Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 2862–2871

polymer

www.elsevier.com/locate/polymer

Control of pore formation in macroporous polymers synthesized by single-step γ-radiation-initiated polymerization and cross-linking

Ágnes Sáfrány[a,*], Barbara Beiler[a,b], Krisztina László[b], Frantisek Svec[c]

[a]*Radiation Chemistry Department, Institute of Isotopes, CRC Hungarian Academy of Sciences, P.O. Box 77, H1525 Budapest, Hungary*
[b]*Department of Physical Chemistry, Budapest University of Technology and Economics, Budapest, Hungary*
[c]*Department of Chemistry, University of California, Berkeley, California, USA*

Received 27 October 2004; received in revised form 9 February 2005; accepted 11 February 2005
Available online 2 March 2005

Abstract

Pore formation during the γ-radiation-initiated synthesis of porous polymer monoliths has been systematically investigated. The major advantages of this approach include absence of typical free radical initiators and ability to obtain monoliths with the same chemical structure in a variety of sizes, shapes and porous characteristics. Monomer concentration, type of porogenic solvent, temperature, irradiation dose, and dose rate are variables mostly affecting the properties of the final polymer monolith. Monoliths prepared from diethyleneglycol dimethacrylate in the presence of 60–80 vol.% of lower alcohol such as methanol and 2-propanol with large channel-like pores in the micrometer range exhibit both good flow-through characteristics and appropriate rigidity. The optimum doses and dose rates were found in the range 20–40 kGy and 10–16 kGy/h, respectively.

Keywords: Synthetic polymers; Radiation polymerization and cross-linking; Porous monolithic column

---

1. Introduction

In the past several decades macroporous crosslinked polymers mostly in form of spherical particles have been used in a variety of applications ranging from chromatographic separation and purification, adsorbents, immunodiagnostics, to combinatorial chemistry. The important characteristic of such polymers is the retention of their porous structure even in the dry state. Their morphology is rather complex. It typically consists of microglobules aggregated in larger clusters. The pores are actually the irregular voids between these clusters (macropores), between the individual microglobules (mesopores) and within the microglobules (micropores). In a search for enhanced and simple to prepare chromatographic separation media, several groups found that macroporous polymers in the shape of a continuous rod could be a useful alternative to columns packed with particles [1–4]. Such a porous polymer rod, often called 'monolith', is characterized by a system of interconnected pores with a bimodal distribution: the small pores provide the desired surface area required for the specific interactions, while the larger channels allow to achieve a high flow rate at moderate pressures. Therefore, major advantages of using such monoliths in chromatography include an increased speed, capacity and resolution. Moreover, they eliminate most of the problems related to the column packing procedure. These macroporous polymer monoliths are usually prepared by a simple molding process that has been introduced in the early 1990s [5,6] and used by many since. The general procedure comprises polymerization of a monovinyl monomer or a mixture of monovinyl monomers together with a cross-linker in the presence of at least one porogenic solvent initiated by a free radical initiator in an unstirred mold. Decomposition of the initiator in radical polymerization is usually induced thermally at a specific temperature. The variables that control pore size are the percentage of the crosslinker, the type and volume of the porogen, the concentration of the free radical initiator in the reaction mixture, and the reaction temperature. Photo-induced initiation can also be used in which case the synthesis is much faster and can be achieved even at low temperature [7–10]. Detailed reviews of preparation

---

* Corresponding author. Tel./fax: +361 3922548.
E-mail address: safrany@iki.kfki.hu (A Sáfrány).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.02.024

methods for numerous applications have recently been published [11–15].

We have shown previously that it is also possible to prepare monoliths in molds by initiating the polymerization by ionizing radiation [16,17]. This method has the advantage of generating radicals directly on the monomer, thereby avoiding use of any initiator. The polymerization can be carried out at any temperature in a very short time, even within minutes. Owing to the larger penetration depth of ionizing radiation compared to photoinitiated polymerization, the size and shape of the monoliths can be readily optimized for the intended application. Functional groups can be introduced either during the preparation or in an additional step. This method is a modification of the radiation-initiated precipitation polymerization used successfully for the preparation of monodisperse polymer microspheres [18–22]. The characteristic feature of this method is irradiation of a homogeneous solution of a divinyl monomer in an organic solvent without stirring, with phase separation resulting from the insolubility of crosslinked particles in the reaction mixture. The monomer concentration and the type of porogenic solvent are factors most profoundly influencing the properties of the final polymer. Other important factors are the irradiation temperature, the dose, and the dose rate.

This paper presents our systematic study aimed at the development of radiation-initiated polymerization and crosslinking for the preparation of macroporous polymer monoliths. We have chosen to investigate methacrylate-type monoliths, since beside acrylamide-based and polystyrene-based polymer monoliths, they are the most widely studied stationary phases for chromatographic applications [14,16, 23–25] and for affinity processes [26]. We also define the relationship between the porous properties and the synthesis parameters.

2. Experimental

2.1. Materials

Diethyleneglycol dimethacrylate (DEGDMA- Aldrich) monomer was used for the preparation of monoliths. The porogenic solvents were methanol (MeOH-AnalityCals, Carlo Erba), ethanol (EtOH-Reanal), 2-propanol (PrOH-Merck), t-butanol (BuOH-Merck), acetone (Reanal) ethyl acetate (EtAc-Reanal), dioxane (Diox-Aldrich), acetonitrile (AN-Carlo Erba), and tetrahydrofurane (THF-Reanal). All chemicals were HPLC grade and used as received.

2.2. Preparation of monoliths

The monoliths were prepared by using an in situ radiation polymerization method. Teflon tubes approx. 25 mm long and 4 mm ID were placed in plastic bags. Typically two tubes were located in each bag. The tubes were filled with deoxygenated solution of DEGDMA in the selected solvent, sealed under nitrogen and irradiated in a ^{60}Co γ-source both in horizontal and vertical position, but no difference was observed. The effect of the irradiation conditions on the monolith formation was investigated by varying the total absorbed dose in a range of 1–50 kGy at several different dose rates and temperatures. The dose and dose rate was determined by using ethanol–chlorobenzene dosimeter solution. Irradiation at different temperatures was performed by placing the tubes in a device enabling controlled heating or cooling. The temperature was recorded using a thermocouple placed inside the device next to the sample tubes. All monoliths were prepared in duplicates, and the same irradiation condition was repeated several times. After the irradiation was completed, the excess polymer at the outside of the tube was mechanically removed, and the tube was attached to a chromatographic pump (Liquochrom Model 2010, LMIM, Hungary) via standard chromatography fittings. Solvent was pumped through the tube to free the monolith from unreacted components mainly the porogenic solvents, and to determine the flow-through characteristics. The monolith was later removed from the tube and used for further measurements. Removing the monolith was difficult as it stack to the tube and since no shrinkage during polymerization occurred.

Alternatively, cleaned 225 or 450 mm long and 4 mm ID stainless steel chromatographic columns were used, sealed on one side, filled with the polymerization mixture, sealed at the other side, and irradiated. After the irradiation, the column was directly connected to a chromatograph. First the solvent was pumped through to wash the monolith and then acetonitrile or tetrahydrofuran was used as the mobile phase for measurements of the back pressure.

2.3. Conversion measurement

The conversion of the monomer into crosslinked polymer was investigated by irradiating deoxygenated solutions of DEGDMA in selected solvents at ^{60}Co γ-source with doses up to 50 kGy, at constant 16 kGy/h dose rate. After irradiation, the obtained polymer was washed several times with the solvent in an ultrasonic bath and dried until constant weight. The conversion was calculated by comparing the weight of the crosslinked polymer to the weight of the monomer in the feed solution.

2.4. Characterization of porous properties

The morphology of the monolith was observed using scanning electron microscopy (SEM, JEOL JSM 5600LV). Approximately 1 mm thick samples were cut from the monolith, fixed to the sample holder, and sputter-coated with platinum/palladium (JEOL JFC-1300 Auto Fine Coater). The polymer formed outside the tube was also used for SEM measurements, but no difference could be noted between the polymer formed inside and outside of the

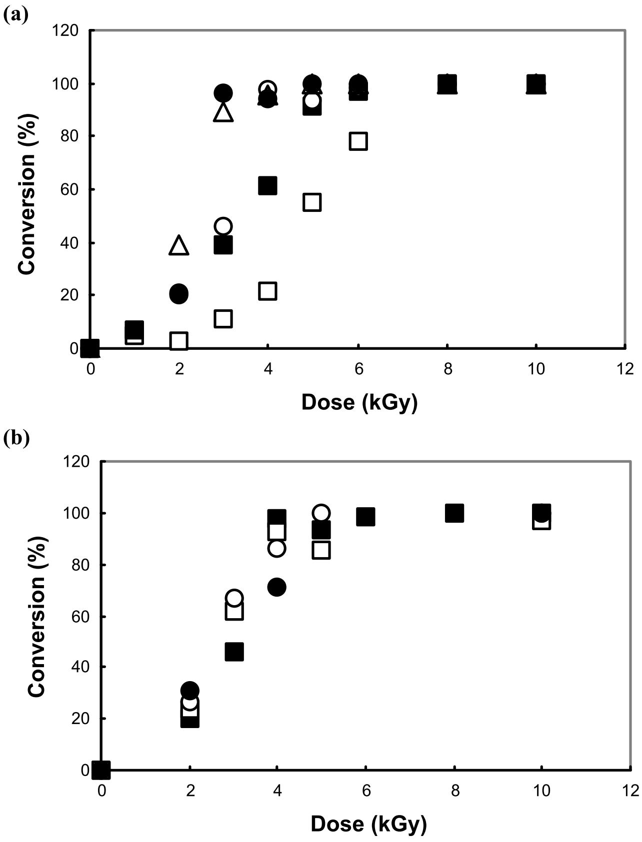

Fig. 1. Reaction kinetics of polymerization/crosslinking in solutions (a) at different DEGDMA concentrations in methanol: 10 vol.% (open square), 20 vol.% (full square),30 vol.% (open circle), 40 vol.% (full circle), and 50 vol.% (triangle); and (b) 30 vol.% DEGDMA in methanol (full square), ethanol(open square), 2-propanol (open circle) and tert-butanol (full circle). The irradiation was done at 25 °C with the dose rate of 16 Gy/h.

tube. The photographs were usually taken with several different magnifications between 500× and 20,000×, but for easier comparison, all SEMs shown in this paper are taken with 5000× magnification.

The pore size distribution of the monolithic materials was determined using an Autopore III 9400 mercury intrusion porosimeter (Micromeritics, Norcross, GA). Nitrogen adsorption/desorption isotherms were monitored at 77 K using an Autosorb-1 (Quantachrome) apparatus. The apparent surface area was calculated using the BET equation.

The flow of selected solvents through the monolith also affords information about the porous properties. For these measurements, the monolith was connected to the chromatographic pump, and acetonitrile or THF was pumped through at a constant pressure. The flow rate was measured at several different pressures in the range of 0.1–0.4 MPa for each sample. All measurements were taken in triplicate, averaged, and recalculated to the pressure of 0.1 MPa and the unit surface area of the monolith. The result is called flux in this paper.

Alternatively, the long columns were connected to the HPLC system, and the pressure was recorded at different flow rates.

3. Results and discussion

The objective of our study was to define the relationship between parameters characterizing the preparation and porous properties of the monoliths. It has been established that the monomer concentration in the polymerization mixture, the type and percentage of the porogenic solvent and the reaction temperature are the parameters of major importance in standard free radical polymerization leading to monoliths. Two more parameters can be used to control the radiation initiated polymerization: the absorbed dose and the dose rate.

3.1. Effect of monomer concentration

When a monomer is irradiated in an organic solvent, free radicals are generated homogeneously in the system. These radicals then initiate the polymerization reaction typically forming linear, branched, and finally crosslinked macromolecules. Since the monomer DEGDMA used in this study has two vinyl groups, both polymerization and crosslinking occur simultaneously. Being insoluble, the crosslinked molecules precipitate and form nuclei for the growing particles. During further irradiation, radicals are generated both on the monomer and polymer molecules in solution and on the precipitated globular nuclei that continue to grow in size, interconnect with neighbors, and finally form the porous matrix. Fig. 1(a) shows the conversion of DEGDMA into cross-linked polymer when irradiated in methanol at a dose rate of 16 kGy/h, while Fig. 1(b) presents the conversion plots for 30 vol.% DEGDMA in selected solvents. Although the process is faster in the more concentrated solutions, the complete transformation of the monomer into crosslinked polymer is accomplished within less than one hour in all cases. To avoid the effect of the conversion on the porous properties of the monolith (the pores are generally larger at lower conversion [27]) and investigate only the effect of monomer concentration on the pore size distribution, only monoliths obtained with 30 kGy were compared. The pore size distribution profiles determined by mercury intrusion porosimetry, and the surface areas calculated from the curves obtained from nitrogen adsorption/desorption of these samples, are presented in Fig. 2.

It should be noted that a direct comparison of the data obtained from nitrogen isotherms and mercury intrusion porosimetry is not appropriate, as each method uses different pore shape model and covers a different range of pore sizes, thus giving complementary information. While mercury porosimetry is best suited for characterization of large and medium sized pores, the nitrogen adsorption/desorption method concerns small pores that contribute

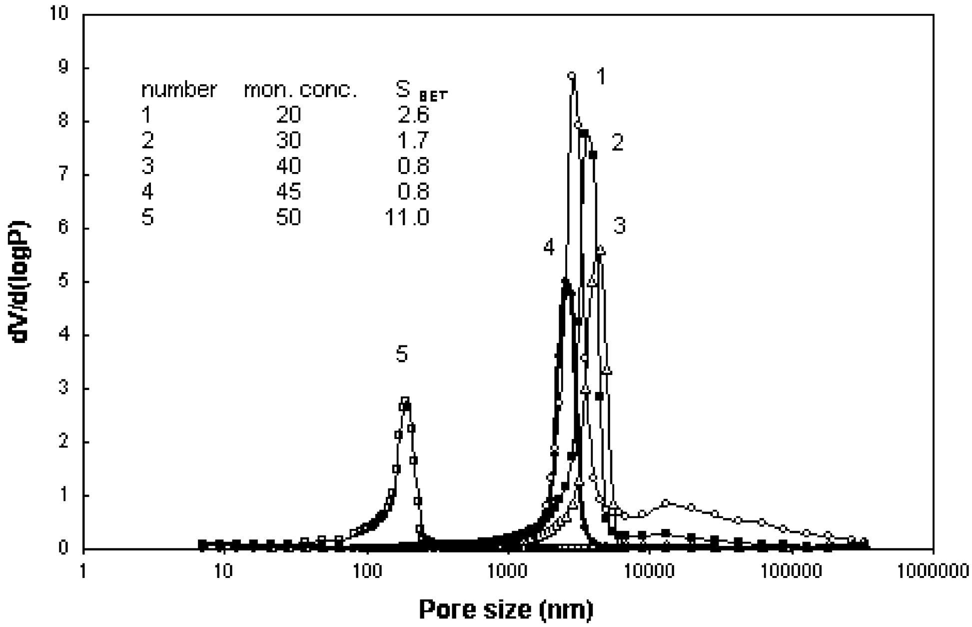

Fig. 2. Differential pore size distribution profiles determined by mercury intrusion porosimetry for monoliths prepared by irradiation of solutions with following DEGDMA concentrations in methanol: 20 vol.% (1), 30 vol.% (2), 40 vol.% (3), 45 vol.% (4) and 50 vol.% (5). The irradiation was done at 25 °C, with dose rate of 16 kGy/h, with the total dose of 30 kGy. The specific surface area, S_{BET} (m^2/g), calculated from nitrogen adsorption isotherms for each sample is also given.

mostly to the surface area. For example, irradiation of 20 vol.% DEGDMA solution in methanol affords polymer monolith with three different types of pores. Most of the pores have a diameter around 3 μm. In addition, macropores with a diameter as large as 30 μm and mesopores with a diameter of around 5 nm can also be observed. With an increasing monomer concentration up to 45 vol.%, the pore size distribution becomes narrower, and the peak at about 30 μm completely disappears. The median pore diameter further decreases to about 170 nm at 50 vol.%. This result is not unexpected since a larger number of nuclei forms in the unit volume during the irradiation of a solution with higher monomer concentration [27]. These nuclei compete for the monomer, and can grow only little in size before they touch each other. Therefore, the voids between microglobules in the clusters of the final matrix—the macropores—have also smaller size. It has been shown earlier [7] that polymer monoliths prepared from mixtures with a higher monomer content have smaller pores. In the present case, since DEGDMA is a divinyl monomer, an increase in its concentration is equivalent to an increase in the percentage of the crosslinker. Both these effects lead to the final structure featuring smaller pores. In fact, the swelling of the nuclei might be the controlling factor, since a more crosslinked nucleus is less likely to swell in both the solvent and the monomer, therefore the size of the final globule should remain relatively small. This shift in the pore size distribution towards smaller pores is accompanied with an increase in specific surface area. Such monoliths with high surface areas might be useful as adsorbents.

The morphology of the polymer monoliths is illustrated on SEM micrographs (Fig. 3) taken with the same magnification. These micrographs reveal the familiar internal structure of monoliths formed from microglobules of relatively uniform size agglomerated into larger clusters. Clearly, monolith prepared from less concentrated monomer solution contains large voids in the micrometer range between the clusters, while the polymer prepared from a 50 vol.% solution has a dense structure with closely packed small globules that are at least one order of magnitude smaller. These micrographs correlate well with the results of porosity measurements.

From the application point of view, monoliths intended for use in various chromatographic separation and purification processes must allow liquid to permeate through the pores at a pressure as low as possible. To test their permeability the monolithic columns were connected to a HPLC pump and acetonitrile and THF were used as the mobile phase. These solvents were pumped trough the monolith with several different pressures during which the flow rates was recorded, and finally all data was recalculated to the pressure of 0.1 MPa. Fig. 4(a) shows the flow rate trough the unit surface area (flux) at a normalized pressure of 0.1 MPa through the monolith prepared from solutions with increasing monomer concentration in methanol. As the results show, the higher the monomer percentage, the lower the permeability. No measurable flow was observed for the column prepared from 50 vol.% solution of monomer even at a pressure of 0.4 MPa. This was not unexpected, since it was shown earlier that a network of large channel-like pores

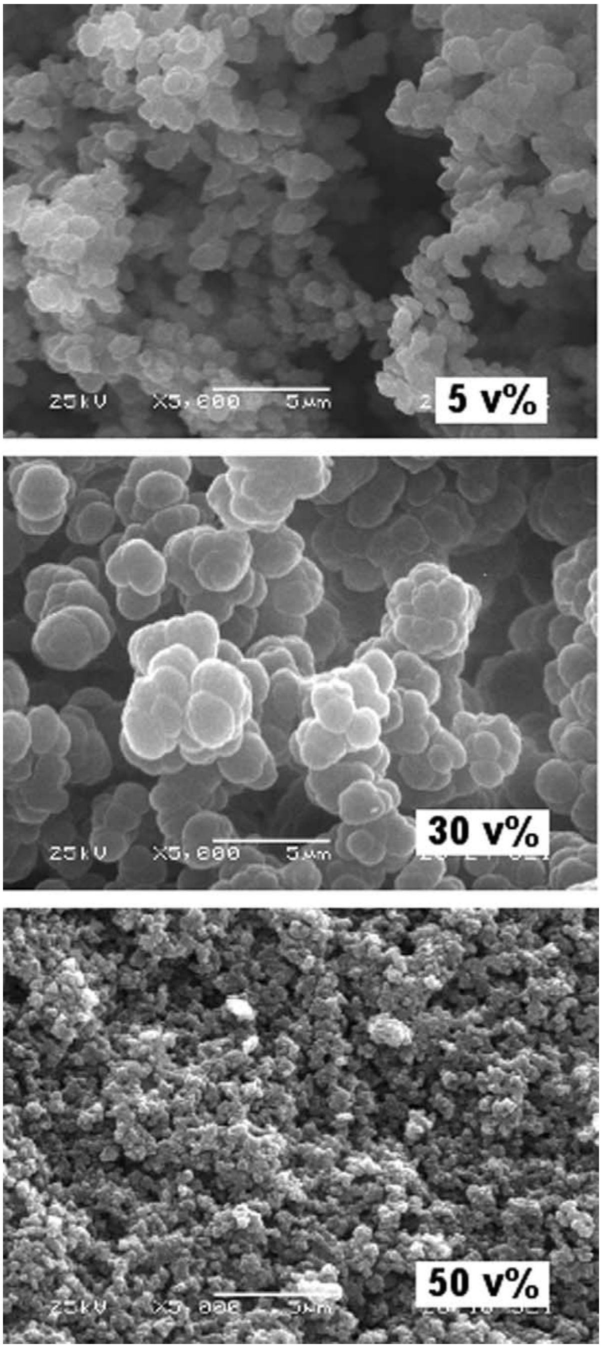

Fig. 3. SEM photographs of monoliths obtained from methanol solutions with different monomer content: 5 vol.% (upper); 30 vol.% (middle); 50 vol.% (lower). The bar represents 5 μm. The irradiation was done at 25 °C, with dose rate of 16 kGy/h, with the total dose of 30 kGy.

with a size in the micrometer range is required to achieve good flow-through characteristic [7] while this monolith has only an order of magnitude smaller pores. Fig. 4(b) shows the effect of flow rate on back pressure for a 25×4 mm ID column containing a monolith prepared from 30 vol.% DEGDMA solution in methanol. The linear fit confirms both incompressibility of the monolith, and high permeability to flow for both solvents used as the mobile phase.

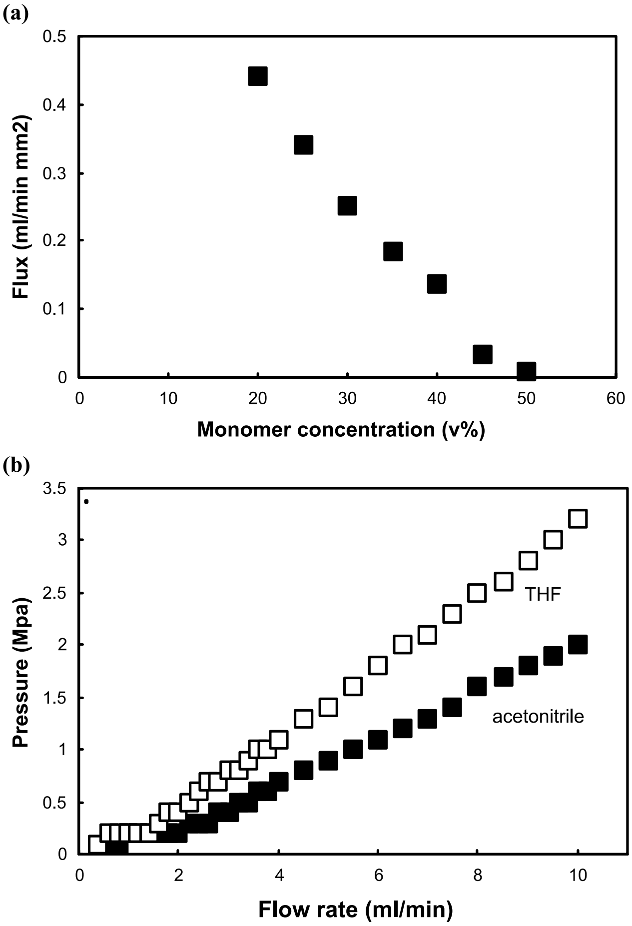

Fig. 4. Flow characteristics of the monoliths measured with columns connected to the chromatograph: (a) Flux dependence on the monomer concentration in the feed solution in methanol. The irradiation was done at 25 °C, with dose rate of 16 kGy/h, up to a total dose of 30 kGy. The flux was obtained by measuring the flow rate of acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa and unit surface area. (b) Pressure response at increasing flow rate for a monolith synthesized by irradiating a 30 vol.% DEGDMA in methanol solution in a stainless steel column (225 mm×4 mm) at 25 °C, with dose rate of 16 kGy/h, and total dose of 30 kGy. Two different eluents, acethonitrile and THF were used.

3.2. Effect of porogenic solvent

The solvent has a significant effect on the porous structure of monoliths, thus providing another tool enabling control of the pore size. Since radiation and photoinitiated polymerization can be carried out at any temperature, these processes afford an additional benefit of allowing the use of a broad range of solvents including those that would be too volatile to be used in conventional polymerization at high temperature, such as methanol or acetone. A series of experiments revealed that polymerization of DEGDMA in alcohol as a solvent resulted in monoliths with large pores. In contrast, solvents such as acetone, THF, ethylpropionate, ethylacetate, and dioxane lead to monoliths with very small pores. These results are similar to those observed for monolith prepared by photoinitiation, and are explained by

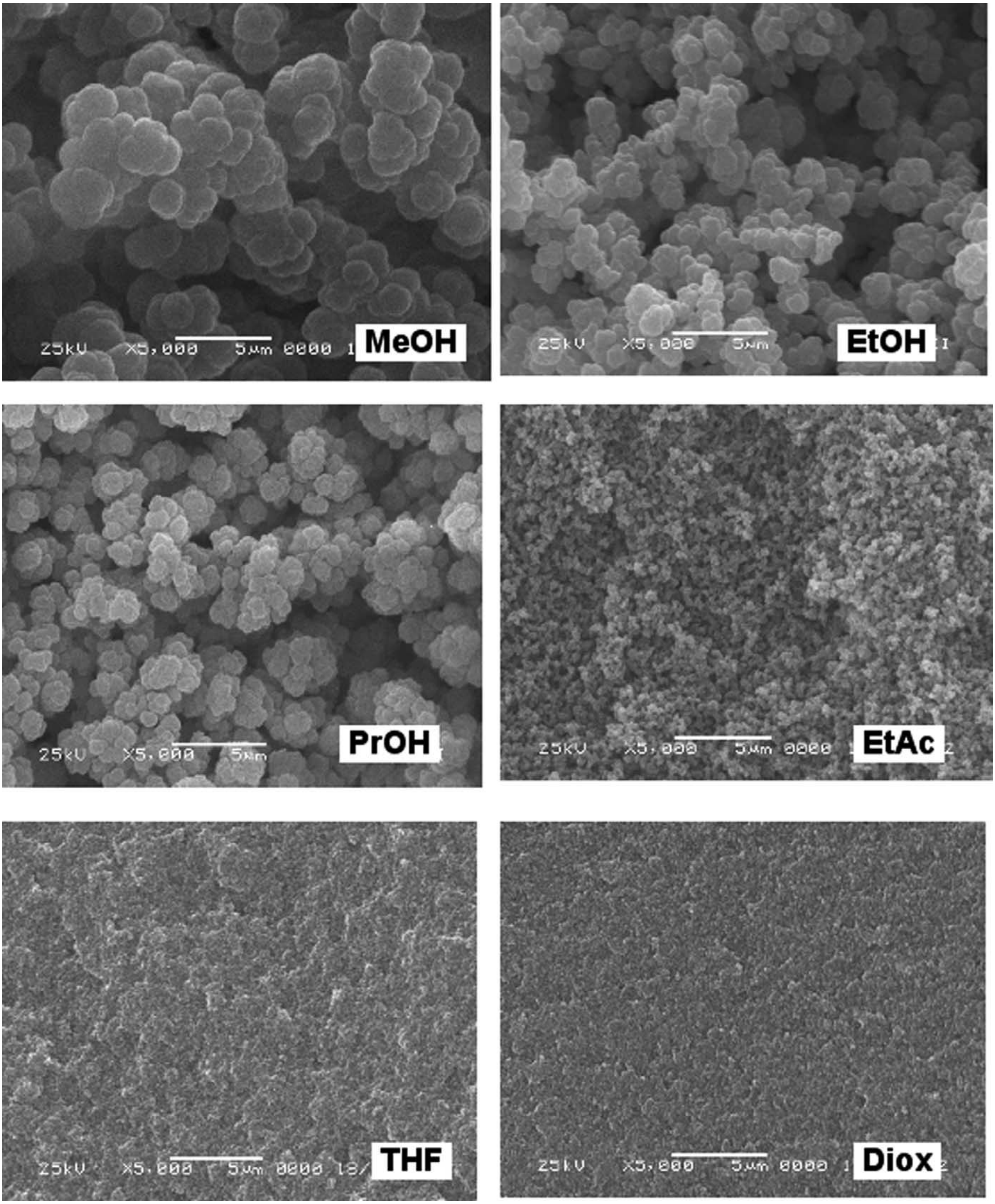

Fig. 5. SEM photographs of monoliths obtained from 30 vol.% DEGDMA in various solvents. The bar represents 5 µm. The irradiation was done at 25 °C, with dose rate of 16 kGy/h, and total dose of 30 kGy.

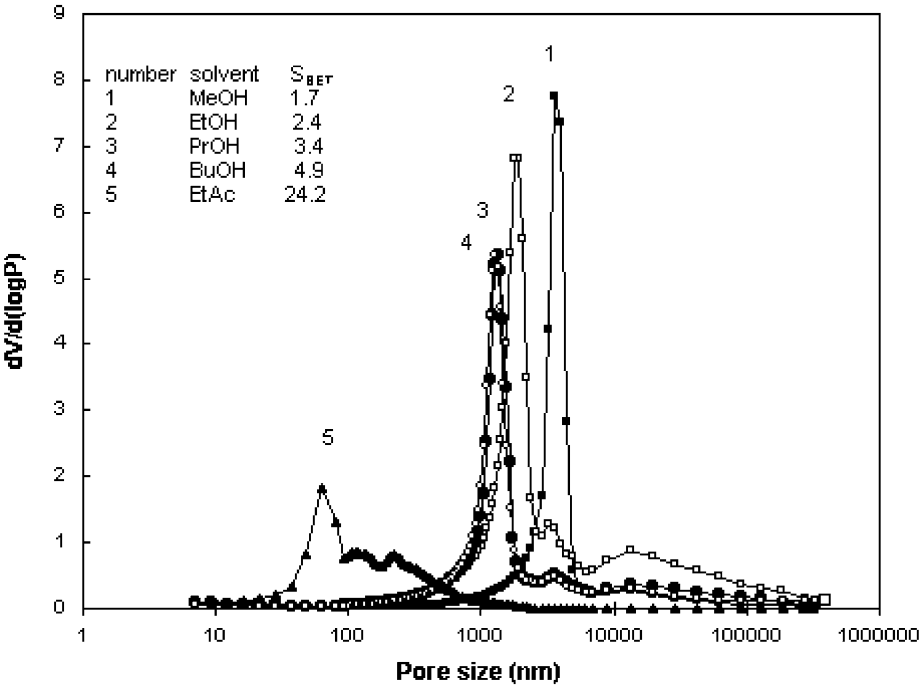

Fig. 6. Differential pore size distribution profile determined by mercury intrusion porosimetry for monoliths prepared by irradiation of 30 vol.% DEGDMA solutions in the following solvents: methanol (1), ethanol (2), 2-propanol (3), tert-butanol (4), and ethylacetate (5). The irradiation was done at 25 °C, with dose rate of 16 kGy/h, and total dose of 30 kGy. The specific surface area, S_{BET} (m^2/g), calculated from nitrogen adsorption isotherms for each sample is also given.

better solubility of monomer in these organic solvents [28]. The polymerization starts from an initially homogeneous solution until the growing crosslinked polymer precipitates. Further polymerization and crosslinking continues both in the swollen nuclei and in solution. When the solvent is a good solvent for the polymer, phase separation occurs later, and the resulting pores will thus be smaller. Since the solubility parameter (δ) of DEGMA was calculated to be 8.5 H [29], all solvents with δ close to that value would be good solvents for this monomer. From the solvents we have used, acetone (9.9 H) [30] THF (9.1 H) [30], ethylpropionate (8.4 H) [30] and ethylacetate (9.1 H) [30] meet this requirement. On the other hand, methanol, ethanol, 2-propanol and t-butanol ($\delta = 14.5$ H; 12.7 H; 11.5 H and 10.5 H, respectively [30]) can be considered as poor solvents. In these solvents due to lower solubility of the monomer and polymer the phase separation will occur earlier and the polymerization and crosslinking will preferentially continue in the nuclei that is more swollen in the monomer than in the solvent. Therefore, the nuclei will be larger, as well as the voids between them.

SEMs in Fig. 5 visualize the porous structure of monoliths obtained using different solvents under otherwise identical preparation conditions. The significant size difference of the microglobules, clusters and channels within the monoliths confirm the profound effect of the solvent type on the morphology. Since all the monoliths have the same chemical composition, this difference is mostly the result of the solubility parameters of the solvents.

The results of mercury intrusion porosimetry and nitrogen adsorption/desorption measurements are shown in Fig. 6. The pore size distribution profile obtained by mercury porosimetry exhibits a rather narrow peak close to median, and one or two small peaks in the range of larger pores. Monolith obtained using methanol solution has a median pore diameter of around 3 μm, with a small percentage of pores having a size of 30 μm. This peak shifts to smaller values with the decrease of the δ value of the solvent. At the same time, all these profiles exhibit small peaks with a decreasing height at 3 and 30 μm. The volume of small mesopores with a size of about 5 nm increases with the decrease of the δ of the solvent, resulting in higher specific surface area. The flow-trough characteristics of the monoliths obtained with acetonitrile pumped through them are presented in Fig. 7(a), and confirm the conclusions derived from porosity measurements. The flux increases with the increasing solubility parameters of alcohol, demonstrating again, that the farther the solubility parameters of the monomer and the solvent are (the poorer the solvent is), the bigger the pores of the obtained monoliths. The reason for these results, as explained earlier, is twofold: early phase separation followed by the preferential swelling of the crosslinked nuclei in the monomer. As a result, monoliths synthesized from methanol solutions afford the best flow-trough characteristics, as shown in Fig. 7(b), where the flow rate obtained at different pressures is compared for two monoliths, one obtained in methanol, the other in t-butanol. Similar results were also observed with methanol used as a porogen for photoinitiated preparation of monoliths [9].

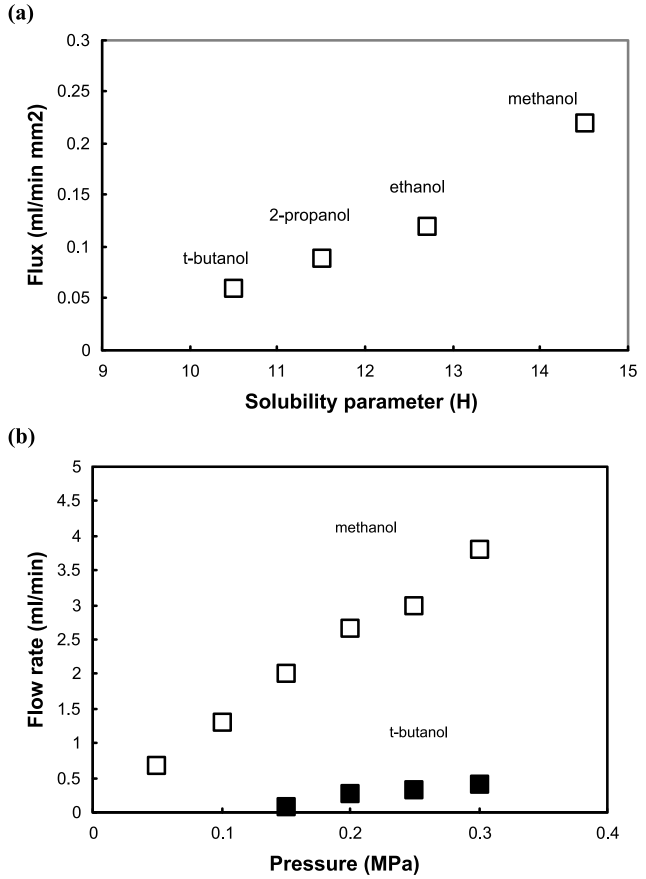

Fig. 7. (a) Flux dependence on the solubility parameter of the porogenic solvent used for the synthesis of monoliths. The monoliths were prepared by irradiation of 30 vol.% monomer solutions in methanol, ethanol, 2-propanol, and tert-butanol at 25 °C, with dose rate of 16 kGy/h and total dose of 30 kGy. The flux was obtained by measuring the flow rate of acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa and unit surface area. (b) Flow rate dependence on the applied pressure trough the monoliths prepared in methanol (open square) and in t-butanol (full square) as described above.

When radiation-initiated synthesis is concerned, the radiolysis of the solvent might be an additional parameter influencing the polymerization and crosslinking mechanism. For example, the chain transfer reactions caused by hydrogen abstraction from the alcohol molecules might enhance the termination of propagation reactions. Since the hydrogen abstraction is most favorable from the α-carbon, this effect is expected to be highest in methanol and lowest in t-butanol solution (methanol has 3, ethanol 2, 2-propanol 1, and t-butanol has no hydrogen on the α-carbon).

Monoliths prepared from DEGDMA solutions in acetone, ethylacetate, THF, dioxane and acetonitrile are clearly ill suited for flow-through applications. However, combinations of two different solvents in appropriate ratio hold promise for the preparation of monoliths with pore sizes in the desired range. Such explorations are in progress, and will be the subject of another publication.

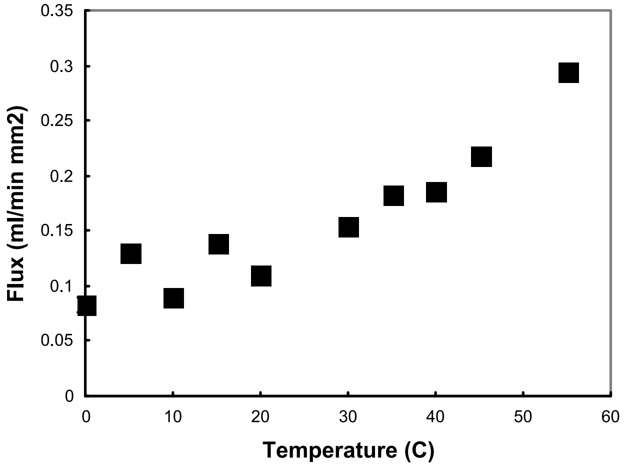

Fig. 8. Flow characteristics of the monoliths synthesized at different temperatures. The feed solution was 30 vol.% DEGDMA in methanol, dose rate of 16 kGy/h, total dose of 30 kGy. The flux was obtained by measuring the flow rate of acetonitrile pumped through the column at different pressures between 0.1 and 0.4 MPa, then recalculated to 0.1 MPa and unit surface area.

3.3. Effect of temperature

Temperature plays a crucial role in tailoring the pore size in thermally initiated polymerization [31]. This can be explained by the effect of temperature on the nucleation rate, and a general rule is that higher reaction temperatures lead to monoliths with smaller pores, mostly as a result of increased initiation rate. In our system with no real initiator present, the kinetics of initiation is not affected by temperature. Therefore, the effect of temperature in the radiation-initiated polymerization can be different. Indeed, the results of the flow characteristic measurements shown in Fig. 8 confirm this assumption: the flux through monoliths increases with increasing synthesis temperature. SEM micrographs (not shown here) support this by revealing larger voids in monoliths obtained at higher temperatures. (Monolith preparation conditions were constant: 30 vol.% DEGDMA in methanol irradiated with 30 kGy with constant dose rate of 16 kGy/h). Since polymers generally dissolve better at higher temperature, and the mobility of the molecules increase, phase separation is expected to occur earlier. In addition, the crosslinked and precipitated nuclei swell better at elevated temperature, and since the polymerization and crosslinking is favored in the nuclei and not in the solvent, larger globules will be formed.

3.4. Effect of dose rate

Changing the dose rate is another tool in radiation initiation enabling tailoring the porous properties. An increase in the dose rate while keeping all other parameters constant, leads to an increased rate of free radical formation, which in turn results in an increase in the rate of polymerization and cross-linking, therefore to earlier phase separation. Earlier phase separation leads to bigger nuclei and bigger pores between them. Indeed, we observed that an increase in the dose rate in the range 2–10 kGy/h almost doubled the flux through the monoliths. With further dose rate increase, the flux levels off. (Monolith preparation conditions were constant: 30 vol.% DEGDMA in methanol irradiated with 30 kGy at room temperature.) The reason for this feature might be that increased rate of reaction also means that the time required for quantitative monomer incorporation becomes shorter. Therefore at some point, the nuclei cannot grow to bigger size before the termination of the reaction. We are currently investigating the effect of the dose rate in more detail and also with even higher dose rates that can only be achieved by using an electron accelerator.

3.5. *Effect of the absorbed dose*

Absorbed dose represents the energy input to the reaction medium, influencing the conversion of the monomer to crosslinked polymer at lower doses and the number of crosslinks between the chains at higher doses. Irradiation can also lead to degradation of the polymer via chain scission, but this was not observed in our case. Therefore, it can be expected that the flux will decrease with the increasing absorbed dose. It should be remembered, that complete conversion of the monomer into monolith is attained at 7 kGy (Fig. 1), at which the extent of crosslinking is rather low. Monoliths prepared by using doses less than 10 kGy have large pores, but they lack proper mechanical strength and collapse after short-time use. After reaching the dose range of 20–40 kGy, the matrices become strong enough to be easily handled and the flow characteristics are suitable for flow-trough applications. Fig. 9 shows the dose effect on the morphology of the monoliths. At doses below the complete conversion the structure of the monolith is already visible, but the pores are closed. This effect also shows the weakness of the matrix since the pores collapsed during the sample preparation. At higher doses, a stable structure forms enabling intended application.

4. Conclusion

The preparation of monoliths by radiation induced polymerization is a good alternative to thermally and photoinitiated polymerization. The characteristic feature of this process is that it proceeds without addition of an initiator and monoliths with various sizes, shapes and porous characteristics can easily be prepared. The pore volume and pore size distribution of the molded polymer monoliths is controlled in a broad range via process variables such as dose and dose rate that are not available in ‘classical’ polymerization processes. Although demonstrated for a system with only one monomer, this process is easily amenable to copolymerizations that are currently under study.

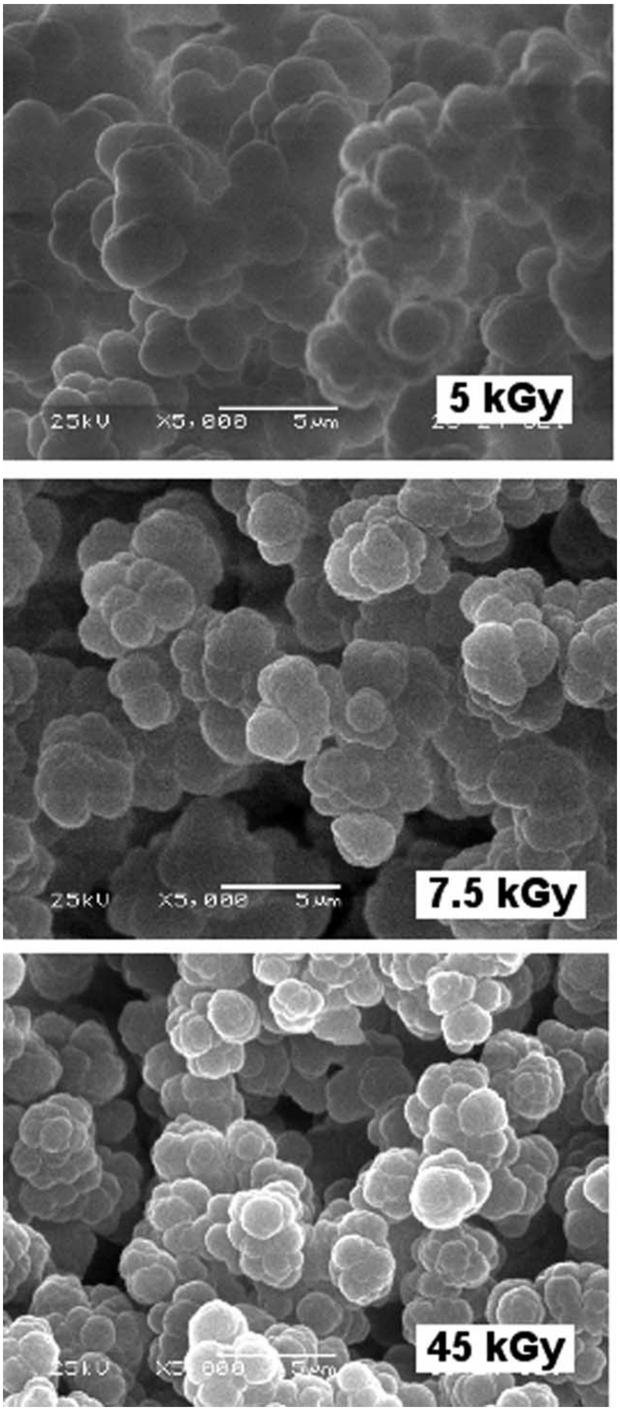

Fig. 9. SEM photographs of monoliths obtained from 30 vol.% DEGDMA in methanol irradiated with different doses: 5 kGy (upper); 7.5 kGy (middle); and 45 kGy (lower). The bar represents 5 μm. The irradiation was done at 25 °C, with dose rate of 16 kGy/h.

Acknowledgements

The help of Péter Hargittai with SEM measurements and the support of this research by the Hungarian Research Fund (OTKA 037285) and the International Atomic Energy Agency (HUN 11512) are gratefully acknowledged.

References

[1] Hjertén S, Liao JL, Zhang R. J Chromatogr 1989;473:273–5.

[2] Regnier FE. Nature 1991;350:634–5.

[3] Minakuchi H, Nakanishi N, Ishuzuka N, Tanaka N. Anal Chem 1996;68:3489–501.

[4] Fields SM. Anal Chem 1996;68:2709–12.

[5] Svec F, Fréchet JMJ. Anal Chem 1992;64:820–2.

[6] Svec F, Fréchet JMJ. Science 1996;273:205–11.

[7] Viklund C, Ponten E, Glad B, Irgum K, Horsted P, Svec F. Chem Mater 1997;9:463–71.

[8] Yu C, Davey MH, Svec F, Fréchet JMJ. Anal Chem 2001;73:5088–96.

[9] Yu C, Xu MC, Svec F, Fréchet JMJ. J Polym Sci, Part A: Polym Chem 2002;40:755–69.

[10] Rohr T, Hilder EF, Donovan JJ, Svec F, Fréchet JMJ. Macromolecules 2003;36:1677–84.

[11] Pucci V, Raggi MA, Svec F, Fréchet JMJ. J Sep Sci 2004;27:779–88.

[12] Buchmeiser MR. J Chromatogr A 2001;918:233–66.

[13] Josic D, Buchacher A. J Biochem Biophys Methods 2001;49:153–74.

[14] Svec F, Tennikova TB, Deyl Z, editors. Monolithic materials: preparation, properties, and applications. Amsterdam: Elsevier Science; 2003.

[15] Svec F. J Sep Sci 2004;27:747–66.

[16] Hilder EF, Svec F, Fréchet JMJ. J Chromatogr A 2004;1044:3–22.

[17] Grasselli M, Hargittai P, Smolko E, Sáfrány Á. NIMB 2001;185:254–61.

[18] Sáfrány Á, Beiler B, Grasselli M. POLYCHAR-10, World forum on polymer applications and theory, January 8–11, 2002, University of North Texas, Denton, USA, Book of Abstract, p. 65.

[19] Molday RW, Dreyer WJ, Rembaum A, Yen SPS. Nature 1974;249:81–5.

[20] Yoshida M, Asano M, Kaetsu I, Morita Y. Radiat Phys Chem 1987;30:39–45.

[21] Naka Y, Yamamoto Y, Hayashi K. Radiat Phys Chem 1992;40:83–8.

[22] Safranj A, Kano S, Yoshida M, Omichi H, Katakai R, Suzuki M. Radiat Phys Chem 1995;46:203–6.

[23] Lee MG. Polymer 2002;43:4307–9.

[24] Coufal P, Cihak M, Suchankova J, Tesarova E, Bosakova Z, Stulik K. J Chromatogr A 2002;946:99–106.

[25] Krajnc P, Leber N, Stefance D, Kontrec S, Podgornik A. J Chromatogr A 2005;1065:69–73.

[26] Platonova GA, Tennikova TB. J Chromatogr A 2005;1065:19–28.

[27] Meyer U, Svec F, Fréchet JMJ, Hawker CJ, Irgum K. Macromolecules 2000;21:7769–75.

[28] Viklund C, Svec F, Fréchet JMJ, Irgum K. Chem Mater 1996;8:744–50.

[29] Naka Y, Kaetsu I, Yamamoto Y, Hayashi K. J Polym Sci, Part A: Polym Chem 1991;29:1197–202.

[30] Weast RC, editor. Handbook of chemistry and physics. 58th ed. Cleveland: CRC Press; 1977–1978. p. C-727–732.

[31] Svec F, Fréchet JMJ. Macromolecules 1995;28:7580–2.