Amine Functionalisations of Glycidyl methacrylate Based PolyHIPE Monoliths

Janja Majer,[1] *Peter Krajnc**[2]

Summary: High internal phase emulsions were employed to prepare highly porous (up to 80% pore volume) monoliths of poly(glycidyl methacrylate-co-ethylenegycol dimethacrylate) by free radical polymerisations of continuous phases of emulsions. Monoliths with cavities approximately 4 μm in diameter and with interconnecting pores approximately 0.7 μm in diameter were obtained. In order to obtain monoliths with ion exchange groups on the surface of pores for chromatography applications, functionalisations with different amines were performed and various reaction conditions tested. FTIR spectroscopy and nitrogen content analysis were used to monitor the functionalisation processes. Monoliths were succesfully functionalised with 1,2-diaminoethane, 1,4-diaminobuthane, 1,8-diaminooctane and tris(diethylamino)amine.

Keywords: glycidyl methacrylate; high internal phase emulsions; polymer monoliths; porous polymers; polyHIPE

Introduction

Macroporous polymers in forms of monoliths are increasingly used in chromatography.[1] Macro porosity enables convective flow of the mobile phase through the monolith thus allowing low back pressures and high effectivity of the supports. Rather big pores are therefore needed and, more importantly, the morphology must exhibit well interconnected porous structure. The polymeric monoliths with macro sized open pores can be prepared by free radical polymerisation in bulk with added porogens, generating a cauliflower- like morphology of aggregated beads or in a more controlled manner using spinodal decomposition resulting in a bicountinuous-like morphology. A very permeable, highly porous monolith can also be prepared by emulsion templating. Using this approach, an emulsion with a high volume fraction of the internal phase (typically over 75%) is prepared and monomers are included in the continuous phase. Upon polymerisation and purification, a porous monolith is produced with an open porous structure, having bigger pores (cavities) of the size of emulsion droplets prior to polymerisation and smaller interconnecting pores formed upon the rupture of polymer film at its thinnest point. Such monoliths, described first by Bonin[2] and patented by Unilever under a trade name *polyHIPE* (poly High Internal Phase Emulsions).[3] Recently, various chemistries have been applied for the preparation of polyHIPE monoliths[4], and even *reversed* polyHIPEs (from water in oil emulsions)[5,6] from water soluble monomers. PolyHIPE structured beads[7,8,9] and membranes[10,11] have also been reported.

Glycidyl methacrylate chemistry is well established for the preparation of polymeric monoliths.[12] Epoxy groups can be functionalised to obtain ion exchange groups and also various types of grafting can be performed in order to improve loading.[13] We alrady reported the preparation of glycidyl methacrylate based polyHIPE monoliths[14] and their permea-

[1] University of Maribor, Faculty of Natural Sciences and Mathematics, Department of Chemistry, Koroška 160, 2000 Maribor, Slovenia
[2] University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Organic and Polymer Chemistry, Smetanova 17, 2000 Maribor, Slovenia
E-mail: peter.krajnc@uni-mb.si

tive properties.[15] For the effective application of GMA monoliths, the compromise between the binding capacity for analyte molecules and the permeability enabling low pressure drops on the other side, is of great importance. Therefore, there are efforts to enhance the binding capacities of monoliths without sacrifising the permeability. One approach is to functionalise the epoxy groups on the surface of the pores with multifunctional amines. If the layer of functionalised groups is thin and the site-site interactions of amine groups are minimal, the permeability of the monolith should not be compromised while the capacity should be enhanced.

Therefore, in this research we investigated the possibility of functionalising GMA based polyHIPE monoliths with two types of amines and the influence of reaction conditions on the resulting structure.

Experimental Part

Materials and Methods

Glycidyl methacrylate (GMA, Aldrich) and ethyleneglycol dimethacrylate (EGDMA, Aldrich) were flushed through a basic alumina column before use to remove the inhibitors. Poly(propylene glycol)-*block*-poly(ethylene glycol)-*block*-poly(propylene glycol) (Synperonic PE/L 121, Sigma-Aldrich), ammonium persulfate (APS, Fluka), N,N,N',N'-tetramethylethylendiamine (TEMED, Fluka), calcium chloride hexahydrate ($CaCl_2{\cdot}6H_2O$, Merck), dimethylformamide (DMF, Fuka), 1,2-diaminoethane (Fluka), 1,4-diaminobuthane (Fluka), 1,8-diaminooctane (Fluka), tris(2-aminoethyl)amine (Fluka), were all used as received.

Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer FTIR 1650 spectrometer (KBR pelets), CHN cumbustion elemental analyses were done on a PerkinElmer CHN 2400 analyser. Scanning electron microscopy (SEM) pictures were taken on a FEI Quanta200 3D (monolithic samples dried and fractured in liquid nitrogen). The swelling properties of solvent were determined by swelling 1mL of powdered polymer in solvent for 24 h. Cavities and interconnecting pore diameters were determined from SEM images.

Preparation of GMA/EGDMA PolyHIPE from Water-in-Oil High Internal Phase Emulsion

9.1 g (64 mmol) of GMA, 3.17 g (16 mmol) of EGDMA and 2.35g of Synperionic PEL 121 surfactant were placed in a reactor and the mixture was stirred with an overhead stirrer at 400 rpm. The aqueous solution was prepared by dissolving 0.2 g ammonium persulphate and 1.79 g of calcium chloride hexahydrate in 100 mL deionised water and 46.2 mL of so prepared aqueous solution was used as the internal phase. It was degassed and added dropwise to the monomer solution under constant stirring. Once all aqueous phase was added, stirring was continued for a further 60 min, to produce a uniform emulsion. Stirring of the emulsion was then reduced to 20 rpm and the reducing agent TEMED (0.0472 g, 0.406 mmol) was added. After 3 min of additional stirring at 20 rpm the emulsion was transferred to the mould (polyethylene container) and cured at 40°C for 24 hours. The resulting monolith was purified via Soxhlet extraction with ethanol for 24 hours and deionised water for further 24 h and dried under vacuum at 50°C.

Functionalization of GMA/EGDMA PolyHIPEs with Amines

55 mg (0.387 mmol of epoxy groups) of polymer was powdered, placed in a 25 mL flask and 20 mL of DMF added. 260 mg (4.33 mmol) of 1,2-diaminoethane or 200 mg (1.62 mmol) of 1,4-diaminobuthane or 285 mg (1.41 mmol) of 1,8-diaminooctane or 457 mg (2.22 mmol) of tris(2-aminoethyl)amine was added and the reaction mixture stirred for 24 h (at 25°C or 50°C or 80°C). The polymer was filtered, washed with the solvent in use, triethylamine, ethanol, ethanol/water (1:1), ethanol and dried under vacuum at 50°C. FTIR spectra were recorded and the amounts of carbon, hydrogen and nitrogen were determined by combustion elemental analysis.

Results and Discussion

There are several factors known to affect the degree of functionalisation of the polymer matrix. Reactive sites must be accessible to the reagent otherwise only the surface of the bulk polymer can be functionalised. This may be appropriate for applications where only the surface is used however higher degrees of functionalisations may be desired for other applications. In the case of functionalisations with difunctional amines, possible post polymerisation cross-linking must also be considered. It has been found previously that when diamino alkanes and multi functional amines were used to transform polyacrylates and polyvinylbenzyl chloride, a substantial amount of additional cross-linking took place.[16,17,18,19] This kind of side reaction is undesired when free amino groups are needed for further functionalisations or end applications. Site- site interactions can be strongly dependent on the temperature and also on the solvent polarity. Furthermore, the chemical structure of the amine influences the degree of cross-linking. When functionalising glycidyl methacrylate based porous polymers for chromatography applications, surface functionalisation is the most important as the mobile phase mostly interacts with the surface of the polymer in the case of convective mass transfer. It is important, however, that one amino group of the functionalising reagent remains free for the interaction with the analyte molecule.

FTIR spectroscopy can be used to monitor the course of functionalising procedure as the epoxy groups of the glycidyl methacrylate are consumed therefore the signal at 908 cm^{-1} should be disappearing. However, due to neighbouring and overlapping signals it is difficult to asses the degree of functionalisation solely by FTIR spectra (Figure 1). Because by amine

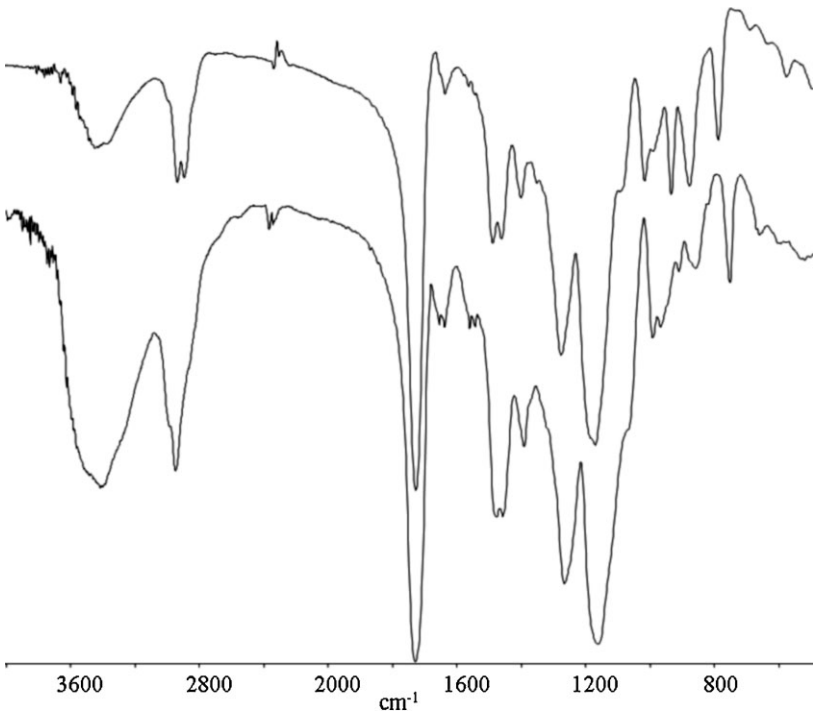


Figure 1.
FTIR spectrum of GMA polyHIPE (upper spectrum) and of 1,4-diamonobuthane derivative of GMA polyHIPE (lower spectrum).

functionalisation nitrogen is introduced into a polymer previously not containing nitrogen, the amount of nitrogen in the polymer gives information about the functionalisation. However, there is a possibility of the second amine group of the bi- or multifunctional amine to react with another epoxy group in the polymer matrix. This lowers the amount of nitrogen present in the polymer after the functionalisation, as one amine molecule replaces two epoxy groups in the polymer. The amount of nitrogen is lower if the degree of functionalisation is low or, if the post polymerisation cross-linking is achieved by bifunctional amine. Therefore, the ultimate test will be the actual capacity of the resulting polymer for the binding of the analyte in question.

PolyHIPE monoliths were prepared similarly to an established procedure,[14] however a redox initiating system was used for the initialization. We found that this gives more control over void size than a thermal radical source. Comparing the morphology to the morphology of the samples prepared previously[14], a less open structure is seen with smaller cavities, approx. 4 μm in diameter (Figure 2).

The degrees of conversion with all bi- and multifunctional amines (see Scheme 1) were found to be between approximately 20 and 45%, as calculated from nitrogen percentage (Table 1). As the batches of polymers for functionalisation were rather small in weight, we found the gravimetry not a very reliable method for determining the degree of functionalisation. Rather low loadings of amines prompted us to perform the reaction at elevated temperatures (initially, we tried to avoid high temperatures as it has been shown previously that higher temperatures enable more post polymerisation cross-linking). In the case

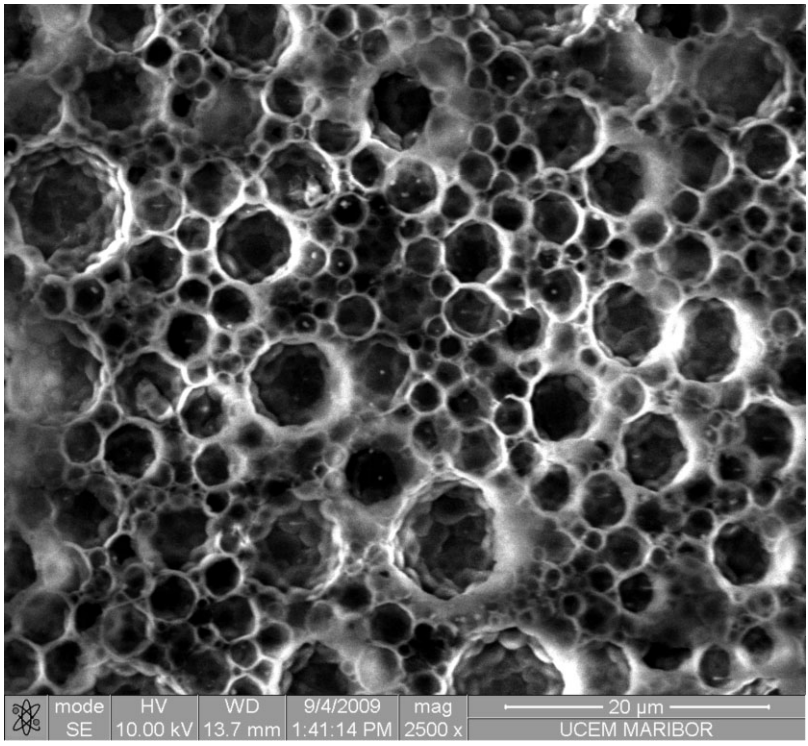
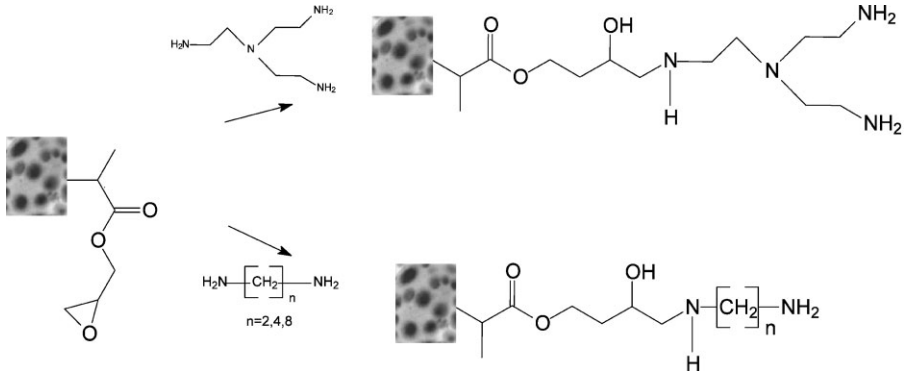


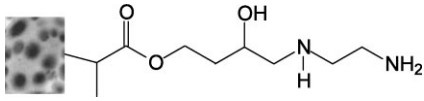
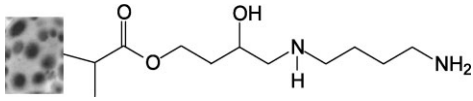
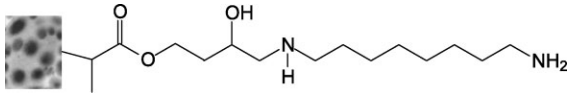
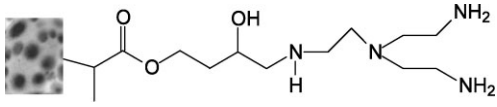
Figure 2.
SEM image of GMA polyHIPE.



Scheme 1.
Amine functionalisations of GMA polyHIPEs.

of reaction with 1,8-diaminooctane, the elevated temperature (to 80°C) still did not result in a very high conversion however it did raise the conversion level from approx. 20% to approx. 36%. 1,8-diaminooctane derivative thus has a loading of amine groups of 2.2 mmol per gram and we believe that half of those are primary. In the case of 1,2-diaminoethane functionalization, the resulted loading was 3.2 mmol per gram and in the case of 1,4-diaminobuthane 2.4 mmol per gram. Comparing to previous results of amine functionalisation of 4-vynilbenzyl chloride based supports[16] and 4-nitrophenyl acrylate based supports[17] these loading are rather low, however it is very likely that due to the macroporous nature functionalised groups are positioned at the surface where they are most needed for the applications with convective mass transfer. Partial hydrolysis of epoxy groups may

Table 1.
Amine functionalised supports.

Functionalized polymer support	Calc. % N[a]	T [°C]	Found % N	Loading of amine groups [mmol/g]
	11.16	50	4.43	3.2
	10.04	50	3.34	2.4
	8.35	25 50 80	1.72 2.32 3.04	1.2 1.7 2.2
	12.46	25 50 80	3.98 5.65 5.17	2.8 4.0 3.7

[a]for 100% conversion and no post polymerisation cross-linking

also be contributing to lower loadings of amine groups. Similarly, a reaction with tris(diethylamino)amine was performed (Scheme 1), and a polymer product with a loading of 2.7 mmol of amine groups per gram was isolated at room temperature and with a loading of 4 mmol of amine groups per gram at elevated temperature. This corresponds to approximately 45% of the epoxy groups being converted to amines. In this case especially, the availability of amine groups will have to be investigated further.

Conclusion

It has been shown that polyHIPE monoliths can be prepared from glycidyl methacrylate and ethyleneglycol dimethacrylate using a redox initiator and that epoxy groups in the polymer matrix can be functionalised with bi- and multifunctional amines to yield polymer supports for chromatography applications and as anchors for solid phase synthesis facilitation. Further research will be needed to determine the exact structure of the resulting polymers (in terms of additional cross-linking) and actual applicability in chromatography and solid phase synthesis.

Acknowledgements: This work has been supported by the Slovenian Research Agency and by the grant SI0039-GAN-00087-E-V1 through the Norwegian Financial Mechanism. Authors are grateful to Prof. Stanovnik from the Ljubljana University for the elemental analyses.

[1] E. G. Vlakh, T. B. Tennikova, *J. Sep. Sci.* **2007**, *30*, 2801.
[2] H. Bartl, W. von Bonin, *Makromol. Chem.* **1962**, *57*, 74.
[3] D. Barby, Z. Haq, *U.S. Patent* 4522953, **1985**.
[4] N. R. Cameron, *Polymer* **2005**, *46*, 1439.
[5, 6] P. Krajnc, D. Štefanec, I. Pulko, *Macromol. Rapid. Commun.* **2005**, *16*, 1289.
[7, 8, 9] D. Štefanec, P. Krajnc, *Polym. Int.* **2007**, *56*, 1313.
[10, 11] I. Pulko, P. Krajnc, *Chem. Commun.* **2008**, *37*, 4481.
[12] M. J. Beneš, D. Horak, F. Švec, *J. Sep. Sci.* **2005**, *28*, 1855.
[13] V. Frankovič, A. Podgornik, N. Krajnc-Lendero, F. Smrekar, P. Krajnc, A. Štrancar, *J. Chromatogr. A* **2008**, *84*, 1207.
[14] P. Krajnc, N. Leber, D. Štefanec, S. Kontrec, A. Podgornik, *J. Chromatogr. A* **2005**, *69*, 1065.
[15] I. Junkar, T. Koloini, P. Krajnc, D. Nemec, A. Podgornik, A. Štrancar, *J. Chromatogr. A* **2007**, *48*, 1144.
[16] P. Krajnc, J. F. Brown, N. R. Cameron, *Org. Lett.* **2002**, *4*, 2497.
[17] I. Pulko, P. Krajnc, *Acta Chim. Slov.* **2005**, *52*, 215.
[18] R. J. Booth, J. C. Hodges, *J. Am. Chem. Soc.* **1997**, *119*, 4882.
[19] M. Zupan, P. Krajnc, S. Stavber, *Polymer* **1996**, *37*, 5477.

