

## Role of Water as a Coporogen in the Synthesis of Mesoporous Poly(divinylbenzenes)

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**ABSTRACT:** The morphology of mesoporous poly(divinylbenzenes) prepared under so called “hydrothermal” conditions and with the monomers diluted in 10 times as much porogen solvent (tetrahydrofuran with 0–20% water) was studied in both dry and swollen states, with nitrogen adsorption/desorption and inverse steric exclusion chromatography, respectively. It was found that the pore volume in the polymer examined just after preparation corresponded to the volume of the porogen used. Such a high porosity can be explained only on the basis of pore formation through microsineresis rather than the macrosineresis mechanism that is common in the synthesis of conventional porous polymer materials. Naturally, drying induces a pore collapse and the addition of water to the porogen influences the ability of the polymer to regain the original pore volume by reswelling in tetrahydrofuran.

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### INTRODUCTION

Crosslinked functional polymers containing pores, even in the dry, unswollen state, are most frequently prepared by radical polymerization of monomers dissolved in a nonpolymerizable solvent. Phase separation during the polymerization then results in the creation of a heterogeneous mixture of domains of a swollen polymer gel and the solvent expelled from it by syneresis. In most cases, deswelling of the crosslinked gel results in the creation of polymer particles surrounded by a continuous liquid phase. The morphology of a majority of the porous polymers thus features hierarchical clusters of polymer microparticles.<sup>1</sup> The volume of pores can be regulated by the amount of porogenic solvent, but in the morphology where pores are interstices between polymer microparticles, there is a limit above which the polymer may become mechanically unstable.<sup>1–4</sup> Moreover, the preparation of porous polymers from mixtures containing more than about 60% of a porogenic solvent has been little investigated.

However, recent research has led to the discovery of a novel route to nanoporous polydivinylbenzene materials exhibiting high surface areas and large pore volumes. The polymerization is performed in an autoclave at elevated temperature and pressure, and requires even more than 90 vol % of a porogenic solvent in the polymerization mixture.<sup>5</sup> The method, dubbed by authors as “solvothetical,” produces materials in monolithic

form and it is thus also possible to use as porogens water-miscible solvents, like tetrahydrofuran or water itself, which are unusable in the conventional suspension polymerization of beaded products. In spite of the high porogen : monomer volume ratio, it was possible to produce relatively compact materials that did not disintegrate into powders.

Extensive studies of the morphology of the solvothermally prepared polymers using conventional nitrogen adsorption/desorption porosimetry of dried samples have shown that they exhibit high specific surfaces, predominantly due to a large volume of mesopores. This is in contrast to the other high-surface styrenic porous polymers, such as e.g., polymer adsorbent Amberlite XAD4 or Tsyurupa-Davankov hypercrosslinked materials, in which the apparent high surface area is predominantly caused by micropores.<sup>6–8</sup> Relations between conditions of the solvothetical synthesis and the morphology of the prepared polymers were examined only on dried products. This is a frequently used approach, but drying induces an extensive collapse of the polymer morphology and hence, between the dry-state morphology and the preparation conditions, it is possible to produce only a phenomenological correlation, without an explanation of the mechanism of the morphology formation during polymerization under solvothetical conditions.

Better insight into the morphology of solvothermally prepared polymers can be achieved through investigation of the swollen

**Table I.** Composition of Reaction Mixtures for the Preparation of the First Series of Samples

Sample designation	Amount of DVB (g)	THF volume (cm <sup>3</sup> )	Water volume (cm <sup>3</sup> )
A-0	2	20	0
A-1	2	20	0.2
A-5	2	20	1.0
A-8	2	20	1.6
A-10	2	20	2.0
A-15	2	20	3.0
A-20	2	20	4.0

state morphology of these materials by inverse steric exclusion chromatography (ISEC).<sup>9–11</sup> It has been found that, in the swollen state, solvothermally prepared polymers contain a much greater volume of mesopores than would be compatible with the conventional notion of the porous structure of macroreticular styrenic polymers in the shape of polymer microparticle clusters. The porosity of a material with this type of morphology is limited due to the danger of disintegration of the agglomerates. The high porosity of the solvothermally prepared polymers could be better explained on the basis of a foam-like morphology, in which the polymeric matrix forms thin walls around bubble-like cavities.<sup>12</sup> This means that the formation of the morphology during the crosslinking free-radical polymerization under “solvothermal” conditions must differ from the macrosynthesis phase separation formation of polymer nodules generally accepted as the mechanism of pore formation during conventional suspension polymerization of monomers diluted in a porogenic solvent. The mechanism of the development of the porous structure during the solvothermal process deserves further investigation.

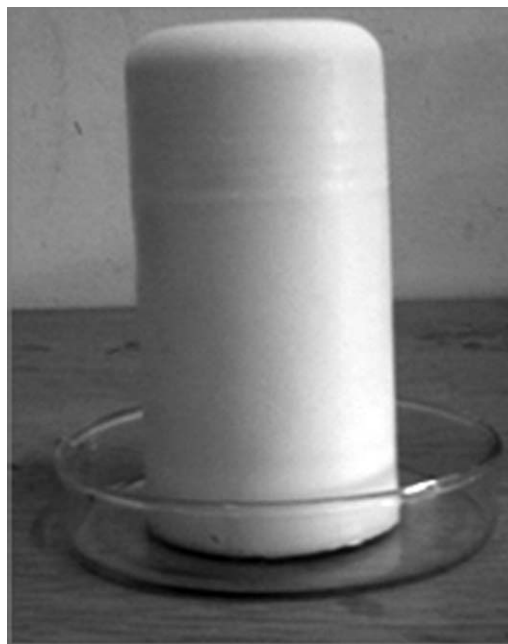
In previous studies of the solvothermal polymerization of divinylbenzene, the best results (in terms of dry-state surface area and pore volume) were achieved with a never before tested combination of tetrahydrofuran,<sup>5,13–15</sup> which is known to be one of the best compatible solvents with styrenic polymers, and water—for styrenic polymers, the totally nonswelling solvent. The admixture of water to tetrahydrofuran (0–10 vol %) had a remarkable positive effect both on the specific surface and, even more significantly, on the pore volume of the dried polymer samples. It appears that water plays an important role in the mechanism of the pore formation, but the data obtained from measurements on the polymer samples deformed by collapse during drying does not constitute a reliable base for the formulation of a hypothesis concerning the mechanism. Hence, we decided to use ISEC to investigate the influence of water on the morphology of the solvothermally prepared polymers in their swollen state.

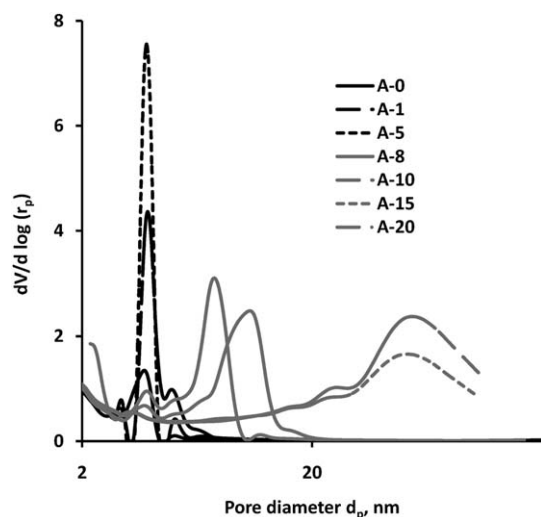
## EXPERIMENTAL

Porous polymer monoliths were prepared under conditions that were essentially identical to those already described elsewhere.<sup>5</sup> In the preparation of the first series of polymer samples (with

A in the designation), a clear, homogeneous mixture of 2.0 g (2.2 cm<sup>3</sup>) of divinylbenzene (tech. grade 80%), 20 cm<sup>3</sup> of tetrahydrofuran (THF), 0–4 cm<sup>3</sup> of water and 50 mg of 2,2' azobis(2-methylpropionitrile) (AIBN) as the initiator was maintained in a closed autoclave under autogenic pressure (2.1 bar) at 100°C for 48 h (see Table I). Higher amount of water in the polymerization mixture would lead to liquid/liquid phase separation already before the polymerization, which was undesirable. After cooling to room temperature, a white, opaque cylinder of relatively soft polymer monoliths, free of any residual solvent, was removed (Figure 1) and left to dry at room temperature overnight. Subsequently, its drying was completed in an oven at 110°C.

In order to investigate the morphology of the polymers in their truly native state, we prepared another series of polymer samples, which in addition to the previously applied assessments in the dry and re-swollen state was submitted to the swollen-state morphology examination also without preliminary drying. The reaction mixtures were composed of 8 g tech.-grade DVB, 80 % (Sigma-Aldrich), 0.2 g AIBN, 80 cm<sup>3</sup> THF and variable volume (0 – 12 cm<sup>3</sup>) water. The concentration of water is encoded in the sample designation – the sample B-0 was prepared without addition of water, while the reaction mixture for the preparation of sample B2 contained 2 cm<sup>3</sup> of water, etc. The samples were prepared in tightly closed 100 m<sup>3</sup> glass Duran bottles (Schott, Germany). For the first 8 hours of the polymerization, the bottles (packed in stainless steel mesh for safety reasons) were immersed in boiling water and then kept in an air oven at 100°C for another 64 hours. The weights of the bottles with the polymerization mixture were measured before and after the polymerization, and proved that no leakage of the bottle content occurred during the reaction.

**Figure 1.** Polymer monolith just removed from the autoclave.



**Figure 2.** Pore size distributions of the dried polymer samples of the A-series determined from nitrogen desorption isotherms.

The morphology of the dried polymers was assessed with nitrogen adsorption/desorption measurements at the temperature of liquid nitrogen using a computerized ASAP 2010 apparatus and associated software (Micromeritics, USA).

For investigation in their swollen state, the polymers of the A-series were ground and sieved in order to separate the particles in the size range 0.125 – 0.25 mm. They were further purified from fines by decantation in methanol and then transferred to THF, in which they were left to swell overnight. The polymers of the B-series were divided into two portions. One was dried and treated similarly to the samples of the A-series and the second was, without first being dried, washed with methanol, as handling of wet polymer in methanol was easier than in THF. Tests performed with cylindrical pieces of polymer B-0 demonstrated that the transfer from THF to methanol did not induce any shrinking of the polymer. The polymers were ground in the methanol and wet sieved in order to separate the particles in the size range 0.125 – 0.25 mm, which were then transferred to THF.

The suspension of the polymer in THF was slurry-packed into a chromatographic column of known volume. The

characterization of the swollen-state morphology of both A and B was performed by ISEC with THF as the mobile phase using standard HPLC equipment connected to a computer data acquisition system programmed for precise evaluation of the elution volumes.

Solutes with known effective molecular sizes (from 320 nm for polystyrene, MW = 10,000 KDa, down to 0.55 nm for n-pentane) were then eluted through the filled column where the polymer acted as the stationary phase. Mathematical treatment of measured elution volumes provided a description of the swollen polymer morphology modeled as a set of discrete pore fractions, each characterized by a single size of pores of simple geometrical shape. A satisfactory fit of the experimental data was achieved with a model consisting of 10 cylindrical pore fractions with diameters in the range 5 – 150 nm. Due to the high crosslinking level of the examined materials, it was assumed that a swollen polymer gel was absent. Details on the experimental procedure and data treatment can be found elsewhere.<sup>11</sup>

## RESULTS AND DISCUSSION

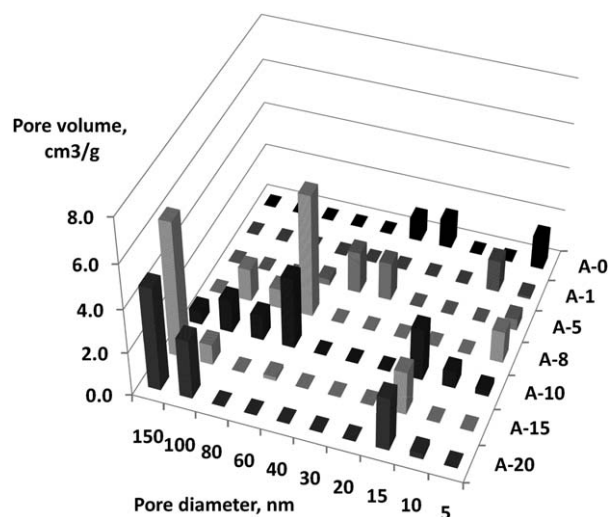
The pore size distribution in dried polymer samples of the A-series series is shown in Figure 2. There is obvious influence of the addition of water to the porogenic solvent on the pore sizes: the increase in water concentration in the porogen led to larger pore sizes.

Table II lists the values of the selected morphological parameters determined from nitrogen adsorption data. BET specific surface areas of the dried A-series polymers were found to be very similar (except for the border members of the series). A very interesting feature of the examined dry pol(DVB) materials was their almost negligible volume of micropores as assessed using *t*-plot analysis.<sup>16</sup> Plotting of the adsorbed amount against the thickness of the adsorbed layer determined on a flat model material enabled to estimate what part of the adsorption corresponded to the volume filling of the micropores and what was due to BET-type multilayer adsorption on the external (mesopore) surface. Typical high surface area styrenic polymers, such as Amberlite XAD-4 (Dow Chemical, USA) contain micropore volumes as high as 0.28 cm<sup>3</sup> g<sup>-1</sup>,<sup>6</sup> almost an order of magnitude higher than what was found in the novel poly(DVB)'s.

**Table II.** Dry-State Porosity of the A-Series Polymers as Evaluated from Nitrogen Adsorption/Desorption Measurements

Sample designation	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Total pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Micropore volume <sup>a</sup> (cm <sup>3</sup> g <sup>-1</sup> )	Mesopore surface area <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )
A-0	561	0.37	0.034	470
A-1	622	0.58	0.018	592
A-5	656	0.58	0.006	620
A-8	638	0.92	0.009	623
A-10	659	0.78	0	636
A-15	646	1.05	0.01	600
A-20	433	1.03	0	513

<sup>a</sup>From *t*-plot



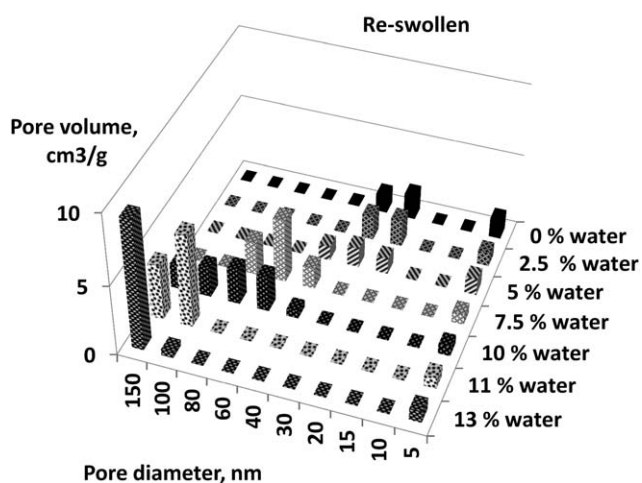
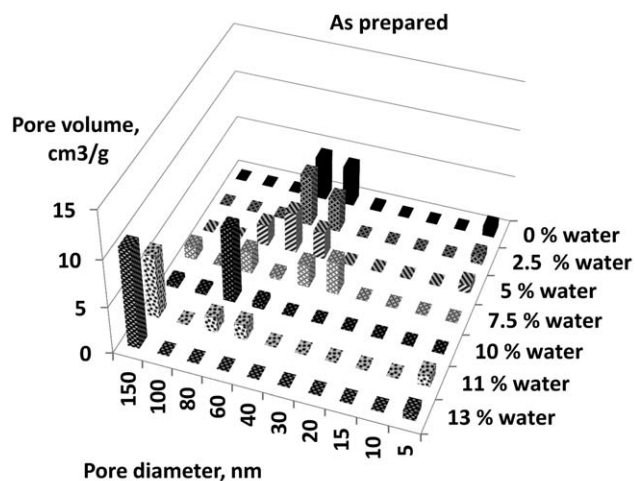
**Figure 3.** ISEC-determined volume distributions of pores of different sizes in the A-series of polymers re-swollen in THF.

Substantial variations in the dependence on the porogen water content were found between the total pore volumes of the dried polymers. The addition of water apparently increased the dry-state pore volume, but this could be due to the varying extents of pore collapse during drying.

As no liquid was observed outside the polymer monolith at the end of polymerization, the original pore volumes created during polymerization should correspond to the volumes of the porogenic solvent used ( $10\text{--}12\text{ cm}^3\text{ g}^{-1}$ ). However, in the dried polymers were found pore volumes only  $0.37\text{--}1.05\text{ cm}^3\text{ g}^{-1}$  (see Table II), which illustrate how great the pore collapse during drying is and how limited is the significance of dry state morphology for formation of ideas about the process of the morphology development during the polymerization. To get a better idea of the character of the polymer morphology in its expanded state, the polymers of the A-series were investigated by inverse steric exclusion chromatography (ISEC), which can provide information on the morphology of the polymers in their THF-swollen state. The results in the form of modeling

**Table III.** Comparison of the Volume of Porogenic Solvent Used in the Polymer Preparation and the Total Volume of Pores in Reswollen Polymer of the A-Series as Determined from ISEC

Sample designation	Volume of porogen per unit of monomer mass ( $\text{cm}^3\text{ g}^{-1}$ )	Total pore volume in reswollen polymer from ISEC ( $\text{cm}^3\text{ g}^{-1}$ )
A-0	10	3.8
A-1	10.1	1.6
A-5	10.5	4.4
A-8	10.8	9.4
A-10	11	9.8
A-15	11.5	9.2
A-20	12	10.1



**Figure 4.** ISEC-determined volume distribution of pores of different sizes in the B-series of polymers in the “as prepared” state as well as in the samples dried and re-swollen in THF.

the morphology as a set of discrete pore fractions of cylindrical shape are shown in Figure 3.

In almost all the polymers, we detected a bidisperse pore structure with one category exhibiting dimensions of  $5\text{--}15\text{ nm}$  in all the samples and the second category displaying growing dimensions with an increased content of water in the porogenic solvent (from  $20\text{--}30\text{ nm}$  in A-0 to  $100\text{--}150\text{ nm}$  in A-20). The total volume of pores in the reswollen polymers was found to be substantially higher than in the dried samples, but values similar to the volume of porogenic solvents used during the polymer preparation were found only at higher water concentrations in the porogenic solvent (Table III). It seemed that the presence of water in the porogen influenced the ability of the polymer morphology to re-expand after collapse during the drying. However, the swollen-state morphology, as evaluated on previously dried samples, evidently remained different from what was created during the polymerization.

Hence, we decided to prepare a second series of samples which could be investigated by ISEC even without an intermediate drying step. Because of logistic reasons, the experimental



**Table IV.** Comparison of the Volume of Porogenic Solvent Used in the Polymer Preparation and the Total Volume of Pores in Reswollen Polymer of the B-Series in the “As Prepared” State and After Drying and Reswelling Determined from ISEC

Sample designation	Volume of porogene per unit of monomer mass ( $\text{cm}^3 \text{g}^{-1}$ )	Total pore volume in the polymers ( $\text{cm}^3 \text{g}^{-1}$ )		
		As prepared <sup>a</sup>	Dried <sup>b</sup>	Reswollen <sup>a</sup>
B-0	10.0	9.9	0.7	4.5
B-2	10.2	9.9	1.5	4.6
B-4	10.5	10.2	1.1	4.6
B-6	10.8	9.9	1.7	9.1
B-8	11.0	9.2	1.7	9.9
B-10	11.2	11.0	–	11.3
B-12	11.5	11.4	–	10.6

<sup>a</sup>From ISEC.<sup>b</sup>From nitrogen adsorption.**Table V.** Amounts of Unreacted Second Vinyl Groups of DVB in Polymer Samples of the A-Series as Determined by  $^{13}\text{C}$  Mas NMR

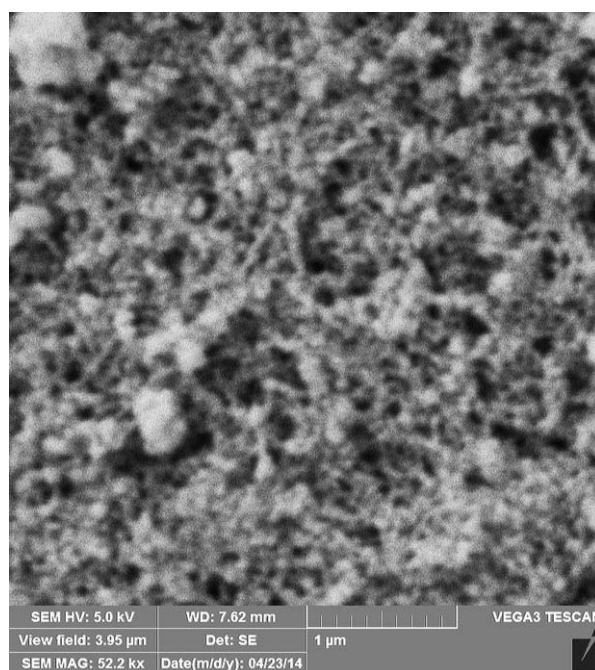
Sample	A-0	A-1	A-5	A-8	A-10	A-15	A-20
Unreacted second vinyl groups (% of starting)	7.6	14.5	20.5	19.0	11.0	9.7	7.7

technique was slightly different and the starting compound, albeit nominally similar (80% tech. DVB), was of different origin. After polymerization, samples of this B-series were divided into two portions—one was ground and wet-sieved and then immediately subjected to the ISEC measurements, and the second prior to grinding and sieving was dried and then reswollen in THF for the ISEC investigation.

The results of the characterization of the swollen morphology for both groups of samples are shown in Figure 4. The results suggest that the morphologies of the “as prepared” polymers with different ratios of water in the porogenic solution were not too different. The morphology appeared to be bidisperse, with a small volume of narrow 5-nm pores and with a predominant amount of the pores in the range 40–80 nm. There was a slight inclination toward a diminution of the narrower pores and an increased diameter of the bigger pores with a higher water concentration, but this tendency was rather weak. Similarly to the A-series, a much stronger influence of the water content in the porogenic solvent was found for the polymers that were dried after preparation and then reswollen in THF.

Table IV compares the total pore volumes in the swollen polymers, as determined by ISEC, with the volumes of porogenic solvent used in their preparation. The pore volumes for the polymers examined immediately after polymerization, without an intermittent drying step, corresponded reasonably well with the volumes of the porogen in all the samples. The collapse of the morphology during drying diminished the pore volume to less than 1/5 of the original value. Subsequent reswelling was able to restore the pore volume to sizes comparable with original values only in the polymers prepared with a water concentration higher than about 5% of the total porogenic solvent volume.

From the comparison of Figure 4 and Table IV it seems that the water addition to the porogenic solvent had a more dramatic influence on the polymer's ability to restore the original morphology by reswelling after drying than on the pore size distribution itself. The observed differences in the “ruggedness” or elasticity of the polymer skeleton could be induced by dissimilarities with regard to actual crosslinking due to a varying conversion of the second vinyl groups of the DVB units.

**Figure 5.** SEM micrograph of dried polymer B-10.

A  $^{13}\text{C}$  MAS NMR assessment of the residual vinyl group content in the polymers of the A-series was carried out according to the approach developed by Law et al.<sup>17</sup> with a Bruker Avance III HD 500 WB/US NMR spectrometer at 125 MHz with magic angle spinning frequency  $\omega_r = 20$  kHz. The results shown in Table V do not exhibit a correlation with the amount of water in the porogen solvent nor with the ability of the polymers to restore their morphology by reswelling of dried samples. However, it is remarkable that the measured amounts of residual vinyls were much lower than the values (around 50%) found in polymers prepared from a similar monomer (80% tech. grade DVB) by conventional suspension polymerization.<sup>17,18</sup>

## CONCLUSIONS

The high porosity of the investigated poly(DVB) together with the relatively narrow pore size distribution is not compatible with the geometrical model depicting pores as spaces between polymer nodules commonly created in the conventional porous polymers by the macrosyneresis mechanism.<sup>19</sup> If the porosity in such system would be higher than 50–60%, the polymer nodules could not be in mutual contact sufficient for mechanical stability of the material. The stable, highly porous morphology of the “solvothermally” prepared poly(DVB)’s is explainable by an inverse geometry, a foam-like structure with continuous polymer phase surrounding relatively voluminous cavities. Even if SEM micrograph (Figure 5) depicts dried, collapsed sample, it supports the presented findings and shows fundamental difference of the investigated poly(DVB) from conventional porous styrenic polymers as presented e.g., by Guyot.<sup>1</sup> Such morphology could be created only by microsyreresis.<sup>20</sup> While macrosyneresis generates polymer microparticles surrounded by a continuous liquid phase, microsyreresis produces droplets of liquid surrounded by a continuous polymer phase. Microsyreresis is induced when mutual interconnection of the growing polymerization centers into a continuous network occurs before the phase separation starts. So far, it has been described only for low-crosslinked materials, especially for cases when deswelling—induced for instance thermally—occurs in an already formed gel matrix.<sup>20–22</sup> Formation of enough extensive interconnected networks before start of the syneresis in the “solvothermal” polymerization of divinylbenzene could be facilitated by very high dilution of monomers by solvation “good” porogenic solvent like THF. Because of the high dilution, in initial stages the polymerization is more favored the growth of polymer chains by adding new monomer unit than formation of crosslinks than mutual interconnection of polymer chains. Solvation of growing polymer chains with “good” solvent also help to keep them in extended configuration rather than forcing them into tighter polymer coils. It is probable that at these conditions is created rather extensive network, which at the start of microseparation of the solvent is hard to break into polymer nodules and instead of it as the discontinuous phase appear liquid nanodroplets. When the porogenic solvent contains a precipitating component like water, the microsyreresis phase separation occurs sooner than with pure THF and there are created bigger pores than with

pure THF—the bigger the bigger water concentration is (see Figure 3). The syneresis pushes the polymer chains together and makes possible their interconnection by crosslinks. The water-rich nanodroplets could effectively compress and orient the grooving polymer chains in the continuous polymer phase. This explains why the polymer morphology created with a THF-water mixture exhibits better elasticity than that prepared with pure THF (or with a very low water concentration), in spite of the similar degree of chemical crosslinking (i.e., similar content of residual vinyls). Existence of microsyreresis in highly crosslinked polymer matrices is only possible explanation of creation of the mesoporous morphology of the “solvothermally” prepared polymers stable even at high porosity reaching 90%. However, proving the hypothesis about the mechanism of this process will require further research.

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