



Preparation of PolyHIPE monolithic materials functionalization by tris(2-aminoethyl)amine



CrossMark

Malësore Pllana-Zeqiri,^a Peter Krajnc,^b Ramiz Hoti^{a,*}

^aDepartment of Chemistry, Faculty of Mathematical and Natural Sciences, University of Prishtina "Hasan Prishtina", 10000 Prishtina, Republic of Kosovo.

^b Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia.

Abstract

The developments of monolithic materials rapidly in nowadays hold an impressively strong position in separation science as well as in other areas of chemistry. In this research are presented functionalization of PolyHIPE monolithic materials by tris(2-aminoethyl) amine. Monolithic polymer supports and scavengers were synthesized via nucleophilic displacement of chlorine in poly(4-vinyl benzyl chloride-co-divinylbenzene) as PolyHIPE materials. Porous copolymers of DVB/DVB were prepared by emulsion templating using high internal phase emulsions (HIPEs) as precursors for monoliths. The properties of the final products synthesized were functionalized with an amino group, at a different ratio of amine/chloromethyl groups, in different time refluxed were explored. PolyHIPE functionalized with tris(2-aminoethyl)amine to yield a product with high degrees of conversion. The extent of the functionalization reactions was investigated by a range of qualitative and quantitative techniques: FTIR, CHN analysis, potentiometric measurements, and (BET) measurements have been performed.

Keywords: Monolithic PolyHIPE; Vinyl monomer; Polymeric scavenger reagents; Mesoporous.

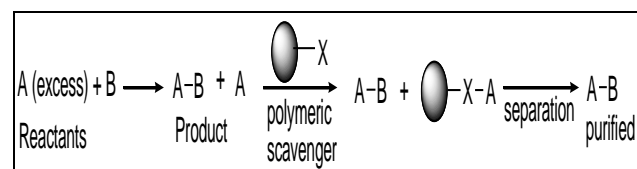
1. Introduction

New technologies have been developed that made it achievable to generate new compounds in a practically unlimited number. The use of polymer support in synthetic organic chemistry is much more, where the simultaneous service of combinatorial chemistry and synthesis in parallel enables. The convenience from polymeric aid is possible to conduct experiments from the computer software.

Scavenging methods may be useful in conventional organic synthesis in situations where a starting material has similar physical properties to the acquired product and is difficult to remove by traditional methods such as extraction, distillation, crystallization, and chromatography while avoiding time-consuming [1, 2], Scheme 1.

For example, if a substrate B is reacted with an excess of the A then the product AB will be comprising of the residual excess of the A removal of this excess reagent in the lead reaction completion can be achieved through employing an appropriate scavenger resin. Therefore, the

scavenger resin is added and reacts by the excess of A, a follow-on in being covalently bonded to the resin. An electrophonic scavenger is a nucleophilic polymer and conversely [3].



Scheme 1. General representation of a reaction involving a polymeric scavenger.

An early report lists dozens of polymeric reagents that have found applications as a catalyst, protecting groups, substrate carriers, analysis (sensor), ion exchange, and detection of reaction intermediates, chromatography, enzyme immobilization, and others.

Scavengers, as good as we do for organic synthesis, have been used as polymer nucleophiles as well as polymeric phosphine reagents, sulfonium salts, halogenating agents, redox, acylating, and

*Corresponding author e-mail: ramiz.hoti@uni-pr.edu.

Receive Date: 14 September 2020, Revise Date: 25 December 2020, Accept Date: 26 February 2021

DOI: 10.21608/EJCHEM.2021.42919.2864

©2021 National Information and Documentation Center (NIDOC)

alkylating reagents [4, 5]. Frechter researched an early example of the polymeric purification of allergenisovalanthylactone (the allergen present in natural oils) [6].

Keating and Armstrong research and give us the first report of the application of a polymer-based reagent to synthesis. Thus, the polymeric polypeptide was obtained with high yields and purity [7]. Through polymerization in a cylindrical glass mold, Tripp et al. were prepared macroporous disks while polyethylene covered porous poly (chloromethyl-styrene-co-divinylbenzene) [8]. To facilitate the work and purification of parallel non-peptide small molecule libraries were used solid-supported (nucleophiles and electrophiles). Most of the polymeric supports used to date have been obtained by various methods in gel or porous form with different porosity. Gel-type beads in swelling are important to enable access to the reactive side. This thus limits the number of solvents that be able to use. Permanently porous beads do not need to require pre-swelling and are consequently appropriate for different solvents.

Last employment by Svec, Frechet, et al. has publicized that porous polymer monoliths under flow-through conditions can exceed many of the issues related to beads. Nevertheless, materials with low surface areas are characterized by high permeability and larger pore sizes. Berkeley Group has functionalized the polymer by grafting on the monolithic surface with relatively large pores [9]. Polymerization, or curing, the continuous phase of a HIPE gives a porous polymeric material known as a PolyHIPE with highly permeable monoliths. Different authors have used a nucleophilic scavenging agent, synthesis ureas, thioureas amides, sulfonamides, and carbamates to remove the excess isocyanate, isocyanide, isociamide, acyl chloride, or sulfonyl chlorides [10, 11]. Scavenger resins, depending on their structure and functionalities, can be used for scavenging of: anhydride [12], acid chloride [13], amines [14, 15], esters, epoxides [16, 17], aldehydes and ketones [18, 19], miscellaneous compounds [20], for metal removal from a reaction mixture [21], functionalized with gold nanoparticles [22], for efficient removal of environmental pollutants [23], in the field of culture heritage to clean surfaces for art conservation and restoration [24], preventing paper documents [25] and many others [26].

The majority usually used method of forming HIPEs is through the slow addition of a porogen (non-continuous phase) to the continuous phase with mixing, although other methods can be used [27].

The aim is to synthesized poly (VBC-co-DVB) polyHIPE monoliths functionalized with tris (2-aminoethyl) amine which can be used as scavengers. Prepared PolyHIPE materials with a 5% degree of crosslinking by divinylbenzene, hydrophobic monomer possessing reactive chlorine, and allowing for the polyHIPE material to be tailored post-polymerization [28]. The resulting porous materials with reactive pendant vinyl groups be able for functionalization with an amino group from tris(2-aminoethyl)amine in different times excess and refluxed are presented in Table 1.

2. Experimental:

2.1. Materials and Methods:

4-Vinylbenzyl chloride (VBC, 90% Sigma Aldrich) and divinylbenzene (DVB, 80%, composed of 80% of divinylbenzene and 20% of ethyl vinyl benzene, Sigma Aldrich) were passed through an inhibitor removal column (Aldrich, Al_2O_3 Fischer Chemical), α, α' -azoisobutyronitrile (AIBN, Fluka), sorbitan monooleate (Span 80, Aldrich), tris(2-aminoethyl)amine (Fluka), tetrahydrofuran (THF dehydrate, Baker), calcium chloride hexahydrate ($CaCl_2 \times 6H_2O$, 98%, Sigma Aldrich), triethylamine (Sigma Aldrich), pyridine (Sigma Aldrich), nitric acid (Fluka, 65% aqueous solution), ethanol and methanol (Merck) were also used as received.

2.2. Infrared Spectral Analysis:

A Fourier transforms infrared spectrometer (Perkin Elmer FT-IR 1650 spectrometer) was used to identify the components of the 'pendant chloromethyl groups' located on the internal and external surfaces of the products. The absorption spectra were measured in KBr pellets between 4000 and 500 cm^{-1} .

2.3. Surface Area Analysis of Spherical Porous Polymer Particles:

Nitrogen adsorption and desorption isotherms were measured at 77.3 K using a Micromeritics Tristar II 3020 r (BET) surface area analyzer. The specific surface area of spherical porous poly (DVB-VBC) and immobilization with tris (2-aminoethyl)amine was obtained using the standard BET method.

2.4. Potentiometric measurements:

Potentiometric measurements Chlorine content was determined by potentiometric titration. A Potentiometric measurement was used to perform on a Hanna 8818 Microprocessor pH/mV/ $^{\circ}C$ Metre.

2.5. Elemental analysis:

Quantitative elemental analyzers of polymers were used to determine by C, H, and N elemental analysis, using a Perkin Elmer CHN 2400 analyzer

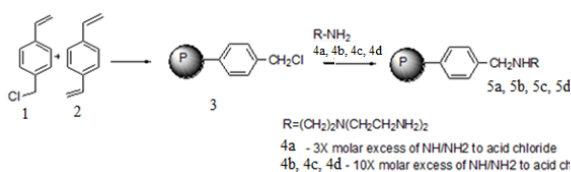
series II (C, H, N, S, and O). We were determined the amount (wt. %) of chemical transformations of functionalized polymers

2.6. Preparation of 4-vinylbenzylchloride/divinylbenzenepolyHIPE material:

HIPE material 4-Vinylbenzyl chloride (5.3 g, 0.035 mol) was placed in a reactor together with divinylbenzene (0.30 g, 0.002 mol), ABIN (0.06 g), and the surfactant sorbitan monooleate (Span 80; 1.04 g), and the mixture was stirred with an overhead stirrer at 500 rpm. An aqueous phase, consisting of 1.79 g $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ till 100 ml deionized water which was previously degassed under reduced pressure for 15 min, was placed in a baffled suspension polymerization reactor. The emulsion was stirred (300 rpm) for another 30 min at room temperature, after addition of the aqueous phase, then transferred to a mold for curing (24 h at 60 °C). The resulting polyHIPE was purified by Soxhlet extraction (distillation water for 24 h and ethanol for 24 h) then dried in a vacuum for 24 h.

2.7. Scavenging Experiments:

PolyHIPE (100mg, 4.01 mmol of chloromethyl groups per gram) was placed in a reactor together (at a molar ratio of amine/ chloromethyl groups 3/1) with 4a (17.64 mg, 0.12 mmol) of tris(2-aminoethyl)amine and refluxed for 1h, and 4b, 4c, 4d (at a molar ratio of amine/chloromethyl groups 10/1) with (58.8 mg, 0.4 mmol) of tris(2-aminoethyl)amine refluxed for 1, 3, 6 h, then mixture dissolved in 5 ml dimethylformamide at 45 °C. The products were washed with DMF, MeOH, NEt_3 , MeOH, MeOH/ H_2O (1:1), MeOH, and THF, dried in a vacuum oven (10 mbar, at 50 °C for 24h), Scheme 2.



Scheme 2. Functionalization of PolyHIPE monolithic materials by tris(2-aminoethyl)amine.

3. Results and Discussions:

The production of VBC-co-DVB PolyHIPE 3 has been functionalized with a nucleophilic amines tris (2-aminoethyl) amine, such is presented in scheme 2.

Functionalization of PolyHIPE monolithic materials by tris (2-aminoethyl) amine 4a (at a molar ratio of amine/ chloromethyl groups 3/1) refluxed for 1h, and with 4b, 4c, 4d (at a molar ratio of amine/chloromethyl groups 10/1) refluxed for 1h, 3h, 6h are presented in Table 1.

FTIR Analysis of Synthesized Spherical Porous Polymer: In the DVB (2) FTIR spectrum monomer showed the peak at 3086 cm^{-1} resulting from the $\nu(\text{C-H})$ stretching vibrations of the vinyl group, the $\nu(\text{C-H})$ stretching vibrations of the group of the benzene ring are presented in $3050\text{-}3010\text{ cm}^{-1}$ and the methyl $\nu(\text{C-H})$ stretching of methyl group appeared at $2950\text{-}2750\text{ cm}^{-1}$. The appearance of the absorption signal at 1635 cm^{-1} resulted from $\nu(\text{C=C})$ stretching mode of the vinyl group, and the signal at $1600\text{-}1500\text{ cm}^{-1}$ corresponds to $\nu(\text{C=C})$ stretching vibrations of the aromatic group [29].

In the VBC (1) FTIR spectrum appeared the peak at 1630 cm^{-1} corresponding to the presence of vinyl bond (C=C), the absorption signal at 1270 cm^{-1} resulted from $\nu(\text{C-Cl})$ stretching vibrations [30], whereas the sharp peak at 710 cm^{-1} is characteristic for chloromethyl group vibrations [31]. In the spectrum of (3) FTIR spectrum spherical porous poly(DVB/VBC), the peak at $3300\text{-}3500\text{ cm}^{-1}$ corresponds to the presence of a low degree of hydroxyl group content in the polymer. This can be explained presumably by the partial hydrolysis of chloromethyl functionality through polymerization [32]. By comparison with the FTIR spectra of the DVB and VBC monomers, the presence of peaks due to C-Cl bonds (1265 and 680 cm^{-1}) was considerably reduced of the C=C peaks 1610 cm^{-1} , confirming the reduction of chlorine, indicates that the copolymerization was successful. Also, signals between $3000\text{-}2854\text{ cm}^{-1}$ associated with C-H bonds stretching from became more intense due to the copolymer backbone formation ($\text{sp}^3\text{ C}$ formation).

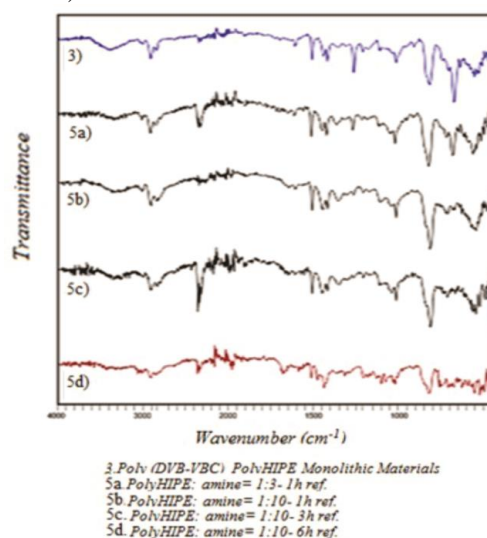


Figure 1. FTIR spectra of VBC/DVB PolyHIPE and functionalized with tris (2-aminoethyl) amine

A slight shift of C-C aromatic stretching modes towards higher wavenumbers was observed and this can be explained by a lower mobility of these aromatic carbons when polymer is formed [33]. As the ratio of amine groups increases by increasing the reflux time, it will become the most identifiable spectrum for characteristic groups. Thus, we will see a clearer spectrum in case 5d, since, for case 5a, the identification spectrum will be less visible. The medium band of $\nu(\text{N-H})$ stretching band at 3409 cm^{-1} clearly demonstrate the modification of compound (3) with tris(2-aminoethyl)amine, as shown in figure 2. Tris(2-aminoethyl)amine showing double absorption band at 1580 cm^{-1} and 1630 cm^{-1} for $\delta(\text{N-H})$ scissoring vibration and absorption band at 1020 cm^{-1} (stretching vibration for C-N) which confirms the presence of amino group.

Potentiometric measurements:

Chlorine was determined by potentiometric titration with AgNO_3 . 0.10 g of a support was placed in a flask and 5 ml of pyridine was added. The mixture was stirred and heated for 2 h at $100\text{ }^\circ\text{C}$. After cooling, 7 ml of HNO_3 and 10 ml of N, N-dimethylformamide were added and the mixture was diluted to 100 ml. Finally, 20 ml of this mixture was titrated with 0.01 M AgNO_3 . The amount of chlorine in the samples is calculated from the volumes of AgNO_3 used by titration.

The results of chlorine analysis indicate signify the possibility to control the degree of reaction of the chloromethyl groups. We were determined the amount (wt.%) of chemical transformations of functionalized polymers.

After washing and drying PolyHIPE starting material's which corresponds with (4.01 mmol of chloromethyl groups per gram) of the polymer product, to give an amino derivative, compound 3 reacted with 4a (0.12 mmol of amine/chloromethyl groups), when loading of chloromethyl groups was reduced 1.79 mmol/g. 1.8 mmol of NH/NH_2 groups per gram was isolated, found a product with a (24 %) degree of conversion, respectively as shown in Table 1.

The results of chlorine analysis indicate signify the possibility to control the degree of reaction of the chloromethyl groups. We were determined the amount (wt. %) of chemical transformations of functionalized polymers. After washing and drying PolyHIPE starting material's which corresponds polymer product 3 with (4.01 mmol of chloromethyl groups per gram). To give an amino derivative compound 3 reacted with 4a, is isolated 5a product when loading of chloromethyl groups was reduced 1.79 mmol/g and 1.8 mmol of NH/NH_2 groups per

gram was isolated, with (24 %) degree of conversion. Compound 3 reacted with 4b, chloromethyl groups were reduced 0.74 mmol/g. is isolated product 5b with approximately (41.6 %) conversion was achieved, after 1h. ref. with (3.05 mmol NH/NH_2 group per gram). While after 3h ref. a product 5c was isolated (with 3.61 mmol, of NH/NH_2 groups per gram) which corresponds to approximately (49.3 %) conversion. Products 5d refluxed for 6h.

Resulted in a higher degree of conversion (62.3 %), while chloromethyl groups were reduced to 0.18 mmol/g (4.56 mmol NH/NH_2 group per gram is isolated) follow-on in high loadings of immobilized of NH/NH_2 groups.

The surface area and so the pore size of the polymer frequently impact the applications for which a particular porous polymer can be used. The specific surface area of spherical porous poly (DVB-VBC) and immobilization with tris(2-aminoethyl)amine was obtained using the standard BET method. This rather low surface area suggested that the material possessed amount of mezo and micropores [34]. In the case of sample 5a (at a molar ratio of amine/chloromethyl groups 3/1) BET surface area was $8.26\text{ m}^2\text{g}^{-1}$. For sample 5b, 5c, 5d (at a molar ratio of amine/chloromethyl groups 10/1) for (1, 3, 6 h. refluxed) BET surface area was 8.28, 8.57, 8.84 m^2g^{-1} gave lower average pore radius and average pore volume, Table 1. The reason is that the mass transfer by diffusion of a flow system with particulate supports is commonly slower and less efficient than convection. Large pores in PolyHIPE monoliths enable low back pressure inflow makes PolyHIPE monoliths generally a material with a relatively low surface area.

In the diagrams below are presented the graphs for Adsorption cumulative pore area and pore volume for sample 3, 5a, 5b, 5c, 5d. Pore volume (nm) was 67.47, 58.82, 58.77, 58.87, and 59.92 (nm).

Table 1. Functionalization of Poly(4-vinylbenzylchloride-co-divinylbenzene) PolyHIPE Monolithic Materials.

Polymer ^[a]	reaction time/h	found %Cl ^[b]	calc. %N ^[c]	found %N	conversion % ^[d]	BET surface area [m ² g ⁻¹]	reactive groups [mmol ⁻¹] ^[e]
3		14,18				7.1	4.01
5a	1	6,36	13,56	3,34	24,6	8.26	1.8
5b	1	2,65	13,56	5,65	41,6	8.28	3.05
5c	3	1,59	13,56	6,69	49,3	8.57	3.61
5d	6	0,65	13,56	8,45	62,3	8.84	4.56

^[a] PolyHIPE monolithic material; products 5a, 5b, 5c, 5d, are derived from 3. ^[b] Determined by potentiometric measurements.

^[c] Calculated mass percentage of nitrogen for complete conversion. ^[d] Conversion determined on the basis of combustion analysis for nitrogen. ^[e] Loading of NH/NH₂ groups in the case of 5a 5b, 5c and 5d; otherwise, loading of % Cl for chloromethyl groups in case of 3.

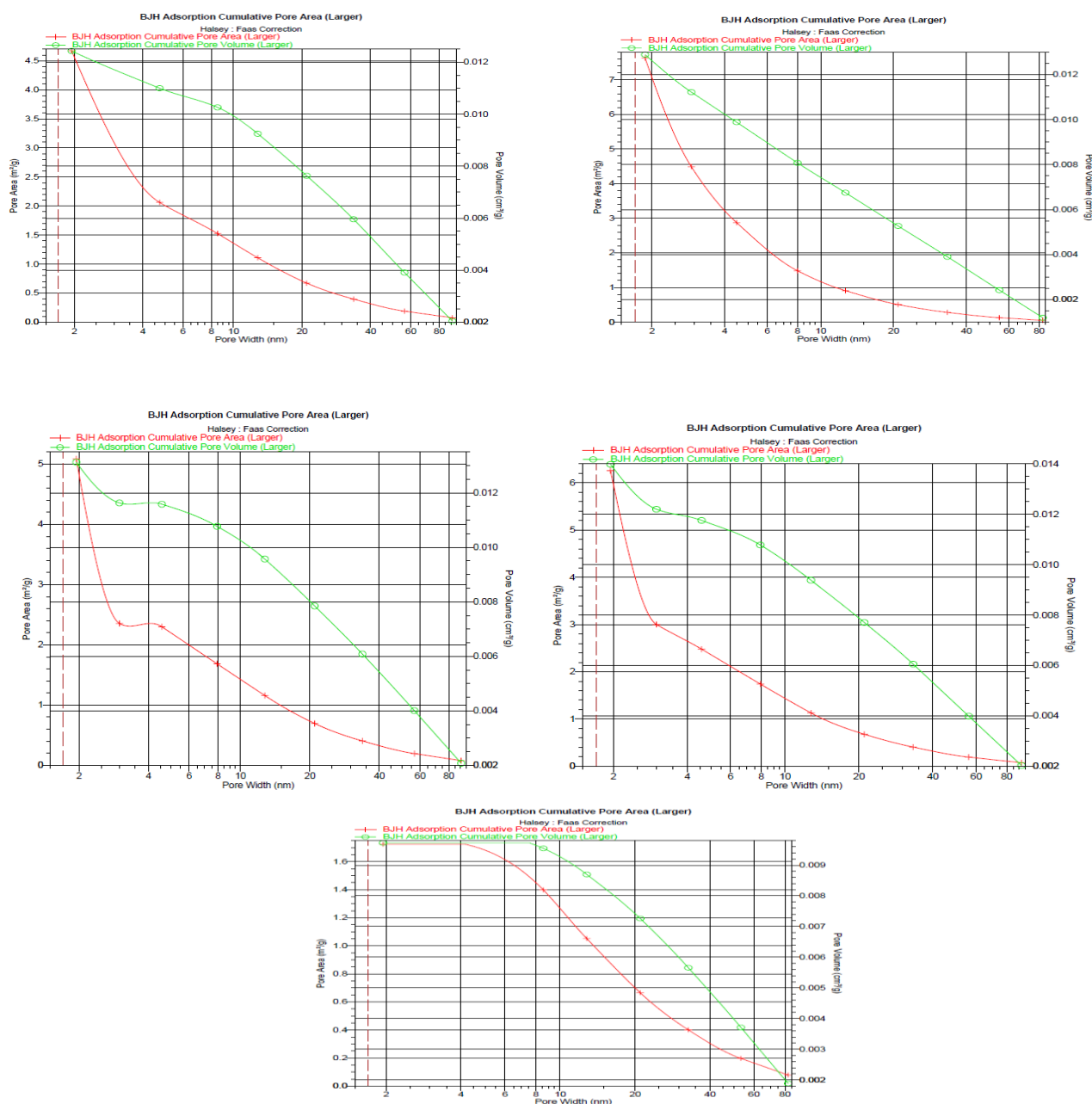


Fig. 2. The variations of adsorption cumulative pore area and pore volume for samples 3, 5a, 5b, 5c, 5d.

4. Conclusions

Our goal was to synthesize and functionalize PolyHIPE with nucleophilic groups, prepared VBC based PHPs with 5 % level of initial crosslinking functionalized PolyHIPE with tris (2-aminoethyl)amine.

These preliminary results indicate that monolithic PolyHIPE supports beneficial materials in organic synthesis procedures lead to transformations.

Monolithic polymer supports and scavengers have been prepared via nucleophilic displacement of chlorine in poly(4-vinylbenzylchloride-co-divinylbenzene)

PolyHIPE materials. Porous copolymers of DVB/DVB were prepared by emulsion templating using high internal phase emulsions (HIPEs) as precursors for monoliths (3) were chloromethyl group loading was 4.01 mmolg⁻¹.

We were done the reactions of monolithic PolyHIPE with tris(2-aminoethyl)amine at 45 °C, bring toward functionalized polymers with amino group, at a molar ratio of 3/1 (amine/chloromethyl groups) and 10/1 (in different time refluxed).

The most identifiable spectrum for characteristic of (NH/NH₂ groups per gram) ratio increases by increasing of rapport ratio and the reflux time. Also is increases the degree of functionalization with amine groups, with the result of product 5a with conversions (24 %) and products 5b, 5c, 5d gave conversions (41.6 %, 49.6 %, 62.3 %).

BET surface area in the case of sample 3 and (for sample 5a, 5b, 5c, and 5d) resulted in a significantly lower

increase of dry BET surface area (from 7.1 m²g⁻¹ to 8.84 m²g⁻¹).

5. Conflicts of interest

There are no conflicts to declare.

6. Acknowledgment

This study has been realized with the support of the University of Maribor, Faculty of Chemistry and Chemical Engineering, PolyOrgLab, Smetanova 17, SI-2000 Maribor, Slovenia.

This work was supported by the projects ofJoin EU-SEE>PENTA-EU@South Eastern Europe, Ministry of Education, Science and Sport, CEEPUS-SI-0708 Mobility grantprogramme.

7. References

- [1] JOHN C. HODGES, Covalent Scavengers for Primary and Secondary Amines, *Synlett***2000**; 2000(1): 152-158. DOI: 10.1055/s-2000-6465. <https://www.thieme-connect.com/products/ejournals/pdf/10.1055/s-2000-6465.pdf>
- [2] S.V. LEY, IAN R. BAXENDALE, G. BRUSOTTI, M. CALDARELLI, A. MASSI, M. NESI, Solid-supported reagents for multi-step organic synthesis: preparation and application, *Il Farmaco*, Volume **57**, Issue 4, 1 April 2002, Pages

321-330. [https://doi.org/10.1016/S0014-827X\(02\)01210-7](https://doi.org/10.1016/S0014-827X(02)01210-7).

- [3] K. SANDHYA, B. RAVINDRANATH, Comparative Efficacy of Polyamine-Based Scavenger Resins, *International Journal of Organic Chemistry*, Vol. **2** No.1, March 2012, 71-74 doi:10.4236/ijoc.2012.21012 Published Online March 2012 (<http://www.SciRP.org/journal/ijoc>).
- [4] AKELAH, A, SHERRINGTON, DC. Application of functionalized polymer in organic synthesis. *Chem. Rev.* 1981, 81, 557-586.
- [5] JASON EAMES AND MICHAEL WATKINSON, Polymeric Scavenger Reagents in Organic Synthesis, *Eur. J. Org. Chem.* 2001, 12132-1224, [https://doi.org/10.1002/1099-0690\(200104\)2001:7<1213::AID-EJOC1213>3.0.CO;2-K](https://doi.org/10.1002/1099-0690(200104)2001:7<1213::AID-EJOC1213>3.0.CO;2-K).
- [6] R. W. ARMSTRONG, A. P. COMBS, P. A. TEMPEST, S. D. BROWN, T. A. KEATING. Multiple-Component Condensation Strategies for Combinatorial Library Synthesis. *Chem Inform* 1996, **27** (27) no <https://doi.org/10.1002/chin.199627324>.
- [7] STEVEN V. LEY, IAN R. BAXENDALE, A ROBERT N. BREAM, PHILIP S. JACKSON, ANDREW G. LEACH, DEBORAH A. LONGBOTTOM, MARCELLA NESI, JAMES S. SCOTT, R. IAN STORER AND STEPHEN J. TAYLOR, Multi-step organic synthesis using solid-supported reagents and scavengers: a new paradigm in chemical library generation, *From the journal: Journal of the Chemical Society, perkin transactions* 1, Issue **23**, 2000. <https://doi.org/10.1039/B006588I>.
- [8] R. PONS, I. CARRERA, P. ERRA, H. KUNIEDA, C. SOLANS. Novel preparation methods for highly concentrated water-in-oil emulsions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 1994,91,259-266. [https://doi.org/10.1016/0927-7757\(94\)02950-4](https://doi.org/10.1016/0927-7757(94)02950-4).
- [9] TRIPP J. A., SVEC F., FRÉCHET J. M. J., Solid-phase acylating reagents in new format: Macroporous polymer disks: Macroporous polymer disks. *J. Comb. Chem.* 3, 604-611, 2001.
- [10] TRIPP, J. A.; NEEDHAM, T. P.; RIPP, E. M.; KONZMAN, B. G.; HOMNICK, P. J., A Continuous-Flow Electrophile Scavenger Prepared by a Simple Grafting Procedure. *React. Funct. Polym.* 2010, 70, 414– 418, DOI:10.1016/j.Reactfunctpolym.2010.03.010.
- [11] HOUCINE RAHALIB DIDIER STIENA, Highly-loaded amphiphilic polyimino resin: quench reagent and solid support for peptide synthesis, *Tetrahedron Letters*, Volume 47, Issue 47, 20 November 2006, Pages 8205-8207. <https://doi.org/10.1016/j.tetlet.2006.09.131>.
- [12] J.J. PARLOW, D.L. FLYNN, Solution-phase parallel synthesis of a benzoxazinone library using complementary molecular reactivity and molecular

- recognition (CMR/R) purification technology, *Tetrahedron*, Volume **54**, Issue 16, 16 April 1998, Pages 4013-4031, [https://doi.org/10.1016/S0040-4020\(98\)00132-X](https://doi.org/10.1016/S0040-4020(98)00132-X).
- [13] S. KIM, H. KO, S. KIM, T. LEE, J. COMB. Chem. Solution-Phase Synthesis of a Library of Biaryl Amides Using Girard's Reagent T as an Acid Chloride Scavenger, *J. Comb. Chem.* 2002, **4**, 6, 549–551 Publication Date: September 28, 2002 <https://doi.org/10.1021/cc020044z>
- [14] P. KRAJNC, J.F. BROWN, N.R. CAMERON, Monolithic Scavenger Resins by Amine Functionalizations of Poly(4-vinylbenzyl chloride-co-divinylbenzene) PolyHIPE Materials, *Org. Lett.* 2002, **4**, 15, 2497–2500 <https://doi.org/10.1021/ol026115k>.
- [15] M. KUMAR MUTHAYALA, A. KUMAR, Synthesis of Ionic Liquid-Supported Sulfonyl Azide and Its Application in Diazotransfer Reaction, *Org. Chem.* 2012, **77**, 19, 8787–8791 <https://doi.org/10.1021/jo301529b>.
- [16] R. KECILI, J. BILLING, M. LEEMAN, D. NIVHEDE, B. SELLERGRÉN, A. REES, E. YILMAZ, SEP. PURIF. TECHNOL. Fast identification of selective resins for removal of genotoxic aminopyridine impurities via screening of molecularly imprinted polymer libraries, *Journal of Chromatography A*, Volume 1339, 25 April 2014, Pages 65-72, <https://doi.org/10.1016/j.chroma.2014.02.073>
- [17] C. LEE, R. HELMY, C. STRULSON, J. PLEWA, E. KOŁODZIEJ, V. ANTONUCCI, B. MAO, C.J. WELCH, Z. GE, M.A. AL-SAYAH, Removal of Electrophilic Potential Genotoxic Impurities Using Nucleophilic Reactive Resins, *Org. Process Res. Dev.* 2010, **14**, 4, 1021–1026 Publication Date: April 14, 2010 <https://doi.org/10.1021/op1000397>
- [18] M.-F. BAKAĀ, J.-C. BARBE, V. MOINE, M. BIROT, H. DELEUZE, Efficient preparation, uses, and recycling of a polymer-bound sulfonylhydrazide scavenger, *Tetrahedron*, Volume 70, Issue 49, 9 December 2014, Pages 9421-9426, <https://doi.org/10.1016/j.tet.2014.10.026>
- [19] R. KECILI, D. NIVHEDE, J. BILLING, M. LEEMAN, B. SELLERGRÉN, E. YILMAZ, Removal of acrolein from active pharmaceutical ingredients using aldehyde scavengers", *Organic Process Research & Development*, **16** (6), 1225-1229 (2012), <https://doi.org/10.1021/op3000459>
- [20] F. BRANDHUBER, M. ZENGERLE, L. PORWOL, A. BIERWISCH, M. KOLLER, G. REITER, F. WOREK, S. KUBIK, Tabun scavengers based on hydroxamic acid containing cyclodextrins, *Chem. Commun.* **49**, 3425 (2013). <https://doi.org/10.1039/C3CC41290C>
- [21] PULKO, I.; SANDHOLZER, M.; KOLAR, M, SLUGOVIC, C.; KRAJNC, P, Removal of olefin metathesis catalyst by 4-nitrophenyl acrylate based polymer supports." *Tetrahedron Lett.* 2010, **51**, 5827-5829. DOI: 10.1016/j.tetlet.2010.08.114
- [22] Cao Y., Lv M., Xu H., Svec F., Tan T., Lv Y., Planar monolithic porous polymer layers functionalized with gold nanoparticles as large-area substrates for sensitive surface-enhanced Raman scattering sensing of bacteria. *Anal. Chim. Acta*, accepted (DOI: 10.1016/j.aca.2015.09.018)
- [23] SHUNSUKE MIZUNO^A, TAKA-AKIASOH^A, YOSHINORI TAKASHIMA^B, AKIRA HARADA^BHIROSHI UYAMA^A, Cyclodextrin cross-linked polymer monolith for efficient removal of environmental pollutants by flow-through method *Polymer Degradation and Stability* Volume 160, February 2019, Pages 136-141 <https://doi.org/10.1016/j.polyimdegradstab.2018.12.014>
- [24] ROKAYA ALY SOBH¹; HANAA NA SR²; WAEL SABRY MOHAMED³, Synthesis and Characterization of Magnetic Sponge Nanocomposite for Cleaning Archeological Lime Stone, *Egypt. J. Chem.* Vol. 63, No.2 . pp.507-514 (2020), <http://ejchem.journals.ekb.eg/> DOI: 10.21608/EJCHEM.2019.18448.2141
- [25] MOHAMED B. GAZY¹; WALEED K. EL-ZAWAWY²; ALAA E. ELSAYED³; TAHA M.A. ELDEBSS⁴; MOHAMED R. HELAL⁵; KHRASHED⁵ Application of Some Polymer latexes in Preventing Paper Documents Forgery Article 1, Volume 62, Issue 1, January 2019, Page 1-14 DOI: 10.21608/EJCHEM.2018.4309.1389
- [26] JUEWEN LIU[†], ALISON STACE-NAUGHTON[†], XINGMAO JIANG[†], AND C. JEFFREY BRINKER^{**†§}, Porous Nanoparticle Supported Lipid Bilayers (Protocells) as Delivery Vehicles. *J. Am. Chem. Soc.* 2009, **131**, 4, 1354–1355, January 12, 2009 <https://doi.org/10.1021/ja808018y>
- [27] S. KOVACIC, P. KRAJNC, Macroporous monolithic poly(4-vinylbenzyl chloride) columns for organic synthesis facilitation by in situ polymerization of high internal phase emulsions *Journal of Polymer Science Part a-Polymer Chemistry*, 2009, **47**, 6726-6734. <https://doi.org/10.1002/pola.23732>
- [28] S. CALDWELL, D. W. JOHNSON, M. P. DIDSBURY, B. A. MURRAY, J. J. WU, S. A. PRZYBORSKI AND N. R. CAMERON. Degradable emulsion-templated scaffolds for tissue engineering from thiol-enephotopolymerisation, *Journal Soft Matter. Soft Matter*, 2012, **8**, 10344-10351, <https://doi.org/10.1039/C2SM26250A>
- [29] D. JERMAKOWICZ-BARTKOWIAK, B. N. KOLARZ, AND A. SERWIN. Sorption of precious metals from acid solutions by functionalised vinylbenzyl chloride – acrylonitrile – divinylbenzene copolymers bearing amino and

- guanidine ligands, *Reactive and Functional Polymers* 65(1):135-142 · November 2005, DOI: 10.1016/j.reactfunctpolym.2004.11.010
- [30] X. HANKUN, F. JUN, G. MINGLI, L. XIAOHUAN, W. XIAOLAN, AND T. SONG. Novel anion exchange membrane based on copolymer of methyl methacrylate, vinylbenzyl chloride and ethyl acrylate for alkaline fuel cells, *Journal of Membrane Science*, Volume 354, Issues 1–2, 15 May 2010, Pages 206-211, <https://doi.org/10.1016/j.memsci.2010.02.028>
- [31] P. A. G. CORMACK, A. DAVIES, AND N. FONTANALS. Synthesis and characterization of microporous polymer microspheres with strong cation-exchange character, *Reactive and Functional Polymers*, Volume 72, Issue 12, December 2012, Pages 939-946. <https://doi.org/10.1016/j.reactfunctpolym.2012.08.003>
- [32] S. SAMATYA, N. KABAY, AND A. TUNCEL, Monodisperse-porous N-methyl-D-glucaminefunctionalized poly(vinylbenzylchloride-co-divinylbenzene) beads as boron selective sorbent, *J. Appl. Polym. Sci.*, 126, 1475 (2012), <https://doi.org/10.1002/app.36912>
- [33] KENNETH S. W. SING, DOUGLAS H. EVERETT, R. A. W. HAUL, L. MOSCOU, ROBERT A. PIEROTTI, JEAN ROUQUEROL, TERESA SIEMIENIEWSKA. Reporting Physisorption Data for Gas/Solid Systems, Wiley online library, 15 March, 2008, <https://doi.org/10.1002/9783527610044.hetcat0065>
- [34] FUMIYASU ONO, SEIJI SHINKAI, HISAYUKI WATANABE, High internal phase water/oil and oil/water gel emulsions formed using a glucose-based low-molecular-weight gelator†, From the journal: *New Journal of chemistry*, Issue 9, 2018, <https://doi.org/10.1039/C7NJ04508E>