

Supporting ruthenium initiator on PolyHIPE

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Abstract

PolyHIPE samples were successfully synthesised using divinylbenzene and styrene as polymerisable continuous phase, aqueous phase containing potassium persulphate and calcium chloride dihydrate, a mixture of emulsifiers (SPAN20, CTAB and DDBSS) and toluene as a porogen. The PolyHIPE samples 1 and 2 and the PolyHIPE sample 3 were designed to be 90 and 92% porous, respectively, based on the aqueous phase content. PolyHIPE samples were found to be porous and open-cell microstructures with the surface area of 370–430 m² g⁻¹.

Alkylidene exchange reactions were carried out between the double bonds of the PolyHIPE and the ruthenium initiator, Ru(=CHPh)(PCy₃)₂Cl₂, for the attachment of the initiator. The amount of initiator loading was determined by phosphorous analysis and for the first time by Rutherford backscattering (RBS) analysis. The loading of the initiator on the PolyHIPE samples, based on phosphorous analysis, was found to be 0.09–0.19 mmol/g. The RBS analysis showed the level of initiator loading to be 0.053–0.097 mmol/g. The level of initiator loading obtained from the phosphorous and the RBS analysis is higher than 0.035 mmol/g reported previously for ruthenium initiator supported on crosslinked polystyrene. However, the level of initiator loading obtained from RBS analysis is lower than that obtained from the phosphorous analysis by ICP-OES. The reason for this discrepancy is believed to be due to inaccuracy of phosphorous analysis as the result of the insolubility of the PolyHIPE supported initiator. © 2006 Elsevier B.V. All rights reserved.

Keywords: PolyHIPE; Supported catalyst; Grubbs initiator; Rutherford backscattering; Supported ruthenium initiator

1. Introduction

Combinatorial chemistry has received much attention as a powerful tool for the discovery of new biologically active molecules for use as pharmaceuticals and agrochemicals [1]. Most of the work in this area is based on using Merrifield resin which consists of partially crosslinked polystyrene beads; polystyrene crosslinked with divinylbenzene (DVB) [2]. The problem with using Merrifield resin is that compound loadings on resin can be low, and therefore quite large amounts of resin are required to obtain only a few milligrams of compound after cleavage. Moreover, how the resin swells in solvents is an important factor when coming to choose the resin. Resin beads that do not become swollen in solvents hinder reaction site accessibility and therefore diminish reaction rates [3].

Ring opening metathesis polymerisation (ROMP) is a well-established living polymerisation technique, in which cyclic and

bicyclic olefin monomers such as norbornene and its derivatives are polymerised to yield unsaturated linear polymers. Well-defined ROMP initiators have been developed by Schrock et al. [4,5] based on tungsten and molybdenum which impart a high degree of control over the initiation and propagation in ROMP but which are very sensitive to water, oxygen and other polar functionalities. This sensitivity limited ROMP to the use of aprotic organic (often chlorinated) solvents and often hampered their evolution from research laboratories to full-scale industrial processes.

During the recent years impressive progress has been made in the development of homogeneous olefin metathesis catalysts [6–9]. This has mainly been due to the synthesis of new ruthenium alkylidene complexes, such as Ru(=CHPh)(Cl)₂(PCy₃)₂ [10,11] and Ru(=CHPh)(Cl)₂(PCy₃)L (where L is an *N*-heterocyclic carbene ligand) [12–16]. These initiators are tolerant of functional groups and even water. Immobilisation of these catalysts on solid supports will be expected to facilitate the work up and make the metathesis reactions more attractive for practical applications. Nguyen and Grubbs presented the first example of immobilising a well-defined ruthenium alkylidene complex on a solid support [17]. In this work

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complex $\text{Ru}(=\text{CH}-\text{CH}=\text{CPh}_2)(\text{Cl})_2(\text{PPh}_3)_2$ was tethered to a series of phosphine-functionalised polystyrene–divinylbenzene (PS–DVB) solid supports by phosphine exchange reaction. These supported catalysts brought about the ROMP of norbornene and cyclooctene, as well as the self-metathesis of *cis*-2-pentene, although at a much slower rate than that of the un-supported catalyst.

Recently, several publications appeared describing new approaches to immobilise ruthenium alkylidene complexes [18]. In most cases, the initiator is attached to the support through the alkylidene unit [19,20]; one example is the supported first generation ruthenium complex known as boomerang, reported by Barrett. It is claimed that during metathesis the catalyst is released to the reaction medium, acts as homogeneous catalyst, and then is recaptured by the support once the substrate has been consumed. This approach is actually not suited for continuous processes. Moreover, the crosslinked polystyrene resin used for the support contains a low content of vinyl group of 0.8 mmol/g and that would be expected to result in low initiator loading. There is one report where a ruthenium alkylidene is bound to a Merrifield resin functionalised with an *N*-heterocyclic carbene ligand, producing an immobilised catalyst that is active for RCM [21]. Mol and coworkers [22] adopted a different approach for the immobilisation of ruthenium alkylidene complex. They replaced the chlorine ligands of the ruthenium complex with carboxylic groups and then attached the catalyst through the carboxylic groups. The supported initiator performed well in RCM but suffered from the catalyst leaching.

PolyHIPEs are highly porous materials obtained by polymerising the continuous phase of a high internal phase emulsion (HIPE) [23–27]. These materials have been used as membranes, absorbents, supports for a variety of heterogeneous catalytic systems, cell and enzymes [28–32]. Many applications of PolyHIPEs in areas such as heterogeneous catalysis, liquid chromatography and solid phase extraction require high surface area [33]. By far, the most studied PolyHIPE system is the styrene/DVB based material [34,35]. High internal phase emulsions of an aqueous phase in a mixture of styrene, DVB and non-ionic surfactant are prepared and polymerised by heating in a sealed container, typically for 24 h at 50 °C. This yields a solid, crosslinked, monolithic polymer material with a permanent, macroporous, open cellular structure.

Our interest in this area is developing a high-loading supported ruthenium initiator and applying the immobilised initiator to ROMP and RCM. The work reported here describes some of our recent results as part of our programme of work aimed at developing a method for preparing high-loading capacity resins based on PolyHIPEs synthesised from predominantly DVB. PolyHIPE synthesised from predominantly DVB has several advantages: the dimethylene group/spacer on the structure means that more stable attachments can be made, the distance from the backbone means the functional group is more accessible to the solvent, allows high level of active (free) double bonds in the resin, and their permanent porosity allows better access to the active sites. To the best of our knowledge the work described here is the first example of supporting ruthenium initiator on PolyHIPE.

2. Experimental

2.1. Materials

Divinylbenzene (DVB, which includes 20% *m*- and *p*-ethylstyrene) (Aldrich), was purified by passing through a column of alumina to remove the inhibitor. Bromine, toluene, potassium persulphate, calcium chloride dihydrate, styrene and the surfactants were purchased from Aldrich and used as received. The surfactants used in this work are listed in Scheme 1.

The Grubbs first generation ruthenium initiator was synthesised according to literature procedures. All solvents were degassed prior to use.

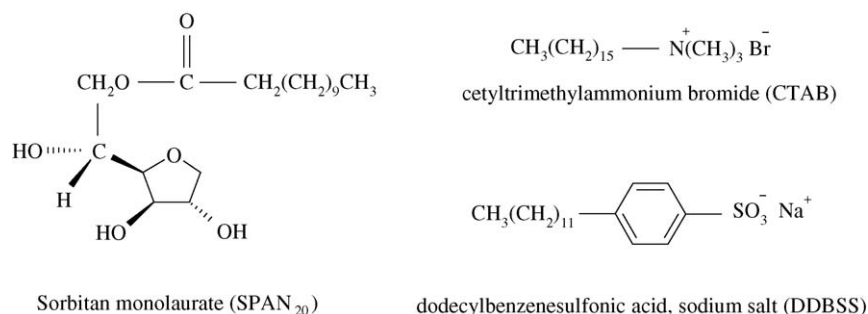
2.2. Characterisation

2.2.1. Elemental analysis

Carbon and hydrogen contents were determined using a CE-440 Elemental analyzer, Exeter analytical, Inc. and bromine content was determined by DX-120 Ion Chromatograph Dionex. Phosphorous analysis was performed by ICP-OES using a mixture of a sulphuric acid and perchloric acid (1:1, v:v).

2.2.2. Surface area measurement

Nitrogen adsorption measurements were performed at 77.3 K on a Micromeritics Tristar 3000 model Analyzer. Samples were degassed at 100 °C overnight under vacuum prior to data collec-



Scheme 1. Structures of the surfactants used.

tion. Surface area measurements utilized a nine points adsorption isotherm collected over 0.05–0.20 P/P_0 and analyzed via the Brunauer–Emmet–Teller (BET) method. Five determinations were carried out for each sample.

2.2.3. Electron microscopy

Environmental scanning electron microscopy (ESEM) was carried out using Philips/FEI XL30 with MCTRL V6.00 software. Prior to analysis, specimens were sputter coated with a thin layer of gold to enhance conductivity.

2.2.4. Solid-state ^{13}C NMR analysis

Solid-state ^{13}C NMR was recorded on a Varian Unity Inova spectrometer with a 5 mm (rotor outside diameter) MAS probe. The spectra were obtained using a cross-polarisation experiment [36]. The spectra are referenced to tetramethylsilane (by setting the high-frequency signal from adamantane to 38.4 ppm).

2.2.5. Ion beam analysis

The Ru content of PolyHIPE materials was determined via RBS analysis. PolyHIPE samples were mounted into the target station of an ion beam accelerator, and bombarded with $^4\text{He}^+$ ions with an energy of 1.8 MeV. At this energy, the scattering cross-sections do not deviate from the Rutherford scattering cross-sections [37], therefore enabling absolute determination of the Ru and C concentrations. $^4\text{He}^+$ ions recoiling from the sample were detected at 170° to the incident beam and their energy analyzed to composition versus depth profile. Typical experimental data are shown in Fig. 3. $^4\text{He}^+$ ions lose less of their energy recoiling from massive nuclei than they do recoiling from comparatively light nuclei, therefore the highest energy recoils detected must originate from the most massive elements in the sample. The elemental markers shown on the abscissa indicate the maximum possible energy of recoils due to each element in the sample.

2.3. Preparation of PolyHIPE

PolyHIPEs (polymerised high internal phase emulsions) are produced from polymerisation of DVB (contains % 20 ethyl styrene) and mixtures of DVB and styrene (80:20, w:w) initiated by potassium persulphate, using a mixture of surfactants (SPAN 20, DDBSS and CTAB), and water (distilled) as the internal phase. The aqueous phase also contained calcium chloride dihydrate. Toluene was used as a porogen. The polymerisation was carried out in an oven at 60°C for 24–48 h. The bottle containing the resulting PolyHIPE was then cut away using a scalpel, and the solid foams were extracted with water then 2-propanol

for 24 h each in a soxhlet apparatus. Solid foams were then dried under vacuum at 50°C to a constant mass.

2.4. Bromination of PolyHIPE samples

PolyHIPE (100 mg, grounded) was placed in a small round bottom flask with distilled dichloromethane (DCM) (3 ml) and stirred using a magnetic stir bar. An excess of bromine (≈ 2 ml) was added to the solution. The resulting mixture was left with continuous stirring for 72 h. The solution was filtered and washed with DCM several times until the filter paper became clear. The samples were left at room temperature (30 min) before drying in vacuum (50°C , 24 h). Samples were submitted to elemental analysis for % Br.

2.5. Attachment of Grubbs initiator to PolyHIPE

In a typical experiment, PolyHIPE (100 mg) was placed in an ampoule containing magnetic stir bar. It was carefully grounded into a fine powder using a glass rod. Grubbs initiator, $\text{Ru}(=\text{CHPh})(\text{PCy}_3)_2\text{Cl}_2$ (150 mg), was placed in a vial, DCM (3 ml) was added and agitated to dissolve the catalyst. The resulting purple solution was transferred into the ampoule and left to stir for 1 h, following which it was removed from the glove box. The DCM was then removed under vacuum and the solid residue was dried for up to 1 h. This process was repeated several times. The unreacted catalyst was removed via cannular filtration. The PolyHIPE supported ruthenium catalyst was washed with DCM, dried and stored under nitrogen.

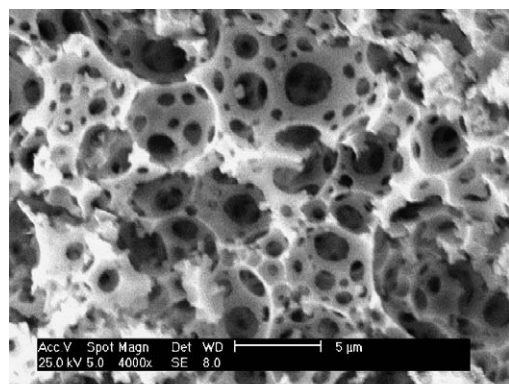
3. Results and discussion

PolyHIPE samples 1 and 2 were prepared from DVB (containing 20% ethyl styrene) and PolyHIPE sample 3 was prepared from a mixture of 80% DVB (containing 20% ethyl styrene) and 20% styrene. PolyHIPE samples were fully characterised and the results are summarized in Table 1. The PolyHIPE samples 1 and 2 and the PolyHIPE sample 3 were designed to be 90 and 92% porous, respectively, based on the aqueous phase content. The internal structures of PolyHIPE samples were characterised using ESEM. The PolyHIPE samples show porous, open-cell microstructures and similar morphologies as shown in Fig. 1a–c.

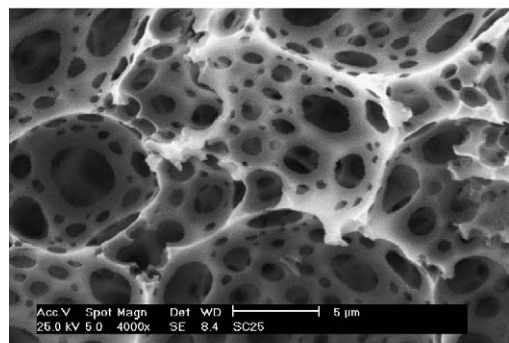
Sample 1 had a surface area of $372\text{ m}^2\text{ g}^{-1}$, and the surface area was increased to $431\text{ m}^2\text{ g}^{-1}$ (sample 2) when the polymerisation time was reduced by the factor of 2. Certain potential applications of PolyHIPE materials, such as supports for catalysts or stationary phases for chromatography, require high surface areas. For example, typical silica packing materials for liquid chromatography have surface areas around $200\text{--}300\text{ m}^2\text{ g}^{-1}$

Table 1
PolyHIPE samples

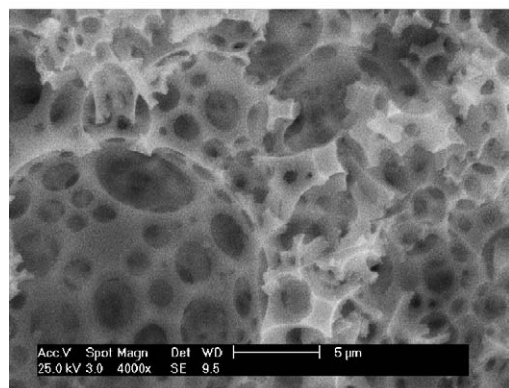
PolyHIPE samples	DVB/styrene	Polymerisation time (h)	Surface area (m^2/g)	% C, found (calc.)	% H, found (calc.)
1	100/0	48	372	83.26 (91.98)	7.28 (8.02)
2	100/0	24	431	83.16 (91.98)	7.20 (8.02)
3	80/20	48	375	85.50 (92.03)	7.37 (7.97)



(a)



(b)

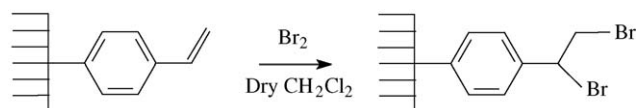


(c)

Fig. 1. ESEM images of (a) PolyHIPE sample 1, (b) PolyHIPE sample 2 and (c) PolyHIPE sample 3. Scale bar = 5 μm .

and heterogeneous catalysts often have values in excess of 500 $\text{m}^2 \text{g}^{-1}$.

It can be seen from Table 1 that there is a large difference between the found and calculated values for carbon and hydrogen which merits an explanation. Generally, the elemental analysis for PolyHIPE samples has not been reported in the literature due to the discrepancies between the calculated and found values for both carbon and hydrogen. It is widely believed, amongst the researchers working on PolyHIPE, which the found values for both carbon and hydrogen tend to be lower than calculated due to the presence of residual surfactants. It is acknowledged that there is always 3–5% of residual surfactant in the PolyHIPE samples. In fact the elemental analysis is reported only for functionalised PolyHIPE samples [30,38,39]. Moreover, the



Scheme 2. Bromination of PolyHIPE samples.

PolyHIPE samples are known to contain residual calcium chloride dihydrate which is used during the preparation. It is highly likely that our PolyHIPE samples contain the residual of surfactants and calcium chloride dihydrate which would be responsible for the discrepancies between the calculated and found values for both carbon and hydrogen in the elemental analysis.

The double bond contents of the PolyHIPE samples were determined by the reaction with bromine. Addition of bromine to vinyl groups led to formation of 1,2-dibromo ethyl groups on the PolyHIPE support (Scheme 2).

PolyHIPE samples, before and after bromination, were analyzed by solid-state ^{13}C NMR, Fig. 2. The spectrum of the PolyHIPE sample 1 before bromination is shown in Fig. 2a. The peaks at 137.4 and 113.4 ppm correspond to methine and methylene carbon atoms of unreacted vinyl groups. The quantitative evidence of a reduction in the number of double bonds after the bromination, is the absence of clear peak maxima at 113 ppm in solid-state ^{13}C NMR of brominated-PolyHIPE 1 sample (Fig. 2b).

Sherrington and coworkers [35,36] carried out arrayed contact cross-polarization (CP) experiments on their PolyHIPE samples and used the integrations to quantify the level of unreacted (free) vinyl groups. The ratio of the intensities of the peak at 127.8 ppm due to the aromatic CH and at 113.4 ppm due to $=\text{CH}_2$ ($\text{ArH}=\text{CH}_2$) revealed the presence of 40% free double bonds in their PolyHIPE samples. We also carried out similar NMR experiments on our PolyHIPE samples to quantify the level of unreacted vinyl groups and found that although our samples appear to have more unreacted double bonds, the procedure is unreliable.

The bromine content of the PolyHIPE samples was determined by the elemental analysis and was related to the reactive double bond contents (mmol/g) and wt.% of double bonds. The calculation is based on the average molecular weight per repeating unit and the mole content of the functional groups determined by elemental analysis [30]. The results are summarized in Table 2.

The calculation shows that PolyHIPE samples prepared here contain 2.17–4.36 mmol/g or 5.86–11.77 wt.% reactive double bonds. The vinyl content for PolyHIPE samples made from the same grade DVB (containing 20% ethyl styrene) is reported to

Table 2
The results of the bromination of PolyHIPE samples

Brominated PolyHIPE samples	% Br found	Bromide (mmol/g)	Reactive double bonds (mmol/g)	Reactive double bonds (wt.%)
1	41.09	5.14	4.36	11.77
2	39.91	4.99	4.16	11.23
3	25.66	3.21	2.17	5.86

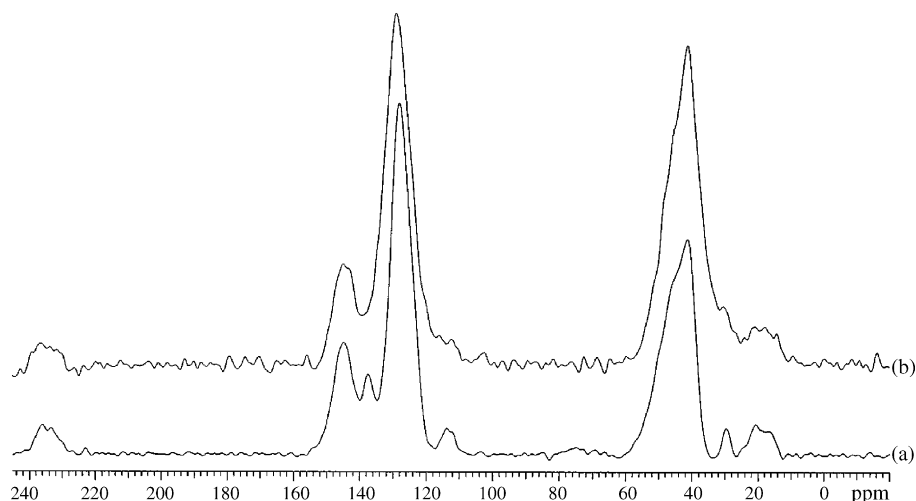
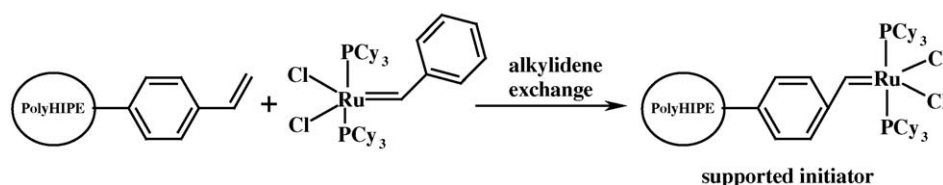


Fig. 2. Solid-state ^{13}C NMR spectra of: (a) PolyHIPE sample 1 and (b) brominated PolyHIPE sample 1.



Scheme 3. Attachment of ruthenium initiator on PolyHIPE support.

be 3.0 mmol/g [38] which is lower than 4.16–4.36 mmol/g found for our PolyHIPE samples (samples 1 and 2).

In order to attach $\text{Ru}(\text{=CHPh})(\text{PCy}_3)_2\text{Cl}_2$ on the PolyHIPE support, alkylidene exchange reactions were carried out between the reactive double bonds of PolyHIPE and the ruthenium initiator, Scheme 3.

The samples were subjected to phosphorous analysis, the results of which were related to the amount of loading of the ruthenium initiator on PolyHIPE support. The results of phosphorous analysis and the loading of the ruthenium initiator are given in Table 3.

Organic solid supports used for various applications are generally based on polystyrene crosslinked with 1–2% DVB. Therefore, the initiator loading on these supports depends on the level of reactive double bonds which is generally low. The loading of the initiator on our PolyHIPE samples, based on phosphorous analysis, is 0.09–0.19 mmol/g which is higher than the loading of 0.035 mmol/g reported by Mol and coworkers for the ruthenium initiator supported on crosslinked polystyrene [22].

The PolyHIPE supported initiator is insoluble, making phosphorous and ruthenium analysis and therefore the extent of

loading via ICP-OES analysis problematic. The ion beam analysis was therefore used to establish the loading of the initiator. Rutherford backscattering (RBS) analysis (ion beam analysis) is well-established as a technique for quantitative determination of the content of heavy elements in a matrix of lighter elements. Using RBS, the concentration of Ru (and therefore the fraction of catalyst) in the PolyHIPE samples was obtained. Typical RBS data are shown in Fig. 3. RBS has been established as a sensitive technique for quantifying the location and concentration of heavier elements in polymer matrices since the 1980s [40,41], and is discussed in detail elsewhere [37,42]. In

Table 3
Analysis results of supported Grubbs initiator

Supported initiator	Support	% P (mmol/g)	Initiator loading (mmol/g)
1	PolyHIPE 1	0.37	0.19
2	PolyHIPE 2	0.17	0.09
3	PolyHIPE 3	0.35	0.18

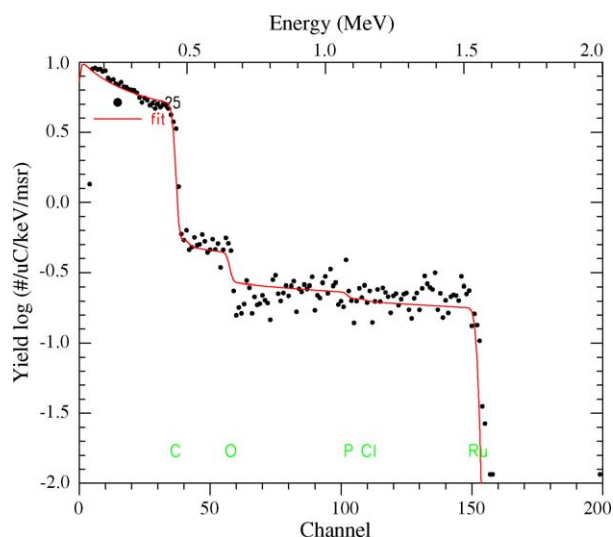


Fig. 3. RBS data for PolyHIPE containing ruthenium initiator.

Table 4
The results for RBS analysis of PolyHIPE sample containing ruthenium initiator

Supported initiator	Atom % Ru	% Ru loading	Initiator loading (mmol/g)
1	0.101	1.04	0.076
2	0.070	0.72	0.053
3	0.130	1.4	0.097

essence, since ruthenium is by far the most massive element in this material, the backscattered $^4\text{He}^+$ ions detected at high energy can only have recoiled from ruthenium. The elemental markers shown on the abscissa of Fig. 3 indicate the maximum possible recoil energy for $^4\text{He}^+$ from the other elements present in this sample. The magnitude of each step in the yield versus energy data in Fig. 3 contains information on the amount of each element detected, and variations in yield between steps can indicate variations in concentration if these are present. The exact relationship between concentration and depth of each element and the observed spectrum was established using the RUMP fitting program [43] to fit the experimental data as indicated by the solid curve.

In addition to quantifying the Ru content, RBS is sensitive to the depth distribution of the elements within the sample. The fit shows excellent agreement with the experimental data for a model in which the composition of the sample was assumed to be invariant with depth, thus demonstrating that over the range of the $^4\text{He}^+$ beam ($\sim 8\ \mu\text{m}$), there is no evidence for depth-dependent loading of the initiator. The loading of the PolyHIPE, expressed as atom % Ru, and as a fraction of the total number of DVB monomers to be functionalised, are shown in Table 4. This method was used for the first time to determine the Ru content in PolyHIPE samples prepared here from which the extent of initiator loading was determined which was found to be 0.053–0.097 mmol/g. The level of initiator loading obtained from RBS analysis is higher than 0.035 mmol/g reported previously for ruthenium initiator supported on crosslinked polystyrene [22]. However, the level of initiator loading is lower than that obtained from the phosphorous analysis by ICP-OES. One explanation for this discrepancy is that phosphorous analysis is not very accurate because of the insolubility of the PolyHIPE supported initiator.

4. Conclusion

PolyHIPE samples (samples 1–3) were successfully synthesised using DVB and styrene as polymerisable continuous phase, aqueous phase containing potassium persulphate and calcium chloride dihydrate, a mixture of emulsifiers (SPAN20, CTAB and DDBSS) and toluene as a porogen.

The PolyHIPE samples 1 and 2 and the PolyHIPE sample 3 were designed to be 90 and 92% porous, respectively, based on the aqueous phase content. PolyHIPE samples showed to be porous and open-cell microstructures with the surface area of 370–430 $\text{m}^2\ \text{g}^{-1}$. The elemental analysis for the PolyHIPE samples shows a large difference between the found and calculated values for carbon and hydrogen believed to be due to

the presence of residual of surfactants and calcium chloride dihydrate.

The PolyHIPE samples, based on the bromination and elemental analysis, contain 2.17–4.36 mmol/g or 5.86–11.77 wt.% reactive double bonds which are higher than those reported for previously prepared PolyHIPEs.

Alkyldene exchange reactions were carried out between the reactive double bonds of the PolyHIPE support and the ruthenium initiator, $\text{Ru}(=\text{CHPh})(\text{PCy}_3)_2\text{Cl}_2$, for the attachment of the initiator. The loading of the initiator in the PolyHIPE samples, based on phosphorous analysis, is found to be 0.09–0.19 mmol/g. RBS analysis was used for the first time to determine the Ru content in PolyHIPE samples from which the extent of initiator loading was determined. The analysis showed the extent of initiator loading to be 0.053–0.097 mmol/g. The level of initiator loading obtained from the phosphorous and the RBS analysis is higher than 0.035 mmol/g reported previously for ruthenium initiator supported on crosslinked polystyrene. However, the level of initiator loading obtained from RBS analysis is lower than that obtained from the phosphorous analysis by ICP-OES. The reason for this discrepancy is believed to be due to inaccuracy of phosphorous analysis as the result of the insolubility of the PolyHIPE supported initiator.

The application of ruthenium initiator supported on PolyHIPE to ROMP and RCM will be the subject of future research and the results will be published elsewhere.

Acknowledgements

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