Scientific paper

Cross-Linked Porous Poly(Acrylic Acid-co-Acrylamide) from High Internal Phase Emulsions: Preparation and Functionalisation

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

[1] *University of Maribor, Faculty of Natural Sciences and Mathematics, Department of Chemistry, Koroška 160, Maribor, Slovenia*

[2] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Organic and Polymer Chemistry, Smetanova 17, Maribor, Slovenia*

** Corresponding author: E-mail: peter.krajnc@uni-mb.si*

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Dedicated to Professor Branko Stanovnik on the occasion of his 70th birthday

Abstract

By using emulsions with high volume fractions of internal phase as polymerisation media porous copolymers of acrylic acid and acrylamide, cross-linked by methylenebisacrylamide, were prepared. The ratio of acrylic acid to acrylamide were varied (molar ratios 70:30, 50:50, 30:70) in order to yield polymers with various loading of acidic functional groups. Porous polymers with an open-cellular architecture were obtained with void diameters between 2.8 μm and 3.9 μm and with interconnecting pores approx. 0.3 μm in diameter. The chemical composition of the polymers influenced the conversion degrees during the process of functionalisation of acidic groups to acid chloride, being the highest in the case of polymer with the lowest content of acrilyc acid.

Keywords: Porous monoliths, copolymers, polyacrylic acid, polyacrylamide, polyHIPE, high internal phase emulsions

1. Introduction

Insoluble polymeric supports represent an important tool in the arsenal of synthetic organic chemistry. Cross-linked polymers were introduced into synthetic methods already in the early 1940's as ion exchangers and more intensely as supports for multi step methods through peptide synthesis by R. B. Merrifield in the 1960's.[1] Later on, the advent of combinatorial chemistry revitalised the use of polymeric supports.[2] Recently, a lot of research is conducted on the method of polymer assisted solution phase chemistry, where a polymer support is utilised for the removal of a species from the reaction medium, i.e. the removal of excess reactants, catalysts or by-products.[3] Such functional polymer supports (frequently called scavengers) facilitate the work-up of the reaction after completion. Furthermore, reagents and catalysts can be immobilised to an insoluble polymeric support and used in a heterogenuous reaction setup. The advanteges of such an approach are mainly due to the simplified separation procedure as the polymer can be removed by filtration. For the same reason it is easy to use an excess of an immobilised reagent. For a polymer to be succesfully applied as a support for reagent, catalyst or scavenger, the reactive sites on the polymer matrix must be accessible to the reaction medium. The morphology of the polymeric support is therefore very important as the vast majority of the reactive sites are situated in the bulk of the polymer. By using low amounts of cross-linker and no porogenic solvents for the polymer preparation, polymeric supports that are almost non-porous are formed and in this case micro porosity is only exhibited when the polymer is swollen in the solvent. Such polymeric supports (reffered to as gels) can only be used in compatible solvents. On the other hand, polymeric supports with permanent porosity are produced when higher amounts of cross-linker and porogenic solvents are used during the preparation

(macroporous or macroreticular polymers). Permanently porous polymeric supports usually have wider solvent compatibility spectrum.

Traditionally, polymeric supports are prepared via suspension polymerisation techniques in a form of beads with a wide range of diameters between submicron level and 1000 μm.[4] For a batch type reaction setup, the beads may be the most suitable form however there is a possibility of running a reaction in a continuous, flow through manner. For such purposes, columns with polymeric supports can be prepared. Recently, there is a growing number of reports of applying flow reaction setups for organic syntheses.[5] In the case of a support for flow through reaction setup, a permanently porous monolithic polymer may be preffered. Convective mass transfer increases speed and efficiency and reduces back pressure which can be very substantial in the case of filling a column with beads that swell in the solvent. Furthermore, channeling of the solution reduces the efficiency in the case of particulate support.[6] In order to keep a low back pressure bigger pores in the polymeric material are preffered however this means lower surface area. To achieve both goals, one can prepare a polymer with large pores and subsequently graft the reactive chains.[7] Another possibility to aquire a desired pore size distribution and thus a material with both good permeability and surface area is to prepare a polymer from a high internal phase emulsion.[8] In a high internal phase emulsion, the volume ratio of the internal (droplet) phase exceeds 74%, which is the volume part occupiable by uniformly sized spheres. If the continuous phase contains monomers, upon polymerisation and the removal of droplets of the internal phase, a highly porous monolithic material can be obtained. The morphology of such a material typically exhibits large voids (in place of the droplets of internal phase) which are connected by smaller pores that are the result of the shrinkage during the polymerisation. Even smaller pores can be the result of the cross-linking of the polymer and the presence of porogenic solvent. Polymeric material prepared applying a high internal phase emulsion are termed polyHIPE materials and have found applications in various fields.[9]

Well established polymer serving as a support for further functionalization is cross-linked poly(4-vinylbenzyl chloride). Commercial availability of precursor monomer adds to the popularity of this type of support. However, for some less reactive nucleophiles, an even more reactive support may be needed. We have shown previously that an immobilised acid chloride can be very useful for the preparation of functional supports.[10] Furthermore, it can be very effective as an electrophilic scavenger of nucleophilic reagents from solution.[11] A possible route to prepare an acid chloride on the polymer matrix is to prepare an activated ester polymeric support, such as the poly(4-nitrophenyl acrylate).[12] This can be hydrolised and further functionalised to an immobilised acid chloride. However, this route requires the preparation of 4-nitrophenyl acrylate prior to polymerisation, hydrolysis of ester groups in the polymer matrix and finally functionalisation to acid chloride. A more convenient route would be to prepare cross-linked poly(acrylic acid) directly from commercially available acrylic acid and functionalise the polymer to acid chloride.

In this paper we are reporting the preparation of highly porous monolithic cross-linked poly(acrylic acid-co-acrylamide) with various acid/ amide ratios by using high internal phase emulsions as porosity templates. Functionalisations towards acid chlorides are also described.

2. Experimental

2. 1. Materials

Acrylic acid (AA, Merck) was purified by vacuum distillation. N,N'-methylene bisacrylamide (MBAA, Fluka) was recrystallized from methanol before use. Surfactants Pluronic F68 (Aldrich) and Triton X-405 (Aldrich), ammonium persulfate (APS, Fluka), N,N,N',N'-tetramethylethylendiamine (TEMED, Fluka), toluene (Merck), acrylamide (Fluka), thionyl chloride (Merck) were used as received. Acetonitrile (Aldrich) was distilled and stored over molecular sieves.

2. 2. Preparation of PolyHIPE Materials from Oil-in-water High Internal Phase Emulsion

For the sample AA100 (75% pore volume, 13% cross-linked): 2.05 g (28.00 mmol) of acrylic acid was added to 6.13 g of deionised water. MBAA (0.77 g, 4.99 mmol), initiator APS (0.15 g, 0.66 mmol) and surfactants Pluronic F68 (0.73 g) and Triton X-405 (1.57 g) were dissolved in the above acrylic acid solution. Toluene (24 mL) was added dropwise to the monomer solution under constant stirring with an overhead stirrer at 350 rpm. Once all toluene had been added, stirring was continued for a further 60 min, to produce a uniform O/W emulsion. Stirring of the emulsion was then reduced to 20 rpm and the reducing agent TEMED (0.075 mL) was added. After 3 min of additional stirring at 20 rpm the emulsion was transferred to the mould (polyethylene container) and cured at 45 °C for 8 hours. The resulting monolith was purified via Soxhlet extraction with acetone for 24 hours and dried under vacuum at 60 °C. Samples AA70, AA50, AA30 (75% pore volume, 13% cross-linked) were prepared via the same procedure, however acrylamide was added to the aqueous phase and the amount of acrylic acid lowered (AA70: 1.42g (19.7 mmol) of acrylic acid and 0.70 g (9.84 mmol) of acrylamide; AA50: 1.16 g (16.09 mmol) of acrylic acid and 1.16 g (16.3 mmol) of acrylamide; AA30: 0.61g (8.46 mmol) of acrylic acid and 1.50 g (21.10 mmol) of acrylamide).

2. 3. Structural Characterisation of the Monoliths

FTIR spectra were recorded on a PerkinElmer FTIR 1650 spectrometer (KBr pellets), scanning electron microscopy (SEM) pictures were taken on a FEI Quanta200 3D electron microscope.

2. 4. Functionalization of AA100, AA70, AA50, AA30 with Thionyl Chloride

500 mg of powdered AA100, AA70, AA50, or AA30 were placed in a 25 mL flask and 15 mL of anhydrous acetonitrile and 4 mL of thionyl chloride were added. The mixture was stirred for 2 h at 60 °C. The resulting polymers were filtered, washed with acetonitrile (5 × 10 mL) and dried under vacuum at 50 °C. The FTIR spectra were recorded and the amounts of chlorine were determined.

2. 5. Chlorine Determination

Chlorine was determined by potentiometric titration with $AgNO_3$. 100 mg of a polymer sample was placed in a flask and 5 mL of pyridine was added. The mixture was stirred for 2 h at 100 °C. After cooling, 10 mL of *N,N*-dimethylformamide and 7 mL of HNO_3 were added and the mixture diluted to 100 mL. 20 mL of this mixture was titrated with 0.1 M $AgNO_3$. The amounts of chlorine in the samples were calculated from volumes of $AgNO_3$ used by titration.

3. Results and Discussion

Common types of high internal phase emulsions used for the preparation of porous polymers is the water-in-oil type (W/O), where aqueous phase is the droplet phase and monomers are in the organic (continuous) phase. However, if water soluble monomers are to be polymerised, for the preparation of monolithic porous polymers the "reversed", oil-in-water (O/W) type has to be used. Supercritical CO_2 is also known to be used as the internal phase.[13] There are not many reports on the use of O/W HIPEs.[14] The preparation of acrylic acid based polyHIPE via such a method has been described recently.[15] Due to low emulsion stability (when compared to W/O styrene or divynilbenzene containing), a use of a redox initiating system was beneficial. In this case, a similar procedure was used. Methylenebisacrylamide was applied as the cross-linking agent (approx.13% mol) in order to obtain an insoluble polymer. Toluene was used as an appropriate oil phase and this yielded a stable enough emulsion for polymer preparation (Scheme 1).

Scanning electron microscopy was used to determine the morphology of the obtained polymeric material. As

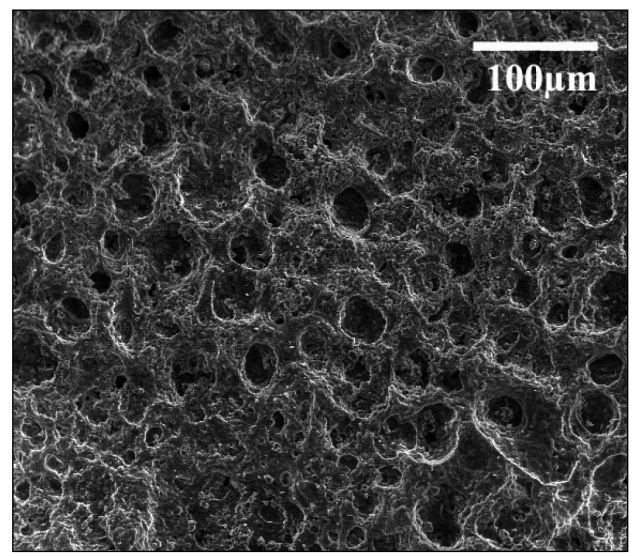
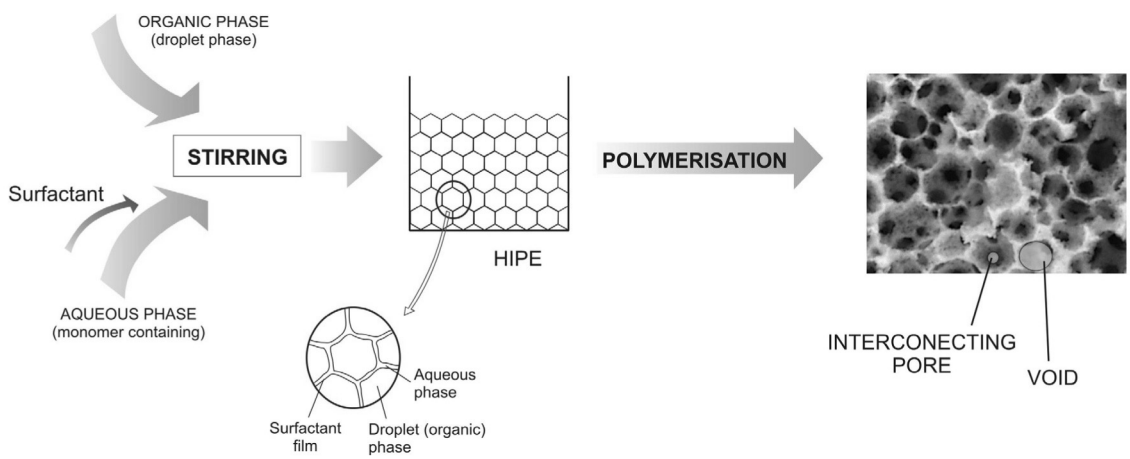


Figure 1. SEM image of AA100.



Scheme 1. polyHIPE preparation

seen from Figure 1, open-cellular connected architecture is evident. However, in terms of the structure, pore size and pore size distribution, the material is unhomogenious suggesting partial phase separation prior to polymerisation.

We were previously successful in the preparation of acrylic acid based polyHIPE material, however pH of the aqueous phase was modified by partial neutralisation with NaOH.[15] In this case, this was avoided as one of the goals was to functionalise the material to an immobilised acid chloride.

In order to modify the stability of the aqueous phase and with a goal to prevent site-site interactions of acidic groups on the polymer matrix (discussed later on), acrylamide was added to the aqueous phase. Emulsions with approx. 30 (AA70), 50 (AA50), and 70 mol % of acrylamide (AA30; in relation to monomer composition, Table 1) were prepared. In all cases, the volume fraction of organic phase (toluene) was 75%. From scaning electron microscopy images (Figure 2) a typical internal structure of polyHIPE material is evident.

The biggest pores (voids) are the result of the droplets of the internal phase being removed after the polymerisation. The proposed mechanism for the interconnecting pores formation states the higher polymer density compared to the monomer solution prior to gelation and thus the shrinkage of polymer film resulting in interconnecting pores. Cryo-SEM investigations support this theory[16] while some authors suggest that the interconnecting pores might be the result of post polymerisation treatement.[17]

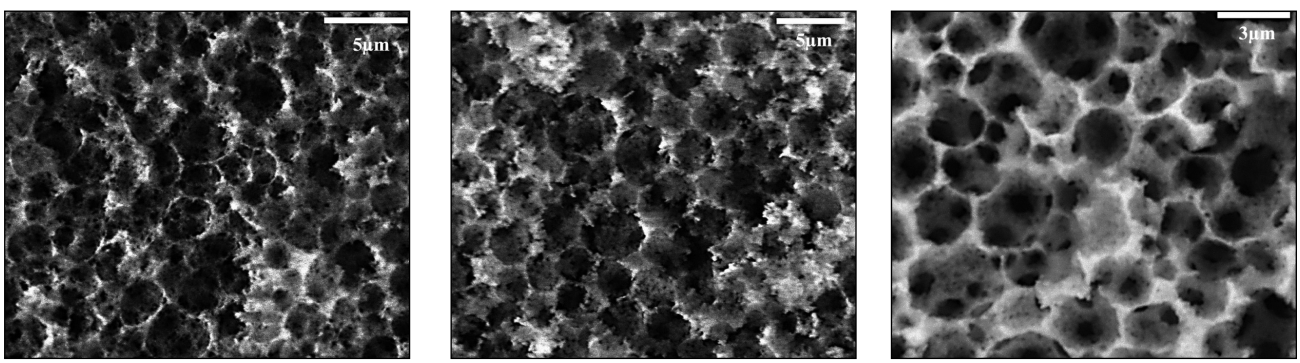
The diameter of the voids of the polyHIPE material is one of the characteristics related to the emulsion stability. As the polymeric material is actually an image of the high internal phase emulsion just before the gelation, the void size tells about the droplet size of the precursor emulsion. Numerous factors affect this and it was not the goal of this work to study this in detail. We did notice an increase in emulsion stability with the increasing acrylamide content, consequently smaller voids (by "increased emulsion stability" a lower rate of droplet coalescence is meant). In the case of the polymer with 33% of acrylamide (AA70), an average void diameter of 3.9 μm was measured, while in the case of polymer with 50% of acrylamide (AA50) 3.3 μm and in the case of polymer with 71% of acrylamide (AA30) the average void diameter was 2.8 μm. The average void diameters were measured by image analysis, applying a correction factor to obtain apropriate values.[18]

Infrared spectroscopy of prepared polyHIPE samples confirmed the chemistry of polymerised acrylic acid, acrylamide and methylenebisacrylamide. Strong absorption at 1730 cm^{-1} could indicate the presence of anhydride, which was surprising considering the aqueous medium of preparation (Figure 3). However, it is known that the neighbouring groups on the polymer matrix can react thus forming a new functional group. Such site-site interactions are especially present when there is a high loading of the functional group.[19] This was certanly the case in our product, as there were no other unfunctional monomers present to "dilute" the acrylic acid in the polymer chains. Despite the water being present it seems that the micro environment excludes the water molecules and preferes the formation of anhydride. These findings also led us to the preparation of poly(acrylic acid-co-acrylamide) with an intent of diluting the acrylic acid reactive groups on the polymer chains and thus diminish the site-site interactions.

Table 1. Composition, morphological features and functionalisations of polyHIPE materials

Sample	Acrylic acid content [mol%][a]	Void diameter [μm]	Chlorine content in functionalised polymer [%]	Degree of conversion [%][b]
AA100	100	30.5[c]	2.5	7
AA70	67	3.9	3.4	14
AA50	50	3.3	5.0	26
AA30	29	2.8	6.2	58

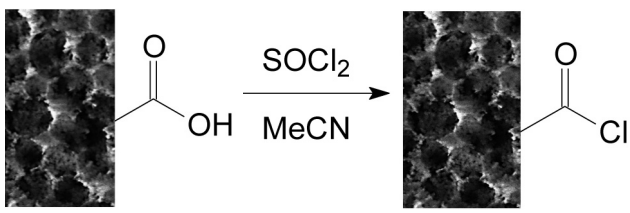
[a] in relation to monomers without cross-linker, [b] calculated from chlorine content, [c] material with different morphology



AA30 AA50 AA70

Figure 2. SEM images of polyHIPE samples

In our further investigations, these samples were used for the functionalisation towards acid chloride (Scheme 2). Thionyl chloride was used as a reagent and acetonitrile as the solvent. The results of the functionalisation procedure support the observation of anhydride formation. FTIR spectroscopy was again used to monitor the transformation while chlorine content in the functionalised polymers was measured in order to determine the conversion level. The highest conversion (approx. 58%; 1.75 mmol acid chloride groups per gram of polymer) to acid chloride was achived in the case of the lowest acrylic acid content material (AA30) which had the "highest dillution" of acidic groups in the matrix. Conversion levels from other samples were consistent with the dillution principle as the levels dropped towards 7% for the sample containing no acrylamide (Table 1). However, it has to be noted that this effect may also be the result of the changed micro environment and thus different accessibility of reactive sites inside the polymer towards the reagents.



Scheme 2. Functionalisation towards acid chloride

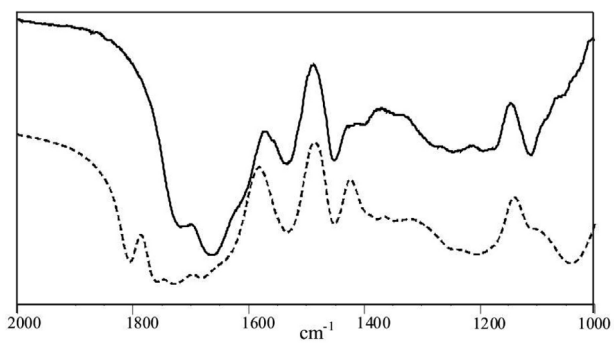


Figure 3. FTIR spectra of sample AA30 and functionalised sample (dotted line)

4. Conclusion

We have shown that copolymers of acrylic acid and acrylamide can be succesfully prepared in the form of highly porous monoliths using a high internal phase emulsion precursor as a porosity template. An "inverse" emulsion polymerisation yields solid porous polymers with typical architecture of open cellular structure. This is a desired structure for numerous applications, including supports for solid phase synthesis. The functionalisation of acrylic acid groups towards acid chloride proceeded much more efficiently when a substantial part of acrylamide was introduced into the polymer suggesting site isolation and the prevention of intra molecular anhydride formation due to site-site interactions. However, further experiments will be needed to obtain a clearer image of the processes, including the possible micro environment influence on the site accessibility.

5. References

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Povzetek

Pripravili smo porozne netopne kopolimere med akrilno kislino in akrilamidom (delež akrilamida med 30 in 70 odstotki), zamrežene z metilenbisakrilamidom, pri čemer smo kot polimerizacijski medij uporabili emulzije z visokim deležem notranje faze. Nastali so visoko porozni polimeri z odprto celično strukturo s premerom praznin med 2.8 μm in 3.9 μm in s povezovalnimi porami s premeri okoli 0.3 μm. Kemijska sestava polimerov je vplivala na stopnje pretvorbe pri funkcionalizaciji do kislinskega klorida; najvišjo stopnjo pretvorbe smo opazili pri najvišjem deležu akrilamida v polimeru.