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Preparation and functionalisation of emulsion-derived microcellular polymeric foams (polyHIPEs) by ring-opening metathesis polymerisation (ROMP)†

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Emulsion-derived microcellular polymeric foams (polyHIPEs) have been prepared by ring opening metathesis polymerisation of a norbornene derivative using a Grubb's catalyst. The resulting material has been further functionalised using the active catalytic sites remaining on its structure.

Microcellular open-celled polymeric foams have found applications in a wide range of areas.[1] Among the different methods available for their preparation, those based on the polymerisation of the continuous phase of a highly concentrated emulsion (HIPE)[2] seem the most attractive by their simplicity and flexibility.

The resulting materials, called polyHIPEs by the pioneering investigators at Unilever,[3] have been studied in detail by different groups around the world.[4] However, in the majority of the applications proposed so far, the polymerisable phase was a mixture of styrene and divinylbenzene as cross-linking agent including, in some cases, a functional styrenic derivative.[5] This is mainly due to the fact that the monomers used have to be hydrophobic in order for the HIPE to be stable[6] (at least in the more studied case where the disperse phase is an aqueous solution). The few attempts to prepare non-styrenic polyHIPEs, if succesful, were rather tedious and required the development of new kind of stable, non-aqueous, HIPEs.[7]

During the course of our studies on the development of new kinds of microcellular foams of the polyHIPE type, we considered that the use of ring-opening metathesis polymerisation (ROMP) would be an attractive alternative. The advantages of ROMP are numerous: (i) the monomers used are readily available unsaturated constrained rings such as norbornene and its derivatives; (ii) these monomers can be expected to be hydrophobic enough to allow the formation of stable inverse HIPEs in conditions close to those used with styrenic monomers; (iii) the ruthenium carbene ROMP catalysts, now available, such as those developed by Grubbs[8] are water tolerant[9] and even air stable in some case;[10] (iv) their very high activity allows their use in very low amounts (down to 0.001% molar); (v) the polymerisation has a living character,[11] so the metal–carbene termination is expected to remain active after the preparation of the polyHIPE. Therefore it should be possible to graft a second macromolecular chain onto the material.

ROMP has already been used for the preparation of monolithic rigid rod porous materials.[12] The porous structure was generated by phase separation using a solvent called porogen.[13] The morphology of the material obtained using this method is completely different from that usually observed in the case of the polyHIPE approach,[14] thus the applications for both materials may be different. The first step to obtain a polyHIPE by ROMP is the preparation of a stable HIPE with a suitable monomer. In order to obtain an insoluble material we needed a difunctional monomer to generate a cross-linked matrix. We chose the tetracyclo [6,2,1^{3,6},0^{2,7}]dodeca-4,9-diene (BVD)[15] **I** for the high reactivity by ROMP of both its two unsaturated sites[16] (Fig. 1). The surfactant used was a commercial mixture of polyglycerol ester of fatty acids[17] known for its high efficiency in the stabilisation of HIPEs.[18]

A BVD-containing HIPE was easily prepared by slow addition, at room temperature, of an aqueous solution of NaCl to a mixture of monomer plus surfactant under rapid stirring (2400 rpm). The water fraction was fixed at 90% by volume. The resulting thick white opaque cream is stable for more than 10 days at room temperature and even after several hours at 60 °C. Therefore, this HIPE appeared suitable for polymerisation by ROMP. The catalyst used was the $RuCl_2$–$(PCy_3)_2$(= CHPh) **II** known for its high reactivity and great water tolerance.[19] Furthermore, it has already being used for ROMP in a direct mini-emulsion.[20] Its oxygen sensitivity prompted us to perform all our polymerisations under a nitrogen blanket with deoxygenated solvents.

In our first attempts, direct addition under stirring at room temperature of a dodecane solution of catalyst **II** to a preformed emulsion of **I** gave a rapid but only limited degree of polymerisation with concomitant coalescence of the bulk: the polymerisation rate was too fast compared with the time needed for an homogeneous diffusion of the hydrophobic catalyst solution inside the continuous monomeric phase.

Attempts were made to prepare the HIPE from an aqueous phase consisting of a microemulsion of a dodecane catalyst solution. The idea was to obtain a homogeneous distribution of the catalytic species through the HIPE, the catalyst transferring from the micelles to the continuous phase during the phase inversion.[21] Unfortunately, the resulting HIPE was too unstable to lead to a rigid monolith after polymerisation: we only obtained a powder of insoluble polymer.

We finally succeeded in our goal by cooling a dodecane solution of the monomer plus surfactant at −15 °C before adding the catalyst solution (2×10^{-3} molar%). At this temperature the polymerisation rate is very slow. A HIPE containing an homogeneously distributed catalyst was then obtained by rapid addition, under stirring, of a 20 wt% NaCl aqueous solution pre-cooled at −15 °C. The resulting HIPE was

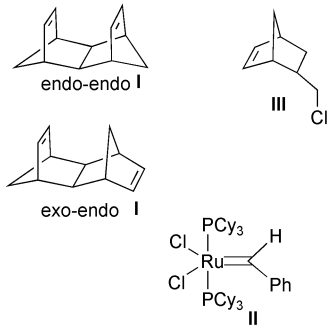

Fig. 1

† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b208832k/

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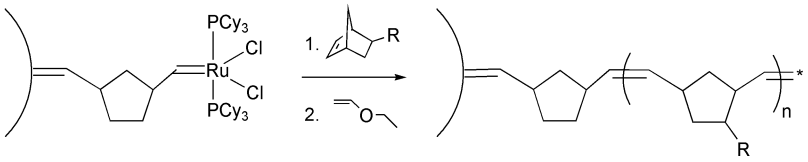

Fig. 3

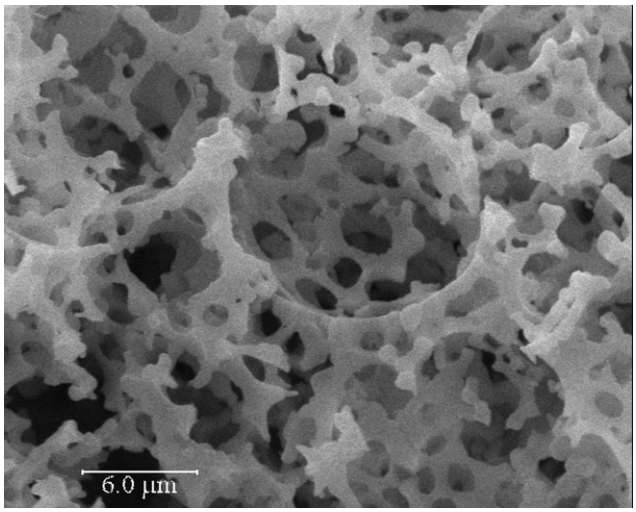

Fig. 2

left to return to room temperature then cured at 60 °C for 5 hours. The resulting hard monolith was boiled in deoxygenated water for 24 h to remove all the salt, then extracted with THF in a soxhlet apparatus for 24 h. After drying under vacuum at 60 °C until a constant weight, a soft, elastomeric but self-sustaining monolith was obtained. Its morphology was typically that of a polyHIPE with a cell size of about 15 μm and window diameter around 4 μm (Fig. 2).

The monomer conversion is almost quantitative. The nitrogen adsorption measurement using the BET treatment indicates a specific surface area of about 5 $m^2\ g^{-1}$, compatible with a polyHIPE without mesoporosity on the walls.[22] This observation suggests a collapse of the polymeric film as dodecane is expected to play a porogenic role.

In order to test the living character of ROMP in our case, a polyHIPE was prepared as described above but, after the soxhlet extraction, the monolith was immersed in a THF solution of 5-chloromethylbicyclo[2,2,1]hep-2-ene[23] **III**, and heated at reflux for 48 hours.

After cooling, the monolith was reacted with ethylvinyl ether as an endcapping reagent then treated as previously. Weight increase and elemental analysis are concordant and consistent with a grafting of a functional polymer on the walls of the monolith of 1.5 mmol g^{-1} (Fig. 3).

In conclusion, we have prepared, for the first time, a functional polyHIPE by ROMP. This material possesses the same internal structure as conventional polyHIPEs prepared by radical polymerisation of styrenic monomers. However, it is much less brittle and easier to handle. The availability of both monomers and catalyst, as well as the ease of functionalization of these materials by grafting of a non cross-linked macromolecular chain should allow this new approach to enlarge the potential applications of the polyHIPEs materials.

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