Synthesis of emulsion-templated porous polyacrylonitrile and its pyrolysis to porous carbon monoliths

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PolyHIPEs are emulsion-templated polymers synthesized within high internal phase emulsions (HIPEs). The miscibility of acrylonitrile (AN) with water has made it difficult to synthesize PAN-based polyHIPEs. This paper describes the successful synthesis of PAN-based polyHIPEs by crosslinking through copolymerization with divinylbenzene (DVB), by stabilization with a polyglycerol polyricinoleate surfactant, and by initiation with both oil- and water-soluble initiators. The PAN-based polyHIPEs had porosities of over 86% and porous structures that were different from those of typical polyHIPEs. This paper also describes the production of porous carbon monoliths through the pyrolysis of these PAN-based polyHIPEs. Pyrolysis did not produce significant changes in the porous structures, which were quite similar to those of the original polyHIPEs. The porosities were around 95% and the carbon monoliths were largely macroporous and mesoporous, with some microporosity. These results indicate that PAN-based polyHIPE templates can be used for the a priori design of porous carbon monoliths.

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1. Introduction

Porous polymer systems termed polyHIPEs can be produced through an emulsion templating synthesis in which the external phase of a high internal phase emulsion (HIPE) is polymerized and then the internal phase is removed through drying [1–7]. A HIPE is formed when the volume fraction of the internal phase of an emulsion is over 0.74, which is the maximum packing fraction of uniform spheres [4–8]. During polymerization, ruptures can occur at the thinnest point within the film of continuous phase separating droplets of the internal phase [4]. A preponderance of such ruptures leads to the formation of a highly interconnected internal phase. The highly interconnected internal phase can then be removed through drying. PolyHIPEs are usually crosslinked in order to enhance their stability and their resistance to collapse under the capillary stresses generated during drying [4]. The crosslinking is usually achieved through copolymerization with a crosslinking comonomer. A typical porous structure for polyHIPEs consists of empty voids, evacuated internal phase droplets, that are highly interconnected through holes in the polymer walls.

The interest in polyHIPE materials is driven by the large number of applications involving porous polymers (catalyst supports, separation membranes, ion exchange resins, tissue engineering scaffolds, etc.) and by the ability to adapt the molecular structures and the porous structures of polyHIPEs to particular applications. A wide variety of polyHIPEs and polyHIPE-based materials have been synthesized including copolymers [9,10], interpenetrating polymer networks (IPN) [11], crystallizable side chain polymers [12], hydrogels [13–15], biocompatible polymers [16–18], degradable polymers [19], step-growth polymers [20], bicontinuous polymers [21], functional surfaces [5,22,23], organic-inorganic hybrids [24,25], and composites [26–29]. Porous silica monoliths have been produced through the pyrolysis of porous hybrid polyHIPEs and nanocomposite polyHIPEs [25,30].

Porous carbon is also used for a wide variety of applications including gas separation, water purification, catalyst supports, and electrodes for capacitors and for fuel cells [31]. Porous carbon can be synthesized using various methods. These methods often include the pyrolysis of a polymer that produces a high degree of char either within a porous structure or within a blend containing a polymer that does not produce char [32]. Polycrylonitrile (PAN) fibers are commonly used as precursors for carbon fibers. PAN undergoes a cyclization reaction at high temperatures producing a ladder polymer and imparting an unusually high thermal stability [33]. It should be possible to design the pore sizes and porous structures of carbon monoliths a priori through the synthesis of porous polymer templates [31]. Unfortunately, the miscibility of AN with water makes it difficult to form AN-based HIPEs for the synthesis of PAN polyHIPEs [32].
2. Experimental

Forming HIPEs containing AN, polymerizing the AN within the HIPEs, and drying the PAN-based polyHIPEs without collapse all posed a great challenge. The procedure described below reflects one of the only systems that consistently produced highly porous PAN-based polyHIPEs.

2.1. Materials

The monomer was acrylonitrile (AN, Merck-Schuchardt) and the crosslinking comonomer was divinylbenzene (DVB, which contains 40% ethylstyrene, Riedel-de-Haen). AN was used as received. DVB was washed to remove the inhibitor, three times with a 5% sodium hydroxide (NaOH, Carlo Erba) solution followed by three times with deionized water. The structure of the organic-soluble emulsifier, polyglycerol polyricinoleate (PGPR, C57O9H104, Palsgaard 4125), is illustrated in Scheme 1. The water-soluble initiator was potassium persulfate (KPS, Riedel-de-Haen) and the organic-soluble initiator was benzoyl peroxide (BPO, Fluka). Potassium sulfate (K2SO4, Frutarom, Israel) was used to stabilize the HIPEs.

2.2. Synthesis

The HIPEs were formed in 500 ml polypropylene beakers by adding the internal aqueous phase (water, initiator, and stabilizer) drop-wise to the external organic phase (monomers and emulsifier). The detailed procedure for polyHIPE synthesis was as follows: the external organic phase was placed in the beaker and stirred with a magnetic stirrer. The aqueous phase was added drop-wise with constant stirring and the resulting HIPE was covered with a plastic film. Polymerization took place in a circulating air oven at 65 °C for 24 h. The water was removed from the polyHIPE by drying at room temperature in a vacuum oven for about 3 days, until a constant weight was reached. Soxhlet extraction was used to try and remove salts and emulsifier from the polyHIPE. The polyHIPE was placed in a Soxhlet apparatus using water for 24 h and then methanol for 24 h. The polyHIPE was then dried in a convection oven at 60 °C for 24 h.

The AN content in the AN/DVB mixture, w_{AN}, was varied from 82.5 to 94.8 wt %. The external phase content was 11.8 wt %. A number of similar AN-based polyHIPEs containing external phase contents of up to 23.1 wt % were also synthesized. The polyHIPE sample names listed in Table 1 reflect the AN content in the AN/DVB mixture with AN83 containing 82.5 wt % AN in the AN/DVB mixture. A typical HIPE recipe (for AN83) is listed in Table 2.

2.3. Pyrolysis

The polyHIPEs were pyrolyzed by heating to 250 °C under O2 at a rate of 10 °C/min and then heating to 960 °C under N2 at a rate of 10 °C/min.

2.4. Characterization

The densities, \( \rho \), were determined using gravimetric analysis. The porosities, \( p \), of the polyHIPEs were calculated using Equation (1) by assuming a wall density, \( \rho_w \), of 1.2 g/cm³ for the polymer [34].

\[
p = \left(1 - \frac{\rho}{\rho_w}\right) \cdot 100\%
\]

The porous structures were investigated through high resolution scanning electron microscopy (HRSEM, Zeiss LEO 982) of cryogenic fracture surfaces. The uncoated polyHIPE samples were viewed using an accelerating voltage of 4 kV. The molecular structure of the polymer was characterized using Fourier transform infrared spectroscopy (FTIR, Equinox 55, Bruker) from 400 to 4000 cm⁻¹ at a resolution of 4 cm⁻¹ with a photoacoustic attachment (MTEC Model 300). The FTIR spectra were collected from the polyHIPEs without any sample preparation.

The specific surface areas were determined using the single-point BET (Brunauer–Emmett–Teller) method, with nitrogen adsorption at 77 K (Quantachrome). The pore size distribution for macroporosity was determined using mercury porosimetry from 0 to 4000 kPa (Micropore 120, Carlo Erba Instruments) and from 0.1 to 200 MPa (Porosimeter 2000, Carlo Erba Instruments). Mesoporosity, microporosity, and the BJH (Barret–Joyner–Halenda) surface area were determined using nitrogen adsorption from 0 to 127 kPa (Micromeritics ASAP 2010).

The composition of the surface was characterized using X-ray photoelectron spectroscopy (XPS, Thermo VG Sigma Probe with Al x-ray source).

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>w_{AN}, wt %</th>
<th>( \rho ), g/cm³</th>
<th>( p ), %</th>
<th>( m_w ), %</th>
<th>( v_w ), %</th>
<th>( \rho_p ), g/cm³</th>
<th>( p ), %</th>
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</thead>
<tbody>
<tr>
<td>AN95</td>
<td>94.8</td>
<td>0.17</td>
<td>86</td>
<td>31.7</td>
<td>73.7</td>
<td>0.25</td>
<td>86</td>
</tr>
<tr>
<td>AN90</td>
<td>89.7</td>
<td>0.17</td>
<td>86</td>
<td>67.8</td>
<td>54.3</td>
<td>0.12</td>
<td>93</td>
</tr>
<tr>
<td>AN85</td>
<td>84.7</td>
<td>0.13</td>
<td>89</td>
<td>61.1</td>
<td>37.6</td>
<td>0.08</td>
<td>96</td>
</tr>
<tr>
<td>AN83</td>
<td>82.5</td>
<td>0.12</td>
<td>90</td>
<td>89.3</td>
<td>85.4</td>
<td>0.09</td>
<td>95</td>
</tr>
</tbody>
</table>
K source). Low resolution XPS was used to characterize the atomic composition and high resolution C1s XPS was used to characterize the carbon bonds. The high resolution C1s XPS data was fit by removing the background and optimizing the sum of two or three peaks, all of which were set to have the same full width at half maximum (FWHM).

3. Results and discussion

3.1. Molecular structure

FTIR spectra of three polyHIPEs based on HIPEs with different DVB contents are seen in Fig. 1. The bands at 713, 1452, 2852, and 2930 cm\(^{-1}\) are associated with the methylene group. The band at 2240 cm\(^{-1}\) is associated with the nitrile group of AN. The variation of the height of the band at 2240 cm\(^{-1}\) normalized by the height of the band at 2930 cm\(^{-1}\) in Fig. 2 represents the variation of the nitrile content in the polyHIPEs. The normalized height of the nitrile band is seen to decrease with increasing DVB content in a linear fashion.

The prominent bands at 3533 and 1734 cm\(^{-1}\) in Fig. 1 represent hydroxyl groups and carbonyl groups, respectively. These bands are associated with residual PGPR. Previous work on polyHIPEs containing sorbitan monooleate (SMO) as an emulsifier with no PGPR has shown that extraction with water and methanol removes the SMO [36]. This may not be the case with PGPR, which could remain in the polyHIPEs following the extractions.

The polymerizations produced white monoliths with yields of around 90%. Based on the HIPE volume fractions, the densities expected for these polyHIPEs were around 0.1 g/cm\(^3\). The polyHIPE densities ranged between 0.12 and 0.17 g/cm\(^3\) (Table 1), depending on the DVB content. The polyHIPE density was higher for the lower DVB contents, indicating that the crosslink density and chain stiffness in those polyHIPEs were not high enough to prevent partial collapse from the capillary stresses generated during drying. The polymer network was sufficiently stiff and crosslinked to resist the capillary stresses when there was 15 wt % DVB in the monomer mixture. The corresponding porosities ranged from 90% for the higher DVB contents to 86% for the lower DVB contents (Table 1).

The porosity structure of AN83 is seen in the SEM micrographs in Fig. 3. The polyHIPE has an open-cell, highly interconnected porous structure with voids between 5 and 20 μm, however it is quite different from a typical polyHIPE structure [7]. Interestingly, all the AN-based polyHIPEs exhibited this structure, regardless of DVB content. The differences in density that result from the partial collapse at low DVB contents is not reflected in the porous structures seen in the SEM micrographs. Increasing the external phase content produced porous structures that seemed more closed-cell in nature (not shown) reflecting an increase in wall thickness which can limit interconnectivity.

3.3. PolyHIPE surfaces

The atomic composition of the AN83 surface from XPS is listed in Table 3. Based on the monomer feed composition, a nitrogen content of 20.4% was expected from the XPS analysis. The nitrogen content of 10.9 at % was surprisingly low for a polymer based on 82.5 wt % AN in the feed. The FTIR results indicated that residual PGPR was present. The surfactant is preferentially located at the HIPE’s water–oil interface [4] and, therefore, the residual surfactant is expected to be preferentially located on the polyHIPE’s surface. An analysis of the surface composition from XPS was based upon the following three assumptions: (1) the nitrogen content represents the number of AN units in the polymer; (2) the AN/DVB ratio in the polymer is the same as that in the feed; (3) the oxygen content represents the number of PGPR molecules. The atomic contents calculated on the basis of these three assumptions are also

![Fig. 1. FTIR spectra of: (a) AN95; (b) AN90; (c) AN85.](image1)

![Fig. 2. Variation of normalized nitrile band height with DVB content.](image2)

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic phase</td>
<td></td>
</tr>
<tr>
<td>AN</td>
<td>8.0</td>
</tr>
<tr>
<td>DVB</td>
<td>1.7</td>
</tr>
<tr>
<td>PGPR</td>
<td>1.9</td>
</tr>
<tr>
<td>BPO</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td>11.8</td>
</tr>
<tr>
<td>Aqueous phase</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>87.5</td>
</tr>
<tr>
<td>K2SO4</td>
<td>0.5</td>
</tr>
<tr>
<td>KPS</td>
<td>0.2</td>
</tr>
<tr>
<td>Total</td>
<td>88.2</td>
</tr>
</tbody>
</table>

Table 2

Typical HIPE recipe (AN83).

![Figure 3. SEM micrographs of polyHIPEs.](image3)
The negligible differences in the atomic contents between the prediction of the model and the experimental results support the validity of the analysis. According to the recipe in Table 2, the external phase of the HIPE contained 16.1 wt % PGPR. Based on the XPS analysis, the polyHIPE surface consists of 48.2 wt % PGPR, 42.7 wt % AN, and 9.1 wt % DVB. These results confirm that, as expected, the PGPR is preferentially located on the polyHIPE's surface.

The high resolution C1s XPS spectrum from AN83 and the three peaks used to fit the experimental results are seen in Fig. 4. The positions of the Gaussian peaks used to fit the data are: (1) 285.0 eV (C–C); (2) 286.6 eV (C=N, C=N, C=O); and (3) 289.0 eV (O=C=O). The peak FWHMs were 1.4 eV. The contributions of each peak to the overall spectrum in the optimized fit are listed in Table 4. The contributions of the various groups can also be calculated using the surface composition that was derived from the previous analysis. A comparison of the results from the previous analysis with the results from the curve fit to the C1s spectrum (Table 4) yields an average error of 18%. The correspondence between the results from the previous analysis and the results from a fit to the C1s spectrum is quite reasonable and supports the derived surface composition.

3.4. Pyrolyzed polyHIPEs

Pyrolysis of the polyHIPEs produced significant mass losses, \( m_L \), and volume losses, \( v_L \), in the samples (Table 1). An \( m_L \) of 32.1% is expected from an ideal PAN pyrolysis in which all the hydrogen and nitrogen are removed and all the carbon remains. The \( m_L \) of 31.7% for AN95 is similar to the ideal \( m_L \). However, increasing the DVB content from 5% to 10% yields a significant increase in \( m_L \) which rises to 67.8%. This increase in \( m_L \) reflects the profound disruption of AN cyclization that hinders the ability to form thermally stable structures. Increasing the DVB content to 17% produces an \( m_L \) of almost 90%. In general, the densities of the pyrolyzed polyHIPEs were lower than those of the original polyHIPEs (Table 1). The one exception is AN95, whose density increased upon pyrolysis. The DVB crosslinking is expected to prevent polyHIPE collapse during pyrolysis as the temperature rises above the PAN glass transition of...
85 °C. The relatively low degree of crosslinking in AN95 can result in partial collapse during pyrolysis. The reduction in density for the other pyrolyzed polyHIPEs yields an increase in porosity, especially since the density of the carbonaceous wall material following pyrolysis is higher than that of the original PAN-based polymer in the polyHIPE. The porosities in the pyrolyzed polyHIPEs can reach as high as 96% (Table 1).

In spite of the significant reductions in sample mass and volume, the porous structure of the pyrolyzed polyHIPE (Fig. 5) is quite similar to that of the original polyHIPE (Fig. 3). This holds for all the other pyrolyzed polyHIPEs and is similar to the results for pyrolyzed hybrid polyHIPEs and nanocomposite polyHIPEs [25,30]. The lack of crystalline peaks in the X-ray diffractions from the pyrolyzed polyHIPEs (not shown) indicate that they are amorphous materials.

The carbon monoliths have the macroporous structure seen in Fig. 5 as well as mesoporosity and microporosity. The BET surface area of the pyrolyzed AN90 was 26.5 m²/g, which is about an order of magnitude lower than that of other macroporous carbonaceous materials [32]. The BJH surface area was 16.4 m²/g and the BJH to BET ratio indicates that the mesoporous content was 61.9%. The size distribution of micropores in Fig. 6 exhibits a peak at around 0.85 nm and a median pore diameter of 0.91 nm. The total volume of the pores from 1.7 to 300 nm was 0.032 cm³/g and the total volume of the macropores was significantly larger, 0.987 cm³/g.

Low resolution XPS analysis of the surface of the pyrolyzed AN83 shows that the nitrogen content on the surface is reduced to 3.7 at % by pyrolysis while the oxygen content increases to 8.4 at % (Table 3). The potassium and sulfur in the pyrolyzed polyHIPE originate in residual initiator and stabilizer. The amounts of residual potassium and sulfur are relatively small. These elements are overwhelmed by the amounts of carbon, nitrogen, and oxygen in the original polyHIPE and, therefore, are not detected by low resolution XPS. During pyrolysis there are significant losses of carbon and nitrogen, enhancing the relative potassium and sulfur contents and, thus, their detectability by low resolution XPS [37].

The high resolution C1s XPS spectrum from the pyrolyzed AN83 in Fig. 7 is quite different from the spectrum from the original AN83 polyHIPE in Fig. 4 and is quite similar to the spectra from other PAN-based carbonaceous materials [38]. The spectrum in Fig. 7 is best fit...
using only two Gaussian peaks with FWHMs of 1.18 eV. The peak at 285.0 eV represents C–C bonds and the peak at 286.2 eV represents C–O and C–N bonds. The contribution of each of these peaks to the total spectrum is listed in Table 4. The nitrogen and oxygen contents listed in Table 3 are reflected in the 16.8% contribution of the C–N and C–O bonds to the spectrum in Fig. 7. These results indicate that the pyrolyzed PAN-based polyHIPEs are highly porous, slightly oxidized, amorphous carbonaceous materials.

4. Conclusions

PAN-based polyHIPEs were successfully synthesized by using DVB crosslinking, PGPR stabilization, and both internal phase initiation and external phase initiation. The PAN-based polyHIPEs had porosities of over 86%. The porous structures were not typical polyHIPE structures and the effects of DVB content on the porous structure were negligible. Extraction in water and methanol did not remove the PGPR from the polyHIPE surface. Porous carbon monoliths were successfully produced by pyrolyzing the PAN-based polyHIPEs. Pyrolysis did not produce a significant change in the overall macroporous structure, in spite of the significant reductions in sample mass and volume. The porous structures of the polyHIPEs can act as templates for the production of porous carbons. The pyrolyzed polyHIPEs, with porosities of around 95%, were largely mesoporous and macroporous with some microporosity.

Acknowledgements

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References