ESI: Synthesis of charged particles in an ultra-low dielectric solvent

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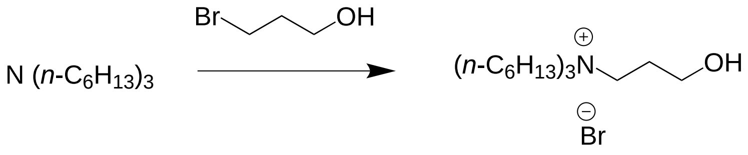
1 Synthesis of Ionic Monomer

The ionic monomer was synthesised in a three-step procedure, detailed below.

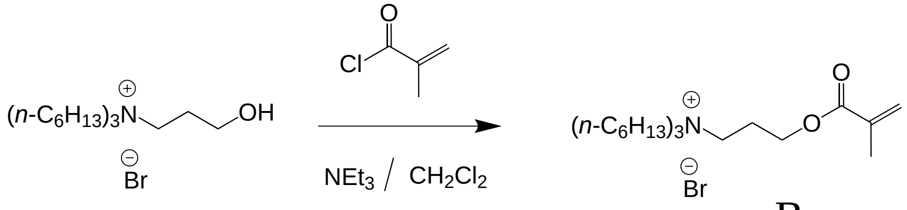
1.1 Stage 1: Alkylation of tri(*n*-hexyl) amine



A

The reaction was carried out by refluxing 1 mole equivalent of tri(*n*-hexyl) amine and 0.9 mole equivalents of 3-bromo-1-propanol at 110 °C for five days. Reaction conditions were chosen to minimize the fraction of un-reacted 3-bromo-1-propanol at the end of the reaction. The aim being to prevent significant formation of non-polymerizable side-products in the next stage. The high temperature and extended period of heating inevitably led to some loss of 3-bromo-1-propanol and a reduced yield. Analysis by ^{1}H-NMR showed that the mixture at the end of the reaction contained approximately 32 mol % product and 67 mol % trihexylamine but crucially less than 1 mol % 3-bromo-1-propanol. Despite the relatively low yield, these conditions were preferred to others tested because of the low 3-bromo-1-propanol content in the final reaction mixture. The reaction mixture was used without further purification in step 2.

1.2 Stage 2: Esterification with methacryloyl chloride



B

To prevent polymerisation of the monomer the procedure was carried out under nitrogen in an ice bath. The methacryloyl chloride was used as received, without removal of the inhibitor. Dichloromethane (dried with molecular sieves) was used as a solvent and reagents were added in the following proportions: 5 ml of dichloromethane per mole of A, 3 mols of methacryloyl chloride per mole of A, and 2.5 mols of triethylamine per mole of A. The amount of each component is given as a proportion of the number of moles of the quaternary ammonium salt (A) produced in the first stage (see Sec. 1.1 for yield). The reaction mixture was reacted for 19 hours with stirring under nitrogen. The reaction was vigorous and an excess of methacryloyl chloride was used to ensure that all of A was esterified . After completion, dichloromethane was removed by evaporation and replaced with ice-cold methanol. Deionised water at ∼ 4 °C was added drop-wise until precipitation was observed; the sediment containing the product B.

Formation of B was confirmed by ^{1}H-NMR and ^{13}C-NMR . Figure 1 presents the ^{1}H-NMR and ^{13}C-NMR spectra of the products of stage 2. Compared to the NMR spectra of the reactants, the spectrum of B showed the appearance of peaks at

4.92 ppm (^{1}H-NMR) and 59 ppm (^{13}C-NMR). These peaks were assigned to the ester protons (labelled (b) in the ^{1}H-NMR spectrum) and the ester carbon (labelled (j) in the ^{13}C-NMR spectrum) confirming that the esterification reaction between A and methacryloyl chloride indeed happened and B was synthesised.

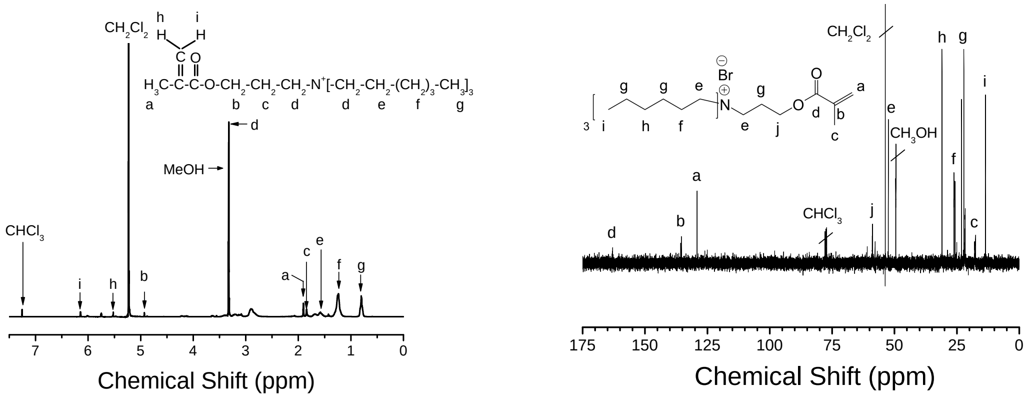
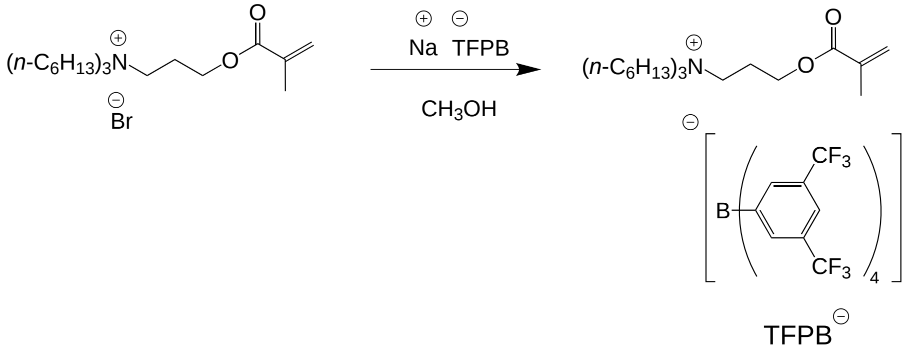


Fig. 1 ^{1}H NMR (left) and ^{13}C NMR spectra (right) of product B

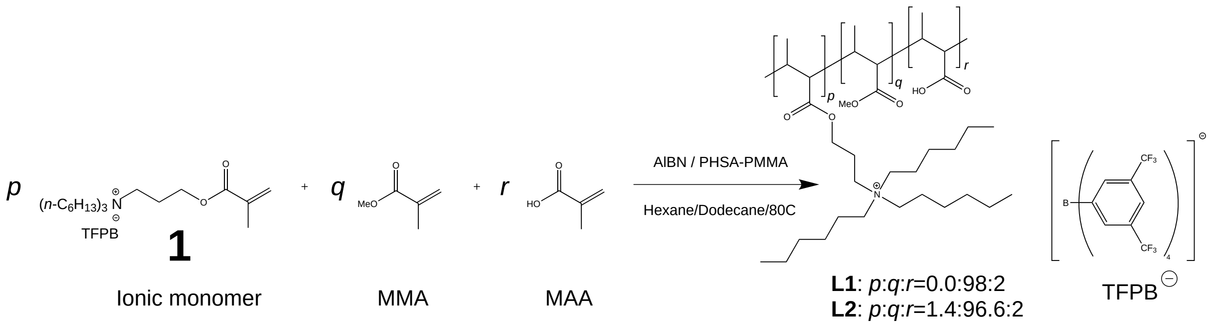
1.3 Stage 3: Ion Exchange



Equivalent amounts of brominated monomer and NaTFPB were reacted in 1000 g per mole of ice-cold methanol for 20 hours, without stirring. To enhance NaBr solubility and product precipitation, twice as much cold water as methanol by volume was added to the mixture gradually by melting frozen deionised water over the mixture. The products were left undisturbed in the ice bath for about an hour during which time it separated into two layers. In order to drive the ion exchange reaction to completion the lower layer was diluted in $\approx$ 3 times its own volume of dry, ice-cold, filtered tetrahydrofuran (THF). The composition of the solvent was adjusted to precipitate NaBr while the hydrophobic TFPB product remains soluble in the mixed solvent. After complete ion exchange, the excess THF was removed by slow evaporation and the product was stored at low temperature prior to its use in particle synthesis.

2 Colloidal Particle Synthesis

Poly(methyl methacrylate) colloids were synthesized using the single-pot, two-stage procedure described by Campbell and Bartlett[1], which was based on that developed earlier by Antl *et al.*[2]. In the first stage, the dispersion polymerization of methyl-methacrylate (MMA) and methacrylic acid (MAA) is initiated by the thermal decomposition of 2,2'-azo-bis-isobutyronitrile



(AIBN), with octanethiol as chain transfer agent, in a mixture of hexane and dodecane. A comb copolymer prepared from poly(12-hydroxy stearic acid) and poly(methyl methacrylate) was used as a particle stabilizer.

The quantities of each component are detailed in Table 1 in the main text. The first stage of the synthesis was carried out in a round-bottom flask in an oil bath at 80°C for two hours; Within ∼15 minutes, the initially clear mixture becomes milky as the newly formed particles become comparable in size to the wavelength of visible light. In the second stage, the stabilizer adsorbed on the colloids was chemically bonded to the surface of the particles to prevent any possible de-sorption when particles are transferred to other solvents. This reaction was carried out by adding the same weight of dodecane as hexane in the first stage, followed by drop-wise addition of diethylamine as a catalyst at a concentration of 0.2 wt% on the total preparation weight. The bath temperature was then raised to 120 °C and the mixture left to react for 20 hours. Afterwards, the suspension was filtered through tightly packed glass wool in a funnel to remove any large aggregates, and then centrifuged for 15 minutes at 20,000 rpm in a Sorvall RC 5B fitted with a SS-34 rotor; the supernatant was then removed and replaced with dodecane. This final step was repeated at least three times to ensure solvent purity. In each case a 65 g preparation was prepared. Samples were checked for agggregation under an optical microscope.

3 Evidence that charges are covalently bound to particles

Potentially the charge on the particle might arise from the physical adsorption of charged species rather than the dissociation of covalently bound ions. In this section we summarise the evidence that the mechanism of charging is dissociation of covalently-bound ions. First, the spectroscopic evidence quoted above demonstrates that at least some of the ionic monomer (B) is prepared. Second, the reaction between an acid chloride and a -OH group proceeds rapidly to completion and we used a three-fold excess of methacryloyl chloride. This will ensure that essentially all of the quaternary salt A is converted into a polymerizable species at stage 2. In consequence, there should be no more than a trace amount of un-reacted species A present in the third stage. All ionic species should be attached to methacrylate units. Third, the particle charge measured is too large to be generated by the adsorption of what could only be a trace amount of non-polymerizable ionic species. For these reasons, particle charging by physical adsorption is unlikely to be significant. Copolymerization is the only plausible route to the measured charge.

References

1 A. I. Campbell and P. Bartlett, *J. Colloid Interf. Sci.*, 2002, **256**, 325 – 330.
2 L. Antl, J. W. Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth and J. A. Waters, *Coll. Surf.*, 1986, **17**, 67 – 78.