Supplementary information

1. Preparation of organic and aqueous phase for the synthesis of poly (DVB-co-VBC-co-styrene) resin (Ps.VBC)

The volume and masse of the components in the organic phase for the synthesis of 15 g of Ps.VBC resin were calculated as follows:

Divinylbenzene (DVB)

DVB ($C_{10}H_{10}$), molecular weight = 130.20 g/mol

Density = 0.921 g/mL

Percentage composition = 12%

$$\text{Mass of DVB} = \frac{12}{100} \times 15 = 1.8\text{g}, \ \text{volume} = \frac{1.8}{0.921} = 1.95 \text{ mL}$$

Vinylbenzyl chloride (VBC)

VBC (C_9H_9Cl), molecular weight = 152.62 g/mol

Density = 1.074 g/mL

Percentage composition = 25%

$$\text{Mass of VBC} = \frac{25}{100} \times 15 = 3.75\text{g}, \ \text{volume} = \frac{3.75}{1.074} = 3.5 \text{ mL}$$

Styrene

Styrene (C_8H_8), MW = 104.15 g/mol

Density = 0.909 g/mL

Percentage composition = 63%

$$\text{Mass of styrene} = \frac{63}{100} \times 15 = 9.45 \text{ g}, \ \text{volume} = \frac{9.45}{0.909} = 10.39 \text{ mL}$$

AIBN and 2-ethylhexanol

The total mass of the co-monomers = 1.8 + 3.75 + 9.45 = 15 g

The total volume of the co-monomers = 1.96 + 3.5 + 10.39 = 15.84 mL

The mass of AIBN stabiliser added was 0.15 g (%1 by weight of the co-monomers and the volume of 2-ethylhexanol (porogen) used was 15.84 mL (1/1 by volume ratio of the co-monomers).

Volume of aqueous phase

The total volume of organic phase used for the suspension polymerisation was 31.68 mL.

But the volume ratio of organic to aqueous phase was chosen to be 1:20; hence, the volume of aqueous phase employed was 634 mL.

2. Theoretical composition of Ps.VBC resin

DVB ($C_{10}H_{10}$)

Molecular weight = 130.20 g/mol

Percentage composition = 12%

$$\text{Mass of DVB} = \frac{12}{100} \times 130.20 = 15.6 \text{ g}$$

VBC (C_9H_9Cl)

Molecular weight = 152.62 g/mol

Percentage composition = 25%

$$\text{Mass of VBC} = \frac{25}{100} \times 152.62 = 38.155 \text{ g}$$

Styrene (C_8H_8)

Molecular weight = 104.15 g/mol

Percentage composition = 63%

$$\text{Mass of styrene} = \frac{63}{100} \times 104.15 = 65.611 \text{ g}$$

Total mass = DVB + VBC + styrene

= 15.624 + 38.155 + 65.611 = 119.39 g

The elemental composition of Ps.VBC resin was calculated as follows:

$$\%C = \frac{(12\% \times \text{mass of C in DVB}) + (25\% \times \text{mass of C in VBC}) + (63\% \times \text{mass of C in styrene})}{\text{Total mass}} \times 100$$

$$\%C = \frac{0.12\,(10 \times 12) + 0.25 \times (9 \times 12) + 0.63\,(8 \times 12)}{119.39} \times 100$$

C = 85.3%

$$\%H = \frac{(12\% \times \text{mass of H in DVB}) + (25\% \times \text{mass of H in VBC}) + (63\% \times \text{mass of H in styrene})}{\text{Total mass}} \times 100$$

$$\%H = \frac{0.12\,(10 \times 1) + 0.25 \times (9 \times 1) + 0.63\,(8 \times 1)}{119.39} \times 100$$

H = 7.11%

$$\%Cl = \frac{(12\% \times \text{mass of Cl in DVB}) + (25\% \times \text{mass of Cl in VBC}) + (63\% \times \text{mass of Cl in styrene})}{\text{Total mass}} \times 100$$

$$\%Cl = \frac{0.12\,(0) + 0.25 \times (1 \times 35.45) + 0.63\,(0)}{119.39} \times 100$$

Cl = 7.42%

3. The volume of AMP required for the amination of 35 g Ps.VBC resin

As shown in (2.), the percentage composition of Cl in Ps.VBC was found to be 7.42% (7.2 g per 100 g resin). Hence, the moles of Cl in 100 g of the resin equals to:

$$\frac{7.42}{35.35} = 0.209 \text{ moles/ 100 g resin}$$

Therefore, the moles of Cl in 35 g of resin = 0.07315 moles/35 g

The amination of Ps.VBC resin with AMP was carried out in the mole ratio of 1:4 resin to APM, thus, the volume of AMP used was calculated as follows:

$$\text{Moles of AMP} = 0.07315 \times 4 = 0.2926 \text{ moles}$$

$$\text{Mass of AMP} = \text{moles} \times \text{MW} = 0.2926 \times 108.143 = 31.643 \text{ g}$$

$$\text{Volume of AMP} = \frac{\text{mass}}{\text{density}} = \frac{31.643}{1.04} = 30.4 \text{ mL}$$

4. Loading of Ps.AMP resin with Mo(VI) complex

12% DVB (C_9H_9Cl), MW = 130.20 g/mol

25% Ps.AMP ($C_{15}H_{16}N_2$), MW = 224.34 g/mol

63% styrene (C_8H_8), MW = 104.15 g/mol

$$\text{Total mass} = (0.12 \times 130.20) + (0.25 \times 224.34) + (0.63 \times 104.15) = 137.32 \text{ g}$$

$$\%C = \frac{(12\% \times \text{mass of C in DVB}) + (25\% \times \text{mass of C in Ps.AMP}) + (63\% \times \text{mass of C in styrene})}{\text{Total mass}} \times 100$$

$$\%C = \frac{0.12\,(10 \times 12) + 0.25 \times (15 \times 12) + 0.63\,(8 \times 12)}{137.32} \times 100$$

C = 87.3%

$$\%H = \frac{(12\% \times \text{mass of H in DVB}) + (25\% \times \text{mass of H in Ps.AMP}) + (63\% \times \text{mass of H in styrene})}{\text{Total mass}} \times 100$$

$$\%H = \frac{0.12\,(10 \times 1) + 0.25 \times (16 \times 1) + 0.63\,(8 \times 1)}{137.32} \times 100$$

H = 7.45%

$$\%N = \frac{(12\% \times \text{mass of N in DVB}) + (25\% \times \text{mass of N in Ps.AMP}) + (63\% \times \text{mass of N in styrene})}{\text{Total mass}} \times 100$$

$$\%N = \frac{0.12\,(0) + 0.25 \times (2 \times 14) + 0.63\,(0)}{137.32} \times 100$$

N = 5.1%

Therefore, 100 g of Ps.AMP contents 5.1 g N.

$$\text{The moles of N in 100 g of Ps.AMP} = \frac{\text{mass}}{\text{MW}}$$

$$= \frac{5.1}{2 \times 14} = 0.182 \text{ moles/100 g}$$

Hence, 35 g of the resin will have 0.0637 moles.

But the loading of Ps.AMP resin with Mo was carried out in the mole ratio of resin to Mo 1:2. Therefore, the corresponding moles of Mo used were 0.1274 moles.

The equivalent mass of $MoO_2(acac)_2$ employed for the Mo loading was calculated as follows:

$MoO_2(acac)_2$, MW = 326.15 g

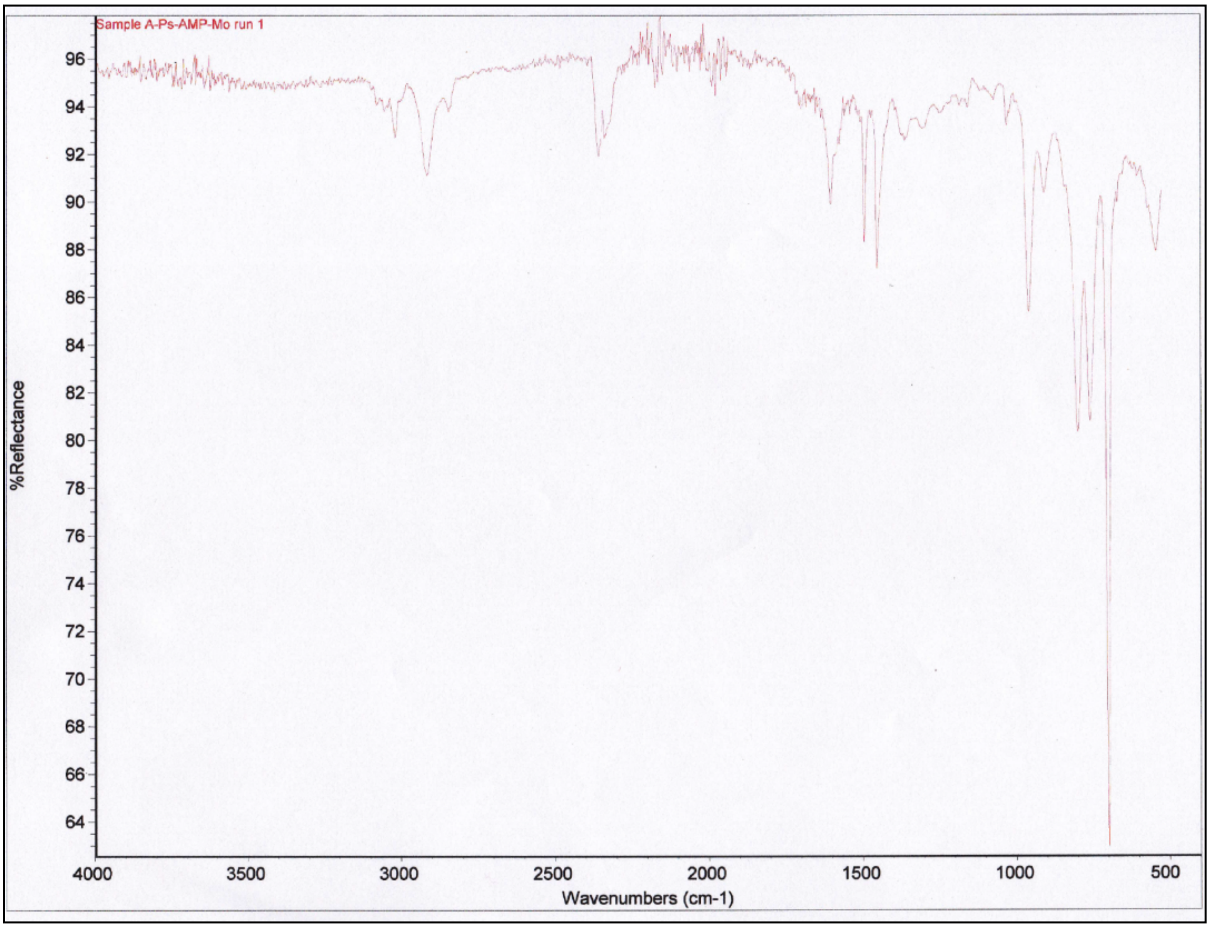
$$\text{Mass of MoO2(acac)2} = 0.1274 \times 326.15 = 41.55 \text{ g}$$

5. Experimental set-up for suspension polymerisation

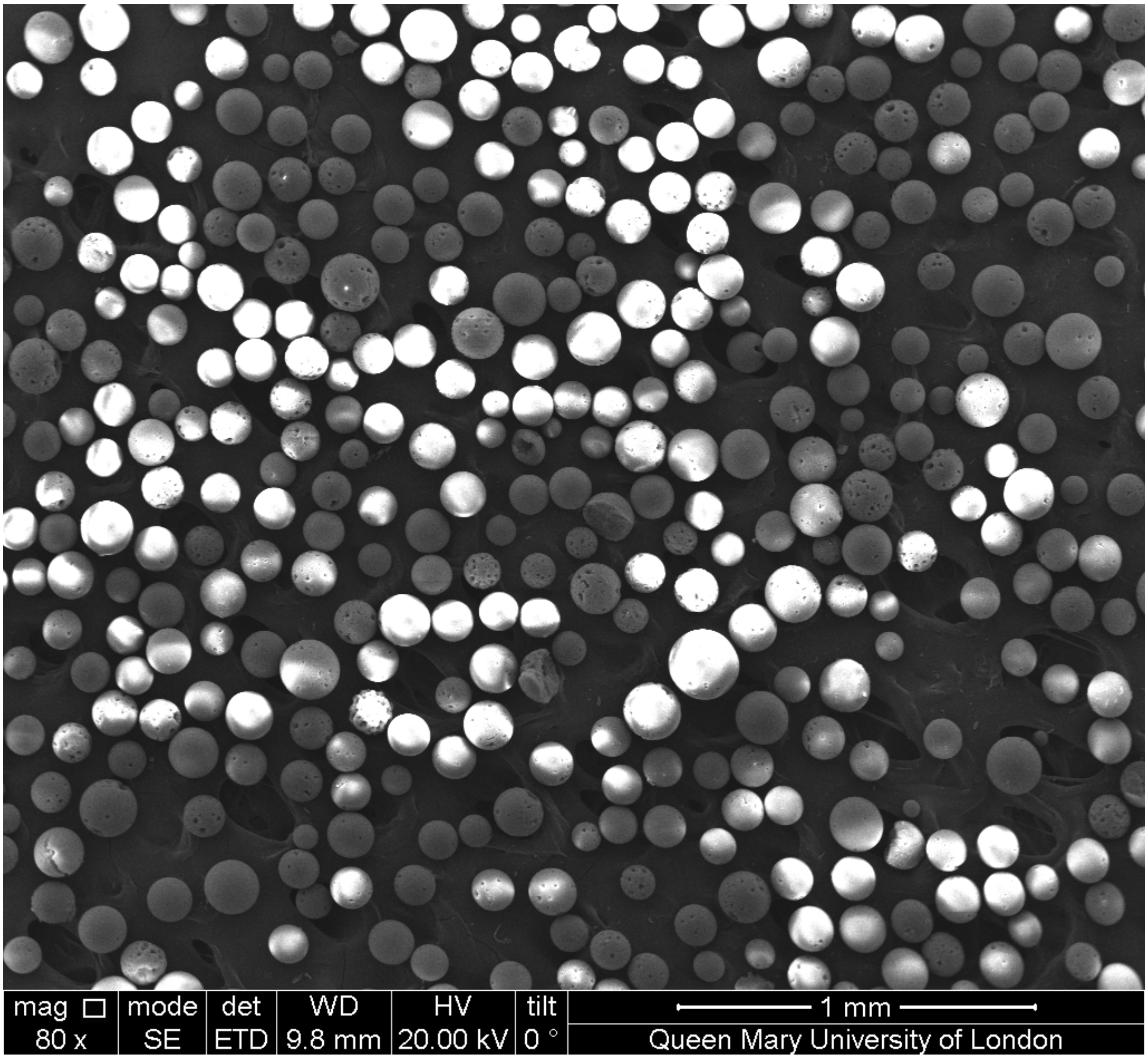
The set-up consists of 1 L jacketed glass baffled reactor, equipped with a condenser, double impeller, digital thermocouple, mechanical stirrer and water bath.

Experimental set-up for suspension polymerisation

6. Catalyst characterisation



FTIR spectrum of Ps.AMP.Mo catalyst



SEM image of Ps.AMP.Mo catalyst