Monolithic Hydrophilic Poly(epoxy-acrylamide) Cryogels: Effect of Monomer Concentration on Cryogel’s Pore Structure and Properties

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ABSTRACT

Hydrophilic macroporous (~ 10-150 µm) polyacrylamide monolithic cryogels with epoxy functionality (Epoxy-MPAAGs) were synthesized at -12 °C by cryogelation technique using acrylamide, N,N’-methylene-bis-acrylamide and allyl glycidyl ether as the co-monomers, with ammonium persulphate and N,N,N’,N’-tetramethylethylenediamine as the initiator system. Total initial monomer concentrations of 5, 10 and 15 % (w/v) were employed. Solid-state diffuse reflectance infrared Fourier transform spectroscopy was used for chemical elucidation of the cryogels whilst scanning electron microscopy depicted the internal pore structure as the pore size distribution became affected by the initial monomer concentrations. Investigation on the influence of the monomer concentration in the range 5-15 % on characteristic properties of the cryogels, including gel fraction yield, degree of swelling, water flow resistance, pore volume and pore size distribution, suggested linearity in the order of relationships, an indication that new cryogels for specific applications can rationally be designed and produced through the variation of monomer concentration.

Keywords: Polyacrylamide, cryogel, pore size distribution

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INTRODUCTION
Monoliths are supports that consist of single continuous pieces of porous materials. These supports can be prepared in various structures such as columns, capillaries, rods, disks, membranes and fibres (Peters et al., 1999, Svec et al. 2003, Mallik and Hage 2006, Jiang et al., 2005 and Jungbauer and Hahn 2004). Owing to their adequate porous structures they can easily operate under high flow rates due to low back pressures. In this regard, fast separations, rapid mass transfer and short analysis time are efficiently attained (Peters et al., 1999, Jiang et al., 2005, Jungbauer and Hahn 2004, Josic et al., 2001, Mallik et al., 2004 and Schuster et al., 2000). Chemical modification of functional groups on the monolith porous surfaces can be easily carried out (Mallik and Hage 2006).

Porous polymeric monoliths have been prepared based on glycidyl methacrylate, silica, and agarose and through cryogelation processes. The poly(glycidyl methacrylate) monoliths have low surface areas compared to the silica-based monoliths (Mallik and Hage 2006). However the silica monoliths are difficult to prepare due to their shrinkage after formation (Minakuchi et al., 1996, Tanaka et al. . . . 2002, Cabrera et al., 1998 and Tanaka et al., 2000). Although the agarose monoliths have very large pore diameters (20-200 µm), their low mechanical strengths limit their applications (Mallik and Hage 2006).

The cryogels (from the Greek kryos - meaning frost or ice) are macroporous heterophase gels in which polycrystals of frozen solvent act as porogens during gel formation (Jungbauer and Hahn 2004 and Lozinsky et al., 2002). Cryotropic gelation/cryostructurization in polymeric systems takes place on moderate freezing of monomer solutions or colloidal dispersions containing monomer or polymer precursors, maintaining the reaction mixture in the frozen state while polymerizing the monomers or polymer precursors, followed by thawing and washing of the resulting polymeric material (fig. 1) (Jungbauer and Hahn 2004 and Lozinsky et al., 2002). Cryogelation is characterized by low critical concentration of gelation (CCG) and high gelation rates contrary to traditional gelation at temperatures above freezing point.

Typical monolithic cryogels are featured by interconnected systems of macropores and unique sponge-like morphology that can permit unhindered diffusion of solutes of practically any size (Lozinsky et al., 2002). Cryogels’ pores are typically 100 to 1000 fold larger than those in other gels (0.03 - 0.4 µm). Their adequate osmotic, chemical and mechanical stabilities make them attractive matrices for biocatalysts and chromatography of large entities such as protein aggregates.

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**Fig. 1:** Cryogelation Process Scheme: Steps Involved in Cryogelation Process.
(Jungbauer and Hahn, 2004)
membrane fragments and viruses. In general, the cryogels have found different applications in the medical, biotechnological and pharmaceutical areas (Lozinsky et al., 2002, Plieva et al., 2005 and 2006).

Previously, hydrophilic macroporous polyacrylamide monolithic cryogels with epoxy functionality (Epoxy-MPAAGs) have been synthesized and studied (Plieva et al., 2005, Plieva et al., 2006 and Plieva et al., 2008). The rational design of the cryogels for particular applications depends on their porous structures and so far the challenge has been on the control of their porous structure (Plieva et al., 2006). The control of monoliths porous structures have been attempted through varying either the concentration of monomer or initiator, the nature of the cross-linker or the final freezing temperature (Plieva et al., 2005 and Plieva et al., 2006). In the present study the influence of monomer concentrations in the initial reaction mixture on the cryogel’s characteristics including pore-volume, gel-fraction yield, degree of swelling, water-flow resistance, average weight and average pore size and the pore size distribution of the produced Epoxy-MPAAGs monolithic cryogels are further explored and affirmed.

The application of spectroscopic techniques for characterization of cryogels is limited by the intended purpose of analysis. Mostly $^1$H and $^{13}$C NMR techniques have been used for the chemical structural elucidation of cryogels (Gusev et al., 1993, Gusev et al., 1990, Kirsebom et al., 2008 and Kirsebom et al., 2009). In this work, solid-state diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been applied for chemical characterization of the Epoxy-MPAAGs monolithic cryogels.

**EXPERIMENTAL**

Materials

Acrylamide (AAm) 99 % electrophoresis grade, $N,N'$-methylene-bis-acrylamide (MBAAm) 99 %, allyl glycidyl ether (AGE) 99 % GC grade, ammonium persulphate (APS) 98 % and $N,N,N',N'$-tetramethylethlenediamine (TEMED) 99 %, were all from Sigma (St. Louis, USA), ethanol from Merck (Darmstadt, Germany), and potassium bromide analytical grade from BDH Chemicals Ltd. (England).

Synthesis of Epoxy-MPAAGs

Approximately 0.5 mL cylindrical blocks of Epoxy-MPAAGs monolithic cryogels were synthesized by free radical addition copolymerization of the monomers AAm, MBAAm and AGE at -12 °C. The total monomer concentrations of 5, 10 & 15 % (w/v) were used in the initial reaction mixtures. The molar ratios AGE/AAm = 0.12 and AAm/MBAAm = 10, were kept constant in all recipes (similar to those prescribed elsewhere) (Plieva et al., 2006 and Plieva et al., 2008). The initiator system comprised of APS and TEMED. The molar ratios: APS/TEMED = 0.5 and (APS+TEMED)/(AAm + MBAAm + AGE) = 0.01 were also kept constant. The respective proportions of the monomers (shown in table 1) were dissolved into about 18.4 mL de-ionized distilled water (ddH2O). The resulting solutions were degassed for about 20 min. by using N2 gas or water pipe vacuum. Appropriate portions of APS were dissolved in 1 mL ddH2O in separate vessels and left under ice bath. Appropriate portions of TEMED were then added and uniformly mixed into the solutions of monomers and cooled under ice bath for about 30 min. Empty glass tubes (i. d. = 7 mm) with single plugged ends were placed inside ethanol cryostat at -12 °C for about 30 min. For the onset of reaction, the APS solutions were mixed with the monomers solutions and quickly poured into the cold glass tubes in aliquots of 0.5 mL. The filled glass tubes were immediately placed in the ethanol cryostat at -12 °C for 1 hr and then transferred into a deep freezer at -12 °C to complete a 20 hrs reaction. The cryogels were allowed to thaw gradually at room temperature while still in the glass moulds before being washed with plenty of ddH2O.
Table 1: Composition of Reaction Mixtures Corresponding to the Initial Monomer Concentration of 5 %, 10 % and 15 % (w/v).

<table>
<thead>
<tr>
<th>Monomer Conc. (%) w/v</th>
<th>Co-monomers</th>
<th>Activator</th>
<th>Initiator</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AAm (g)</td>
<td>MBAAm (g)</td>
<td>AGE (µl)</td>
</tr>
<tr>
<td></td>
<td>71.8 g/mol</td>
<td>154.17 g/mol</td>
<td>114.16 g/mol</td>
</tr>
<tr>
<td>5</td>
<td>0.7</td>
<td>0.18</td>
<td>140</td>
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<tr>
<td>10</td>
<td>1.3</td>
<td>0.35</td>
<td>280</td>
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<tr>
<td>15</td>
<td>2.0</td>
<td>0.53</td>
<td>415</td>
</tr>
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Characterization of the Monolithic Cryogels
The synthesized monolithic cryogels were characterized by determining gel-fraction yield, degree of swelling, water-flow resistance, pore-volume, pore size distribution and degree of swelling.

Gel-fraction yield
The wet cryogels were oven-dried at 60 °C overnight to attain constant dry masses. The gel fraction yield was calculated as: \( \frac{m_{\text{dry}}}{m_{\text{tot}}} \times 100 \% \), where \( m_{\text{dry}} \) is the constant dry mass of the monolith and \( m_{\text{tot}} \) is the total mass of the monomers used to prepare the monolith. A minimum of triplicate measurements was obtained and the average values calculated.

Degree of Swelling, \( S_{w/w} \)
Dried monoliths were soaked into water for about 1-2 min until saturation and re-weighed. The degree of swelling, \( S_{w/w} \), was determined as: \( S_{w/w} = \frac{(m_{\text{swollen}} - m_{\text{dry}})}{m_{\text{dry}}} \), where \( m_{\text{swollen}} \) is the mass of swollen monolith. A minimum of triplicate measurements was taken and the average values are presented.

Flow Rate (Water-flow Resistance)
Monoliths of the same geometrical size and shape (approximately 0.8 cm diameter, 1.1 cm length), were inserted one at a time into a glass column of internal diameter (i. d.) 0.7 cm. The water-flow resistance, taken as the flow rate through the monolith at a constant hydrostatic pressure of 1 m of water, was determined by measuring the cubic (volume) flux (cm³/min) of water eluted through the monolith-packed glass columns in a specified time interval (1 or 2 min). The cubic (volume) flow rates were converted to linear flow rates using the relation: linear flow rate = cubic flow rate / area of cross section. Where the cross-section area, \( A = \pi d^2/4 \) and \( d \) is the internal diameter of the column. Replicate measurements were made and the average flow rates were calculated.

Pore-Volume
Pore-volume (%) of the cryogels was determined through the uptake of cyclohexane. Pre-weighed dry monoliths of constant masses were immersed into the cyclohexane for an hour and re-weighed in their swollen states. The pore-volume (%) was estimated as: \( \frac{(m_{\text{swollen}} - m_{\text{dry}})}{m_{\text{swollen}}} \times 100 \). The averages of replicate determinations were calculated.

Pore Size Distribution
Pore size distribution of the cryogels was analysed by using scanning electron microscopy (SEM). Wet samples of the cryogels were vertically cut into fairly small slices (about 1-2 mm thickness) and successively dehydrated in ethanol (20, 40, 75 to 99.5 %-v/v). The samples were then coated.
with gold-palladium (40:60) and the micrographs were obtained by using a computer assisted JEOL JSM-5600 LV scanning electron microscope. The pore sizes of randomly selected cryogels’ pores were grouped in different classes (with class intervals ranging from 10 µm to 40 µm) and then the % class frequency was calculated as: \( \frac{f_i}{f_t} \times 100 \) where \( f_i \) and \( f_t \) are the number of pores for a particular size class and the total number of selected pores, respectively. IMAGE J software was used for pore size analysis.

Chemical Characterization by DRIFTS
Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) analyses for the native Epoxy-MPAAGs monolithic cryogels were carried out using a computer coupled FTIR-800 Shimadzu spectrometer. Monolithic samples and KBr were oven-dried overnight at around 60 – 70 °C and then finely ground. 5-20 mg of the powdered cryogels were then thoroughly mixed with the KBr in about 1:9 ratio and spectra of KBr-diluted cryogel samples were scanned in the range 4000-600 cm\(^{-1}\) at room temperature against a background spectrum of the anhydrous KBr.

RESULTS AND DISCUSSION

Synthesis of the Epoxy-MPAAGs Monolithic Cryogels
The success of the synthesis of the Epoxy-MPAAGs monolithic cryogels was much dependent on freezing-gelation interplay. Most crucial during the synthesis process was rapid freezing of the reaction mixture such that it takes place before the onset of gelation. It was quite clear that gels of poor quality with no significant difference from traditional ones were formed if by any chance gelation began before freezing. In order to facilitate freezing, both the empty glass tubes (the moulds) and the reaction systems (monomer mixture and initiator system) were ice-cooled for at least 30 min. before the reaction. The manual filling of the reaction mixture into the empty glass tubes was done quickly in order to minimize as much as possible a rise in temperature of the reaction mixture due thermal contact with the surroundings, i.e., limiting the possibility of increasing the gelation rate due to high temperatures. Where necessary, freezing was induced through manual shaking of the reaction mixture inside the glass tubes. In this way, the reacting substances facilitated rapid ice nucleation within the glass moulds.

Cryogelation polymerization reaction (fig. 2) starts with the reaction between the initiator APS and the activator TEMED to form free radicals. The free radicals initiate the reaction of monomers AAm, MBAAm and AGE (epoxy groups enhancer) (Plieva et al., 2006). MBAAm also acts as a cross-linker. The recovery (i.e. percentage good monoliths per batch) determined for seven independent batches for the 10 % cryogels were 93 ± 3 % and for two independent batches of the 5 % cryogels were 95 and 100 %. This shows that the cryogelation process is to a high degree reproducible.
Fig. 2: Polymerization Reaction Scheme: Synthesis of Epoxy-MPAAGs from Respective Monomers - AAm, MBAAm and AGE and Initiating System - APS and TEMED (Mallik and Hage, 2006).

Fig. 3: A Section of the 10 % Epoxy-MPAAGs Monolithic Cryogels in their Glass Moulds

Physical Properties of the Epoxy-MPAAGs monolithic Cryogels
The produced Epoxy-MPAAGs monoliths (fig. 3) were generally white, opaque, soft and spongy cylindrical blocks built up with systems of interconnected pore structures. In their wet states the monoliths appear relatively more opaque as monomer concentration increases. This could be attributed to the anticipated increase in thickness of walls following the increase in monomer concentration, i.e., much more reflection of incident light is expected when thickness of the walls increases. When drops of water of certain volumes were poured from the top of monolithic column (during washing for example), similar volumes of water were instantaneously released as effluent. It was also possible to mechanically squeeze out some water from the monoliths. The presence of the large interconnected pores within the polymeric cryogels facilitates the existence of this capillary bound water, making the cryogels ‘drainage-protected’ (Plieva et al., 2006). Also dry monoliths could re-swell immediately when in contact with water.
In general, the monoliths were exceptionally mechanically stable. Their traditional counterparts that are produced at elevated temperature (above freezing point) are normally brittle, quite fragile, of high flow resistance and poor ability to re-swell after drying (Plieva et al., 2006). The sponge-like morphology, the interconnectedness of pores along with their mechanical stability are typical for cryogels (Lozinsky et al., 2002). When cryogelation follows the freezing-before-gelation mode, polymerization takes place in the non-frozen liquid microphase thus producing the elastic sponge-like macroporous structure with interconnected pores (Plieva et al., 2006). However, the observed spongy and soft morphology kept on decreasing as monomer concentration was increased. Probably this can be attributed to the formation of thicker (denser) walls following the increase in polymer content as the monomer concentration in the reaction system increased (Plieva et al., 2005). In comparison for example; the 15 % Epoxy-MPAAGs cryogels appeared relatively rigid at their removal from glass moulds after thawing. On the other hand the 5 % Epoxy-MPAAGs cryogels appeared to be the weakest of all in terms of mechanical strength. In general, decreasing the initial monomer concentration below 5 % would be associated with the production of more fragile cryogels while increasing the initial monomer concentration above 15 % could risk the formation of more rigid and less macroporous cryogels.

**Effect of Monomer Concentration on Characteristic Properties of Epoxy-MPAAGs Monolithic Cryogels**

The effect of varying monomer concentration in the initial reaction mixture on some selected physical properties of the produced Epoxy-MPAAGs monolithic cryogels was investigated. The selected physical properties included cryogels’ weights, gel-fraction yield, water flow resistance, pore volume and degree of swelling. The corresponding results are graphically summarized in figures 4 and 5.

The results show that an increase in monomer concentration (in the range of 5 to 15 %) in the initial reaction mixture was associated with an increase in cryogels’ weight, gel fraction yield and water flow resistance. For every 1 % increase in monomer concentration, the average polymer weight increased by 6 mg, the gel-fraction yield increased by 1.2 % and the water-flow resistance increased at a rate of 275 cm/hr (figs. 4 and 5). The observed trend can be explained most likely in terms of the anticipated increase of polymer content (growth of thicker walls) at a fixed reaction volume. On the other hand the increase in monomer concentration was associated with a decrease in pore volume and degree of swelling (fig. 4). For every 1 % increase in monomer concentration, the pore volume decreased by 2.4 %, while the degree of swelling decreased by 3.2. Some of the results concur in general with the results of other similar studies though of different gel compositions or gel dimensions in which the degree of swelling and pore volume were observed to decrease with the increase in monomer concentration while water flow resistance increased with monomer concentration (Plieva et al., 2005 and Asnaghi et al., 1997). The above results suggest the existence of tendencies of linearity in the order of relationships between the monomer concentration and each of the above mentioned parameters.

Different trends, however, can be expected above the studied range of monomer concentration due to the effect of factors such as the increase of thickness of cryogel walls and the interplay between the cryogelation rate and the effect of the freezing point depression. It is assumed that smaller pores and thicker walls are a result of higher monomer concentration (Plieva et al., 2005). Most likely when more monomers are reacting whilst producing more polymer content (thicker walls) the volume to be occupied by the forming ice polycrystals might decrease to balance physico-chemical dynamics. Usually the increase in monomer concentration is associated with an increase in cryogelation rate; but on the other hand, this increase in monomer concentration can increase the freezing point depression and lower the rate of ice nucleation. In so doing, the polymer phase network might grow relatively faster against the ice phase ending up with reduced pore volumes. In the case where cryogelation rate is much higher than the rate of ice nucleation, there is a risk of having ‘freezing after gelation’ with the production of closed macropores (not interconnected structure) of higher flow resistance (Plieva et al., 2006).
The influence of the increase in the amount of MBAAm is also significant in determining properties of the resulting cryogel. Increased amount of MBAAm will lead to increased degree of crosslinking for the monolithic cryogels that are formed. Crosslinking compromises significantly solubility and swellability of polymers. Generally, the pore walls of macroporous cryogels result from highly concentrated polymer network of low swelling capacity (Arvidsson et al., 2003). In this regard; the increase in monomer concentration will definitely decrease the swelling capacity even more.

**Fig. 4:** Influence of Monomer Concentration on Pore Volume, Gel Fraction Yield, Degree of Swelling and Weight of Cryogel.
**Fig. 5:** Influence of Monomer Concentration on Water-flow Resistance of the Epoxy-MPAAGs Cryogels.

**Effect of Monomer Concentration on the Pore Structure of Epoxy-MPAAGs Monolithic Cryogels**

In this particular study, SEM has been applied for pore structure analysis. Mercury intrusion porosimetry has been used traditionally for determining the porosity of materials in their dry states (Josic et al., 2001, Viklund et al., 1996 and Zou et al., 2002). The method however is not necessary for cryogels since their porosities are well preserved when analysed in their wet natural states. Environmental Scanning Electron Microscopy (ESEM) has thus been used to analyse the structure of cryogels (in their hydrated natural states) whilst dehydrating them gradually (Plieva et al., 2006). Nevertheless, ESEM is not considered to be suitable for fine structure at the micrometer scale (Plieva et al., 2006). Although the scanning electron microscopy (SEM) operates in dry states, the method is still appropriate for the macroporous polyacrylamide cryogels owing to their excellent mechanical stability, i.e., there is no significant deterioration of their porous structure during sample drying/dehydrating process (Plieva et al., 2006). As evidenced from the SEM micrographs (fig. 6), the produced Epoxy-MPAAGs monolithic cryogels were porous material of micrometer scale. Visual analysis of the SEM pictures (fig. 6), at the same magnification (x 300), shows that 5 % Epoxy-MPAAGs cryogel was the most porous of all, i.e., contained a large volume or number of pores (empty spaces) compared to its polymer content (solid part). Also 10 % Epoxy-MPAAGs cryogel appeared somehow to possess a relatively larger volume of pores than 15 % Epoxy-MPAAGs cryogel. This observation matched consistently with the inferred decrease in the % pore-volumes with the increase in initial monomer concentrations in the reaction mixtures (fig. 4).

The pore sizes of the produced cryogels ranged generally from about 10 µm to about 150 µm (fig. 7). The anticipated influence of monomer concentration on the pore size and pore size distribution was not vivid, i.e., the mode (pore size class of highest % frequency) decreased from 41-50 µm for the 5 % cryogels to 31-40 µm for the 10 % cryogels but still remained at 31-40 µm for the 15 % cryogels. Similarly, it was observed (fig. 8) that there was a decrease in the mean pore sizes when the monomer concentration increased from 5 % to 10 %. On the contrary there was no significant
change in the mean pore sizes from 10 % to 15 % monomer concentrations. Almost certainly there could be significant change in terms of the wall thickness even though pore sizes did not change significantly, e.g., the pore walls of the 15 % cryogel (fig. 6) appear to be the thickest of all. Apparently, this calls for a more detailed systematic study for verification. As suggested earlier one could expect the formation of yet smaller water polycrystals and thicker walls, leading to smaller pores. Possibly, at the monomer concentration of 15 % (w/v) the monomeric system approaches a limit above which the effect of the freezing point depression becomes more pronounced. Freezing efficiency in higher monomer concentration systems might not be as high as in their lower monomer concentration counterparts, especially when freezing temperature is kept constant (as in our case). The increase in viscosity of the unfrozen liquid phase could hinder further crystallization (Plieva et al., 2006). One way to control this could be to lower down the freezing temperature as monomer concentration was varying. This could in turn produce even smaller pores because the lower the freezing temperature, the larger the distribution of small solvent crystals leading to smaller pores, as explained elsewhere (Lozinsky et al., 2002). The SEM was useful in exposing the internal porous structure of the cryogels. On the contrary, the imaging software (IMAGE J software) by which pore sizes are analysed was both so much time consuming and not without user’s subjectivity.

![Fig. 6: SEM Images for the 5, 10 and 15 % Epoxy-MPAAGs Cryogels (Magnification x 300)](image-url)
Fig. 7: Pore Size Distribution for the 5, 10 and 15 % Epoxy-MPAAGs Cryogels

Fig. 8: Mean Pore Sizes of Epoxy-MPAAGs Cryogels versus % Initial Total Monomer Concentration in the Cryogelation Mixture
The cryogelation process was highly reproducible with over 90% secondary amides within the polyacrylamide networks. Also, carbon dioxide is evident in the cryogel samples (Williams and Fleming, 1980 and Pavia et al., 1996). The strong broad peaks near 3200 cm⁻¹ (i.e., 3181.64, 3187.63 and 3190.82 cm⁻¹) have been assigned to N-H stretching due to primary amide of the solid state Epoxy-MPAAGs cryogel samples (Williams and Fleming, 1980 and Pavia et al., 1996). The sharp peak near 2940 cm⁻¹ (2938.80, 2940.13 and 2937.00 cm⁻¹) is due to secondary amide N-H stretch confirming the presence of secondary amide groups in the cryogel samples (Williams and Fleming, 1980 and Pavia et al., 1996). The C=O stretch (1676.42 and around 1690-1700 cm⁻¹) (Williams and Fleming, 1980 and Pavia et al, 1996) and C=N stretch (around 1450 cm⁻¹) (Williams and Fleming, 1980) typifying the presence of the secondary amides within the polyacrylamide networks. Also, carbon dioxide (O=CaO) peaks (2361.92, 2355.37 and 2370.95 cm⁻¹) common in many IR spectra is also evident (Williams and Fleming, 1980). Furthermore the C=O stretch (1116.71, 1116.48 and 1116.52 cm⁻¹) most likely due to ether (or epoxy) groups is apparent (Williams and Fleming, 1980). The IR peaks for the epoxy functional groups were expected at about 1250 cm⁻¹ and in the fingerprint region at about 800 and 900 cm⁻¹ (Williams and Fleming, 1980 and Podgornik and Tramcar, 2005). The peak at about 1315 cm⁻¹ (1313.63, 1319.15 and 1314.54 cm⁻¹) could account for the epoxy functional group. Probably the amount of the epoxy groups incorporated within the cryogels’ networks was insufficient to display strong/intense peaks all over the regions; most likely due to low value of the AGE/AAm molar ratio (AGE/AAm molar ratio of 0.12 was used). Although for confirmation purposes DRIFTS analysis requires supplementary justification from other spectroscopic techniques, it still serves as a useful tool for preliminary functional groups elucidation in epoxy cryogels.

CONCLUSION
Hydrophilic sponge-like macroporous Epoxy-MPAAGs cryogels with pore sizes 10-150 µm have been synthesized by cryogelation polymerization of the monomers AAm, MBAAm and AGE and the influence of the total initial monomer concentration (in the range 5 to 15%) on selected cryogels properties was investigated. The cryogelation process was highly reproducible with over 90% recovery. The Epoxy-MPAAGs cryogels were generally mechanically stable and possessed variable pore volumes swelling degrees and flow properties. The results suggested the existence of tendencies of linearity in the order of relationships between the initial monomer concentration in the
reaction mixture, within the limited concentration range studied, and each of the studied characteric parameters of the cryogels. This observation indicates that rational design of polymeric monolithic cryogels with characteristic properties including, average pore sizes and size distributions, that are suitable for specific applications can be effectively achieved through proper choice of monomer concentration in the initial reaction mixture.

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