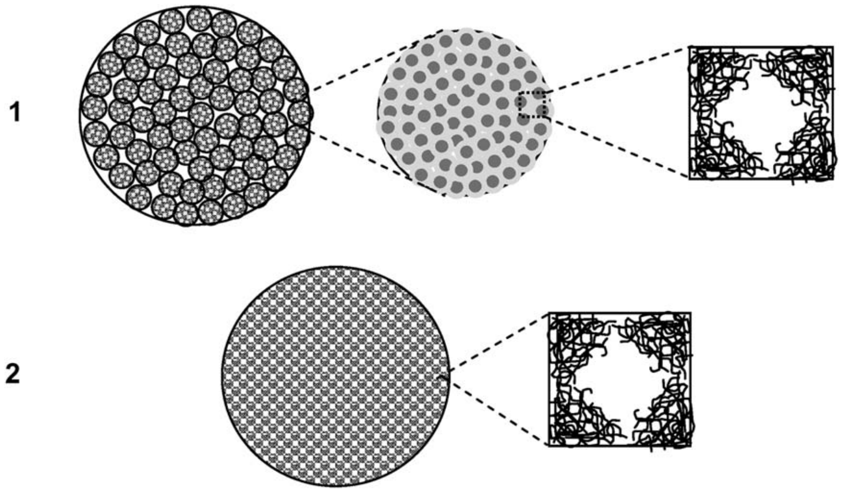

Fig. 3. Schematic depiction of the basic features of the morphology of macroreticular resins prepared using 1 – precipitating porogenes (X1-A) and 2 – swelling porogenes (X2-A).

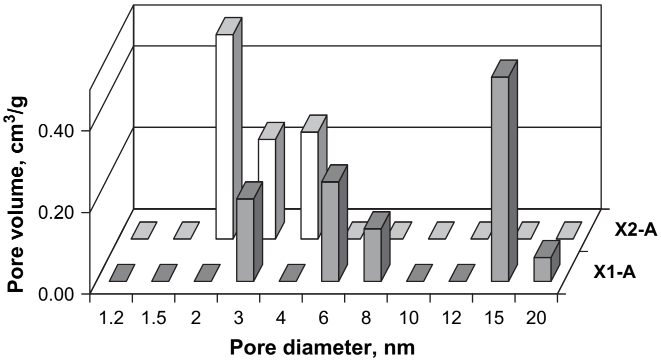

Fig. 4. Pore size distribution in the starting polymers swollen in tetrahydrofuran, as determined by ISEC.

ones. There was practically no change in the overall pore volume, but the pore sizes were shifted significantly toward higher values. Especially strongly it is apparent in the morphology of the swollen polymers evaluated by ISEC, but this effect is well visible even in the morphologies of dried polymers evaluated by the conventional nitrogen porosimetry.

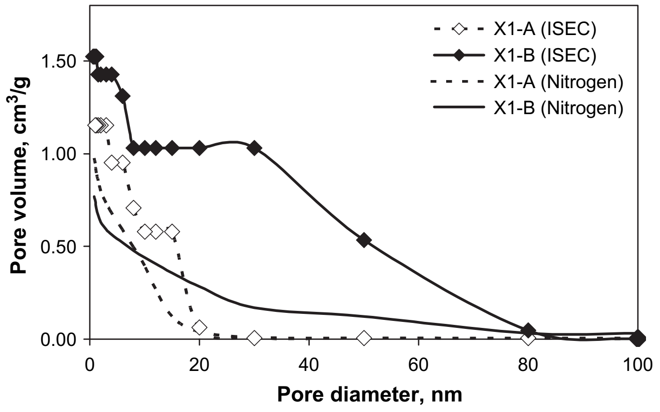

Fig. 5. Cumulative pore volume distribution for polymers X1-A and X1-B determined in dried samples by nitrogen adsorption/desorption porosimetry and by ISEC examination of the swollen materials.

This morphology change can be quite understandable if we consider that some of the newly formed crosslinks may be "glued" together. In so highly crosslinked and therefore rigid materials like the examined polymers there seems to exist a tendency to keep the overall dimension of the whole system almost constant (Table 1) and therefore, in the vicinity of the "glued-together" domains are created more wide channels, as it is schematically depicted in Fig. 6.

Changes in the morphology appearing as division of formerly bigger elements into smaller fragments are very well depicted by atomic force microscopy (AFM) (Fig. 7). It is true that microscopic pictures show always only an extremely small fragment of the investigated sample but Fig. 7 was selected as a typical example from wider number of AFM pictures and it is a good visualization of the morphology changes.

Practically monomodal character of the pore volume distribution of the polymer X2-A prepared using swelling porogenic solvent remained essentially unchanged even after the post-crosslinking.

The additional crosslinks increased the rigidity of the polymer microgel particles, the basic building blocks of the morphology (as depicted in Fig. 3). The increase in the porosity of the dried polymer due to post-crosslinking occurs in the whole range of the pore sizes (Fig. 8). Hence, it looks more like a consequence of diminished extent of the collapse of

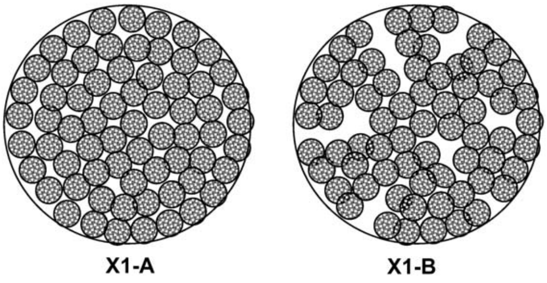

Fig. 6. Schematic depiction of the morphology changes induced by post-polymerization crosslinking in the polymer X1 prepared with precipitating porogenic solvent. X1-A – starting polymer, X1-B – post-crosslinked polymer.

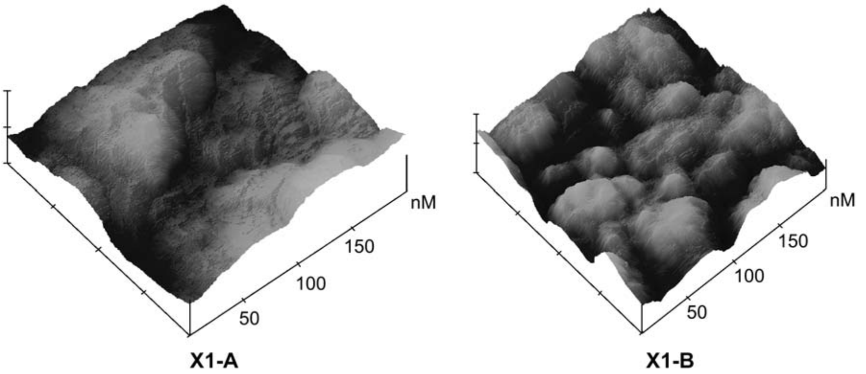

Fig. 7. Atomic force microscopy pictures of the fracture surface of particles of the starting (X1-A) and the post-crosslinked (X1-B) polymers.

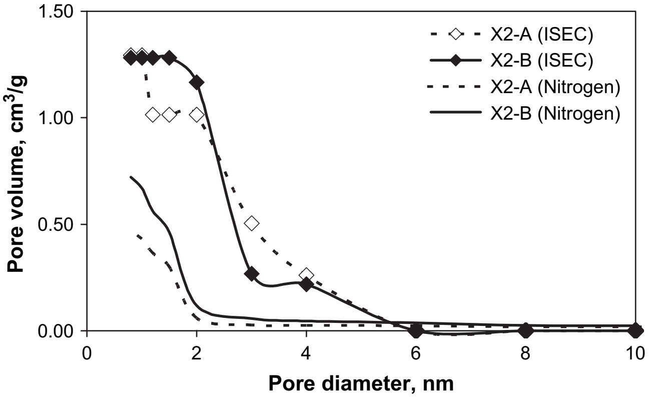

Fig. 8. Cumulative pore volume distribution for polymers X2-A and X2-B determined in dried samples by nitrogen adsorption/desorption porosimetry and by ISEC examination of the swollen materials.

the spaces between microgel polymer particles rather than as creation of a new microporosity in the incompletely collapsed post-crosslinked microgel itself.

4. Conclusions

Residual double bonds remain in styrene-*co*-divinylbenzene polymers after finishing of the polymerization mainly because a part of the divinylbenzene second double bonds did not find a suitable polymerization partner. However, these double bonds are very well able to react with benzene rings of neighboring polymer chains in Friedel–Craft's catalyzed alkylation reaction. The resulting additional crosslinking modifies the polymer morphology mostly by enforcing the existing morphology features by increasing the rigidity of the polymer domains created already in the synthesis of the starting polymer. This mechanism differs from that proposed by Tsyurupa and Davankov for their hypercrosslinked polystyrenes (see e.g. their latest review [22]), who suppose that the newly created crosslinks are homogeneously distributed in the polymer network and promotes the creation of pores by preventing the expanded network fully collapse after removal of a swelling solvent. Evenly spread random formation of the new crosslinks may be possible in the initial stages of the original arrangement proposed for the preparation of hypercrosslinked polymers by Tsyurupa and Davankov by reaction of dissolved linear polymer with crosslinking reagents. However, formation of new crosslinks in fairly dense, already substantially crosslinked network of existing polymer cannot be random but it has to be inevitably influenced by the local configuration of the polymer chains and in our case also by the distribution of the residual double bonds. The residual double bonds are quite probably located in the dense cores of the microgel domains where steric hindrances prevented them to react during the polymerization. Reinforcement of the cores of polymer microgel domains by transformation of the residual double bonds into additional crosslinks by the Friedel–Craft's reaction results then in greater stability of the already existing pores rather than in creation of new pores by incomplete collapse of swollen polymer gel.

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