

pH controlled assembly of a polybutadiene–poly(methacrylic acid) copolymer in water: packing considerations and kinetic limitations

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Copolymer Synthesis

The experimental procedure for the synthesis of the polybutadiene-poly(*t*-butyl methacrylate) (PBd-P(*t*-BuMA)) was performed under high vacuum unless otherwise stated. Breakseals or greasless taps were used for the transfer of reagents from ampoules into a glass mixing vessel. *n*-Hexane (Fisher) was distilled from *n*-butyllithium (*n*-BuLi) before use and tetrahydrofuran (Fisher) was dried over sodium benzophenone then distilled from polystyrenyllithium just before use. Butadiene (Aldrich) was condensed at -70°C into a measuring cylinder and degassed. It was distilled twice onto sodium mirrors and dried over each for approximately 30 minutes before finally being purified over *n*-BuLi. The monomer was kept at a temperature of -30°C throughout the procedure. *t*-butyl methacrylate (Aldrich) was degassed and dried over calcium hydride for 48 hours then degassed once more before distillation onto triethylaluminium (Aldrich, 1cm³, 1.9M, 25wt.% in toluene) under reduced pressure. On stirring a yellow colour was observed indicating reasonable purity. The solution was stirred for 30 minutes before distillation into an ampoule along with THF. *sec*-Butyllithium (Aldrich) was used as supplied. 1,1-Diphenylethylene (DPE) (Aldrich) was distilled from 1,1-diphenylhexyllithium prior to use. Lithium chloride (98%, Aldrich) was dried in an ampoule under vacuum overnight at 120 - 130°C. THF (ca. 3cm³) was distilled into the ampoule under reduced pressure before it was sealed under vacuum.

1,3-Butadiene gas (10.0g, 0.19moles) was polymerized in *n*-hexane (150cm³) at room temperature overnight, using *sec*-butyllithium (5.6mmol) as the initiator. A sample of the polybutadiene (PBd) was taken and precipitated in methanol, collected and dried. The *n*-hexane was removed under reduced pressure and THF (150cm³) distilled onto the polymer. Addition of DPE (2.1g, 0.012mols) produced a deep red solution. LiCl (2.35g, 0.056mol) was added and dissolved with stirring at -30°C. *t*-Butyl methacrylate (9.52g, 0.067mols) was added at -78°C to give a colorless solution. The reaction was terminated with degassed methanol after 45minutes. 2,6-Di-*tert*-butyl-4-methylphenol was added to the solution. The polymer was precipitated in methanol

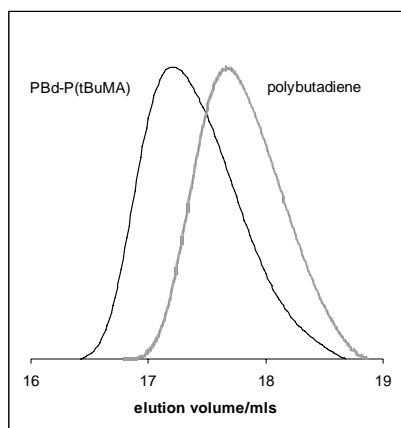
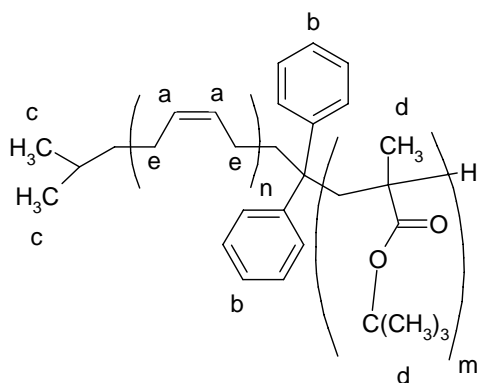


Figure 2 SEC trace of polybutadiene-*b*-poly(*t*-butylmethacrylate) and the polybutadiene homopolymer sample

The ^1H NMR results of the diblock before and after hydrolysis can be seen in figures 2 and 3 respectively. Both samples were run in deuterated chloroform. The only change in the spectrum is the reduction in the integral for peak *d* at $\delta 1.35$ corresponding to the removal of the *t*-butyl group, and where there are two overlapping resonances for the *t*-butyl and the methyl group of the methacrylate in figure 2, there is just the methyl group in figure 3.



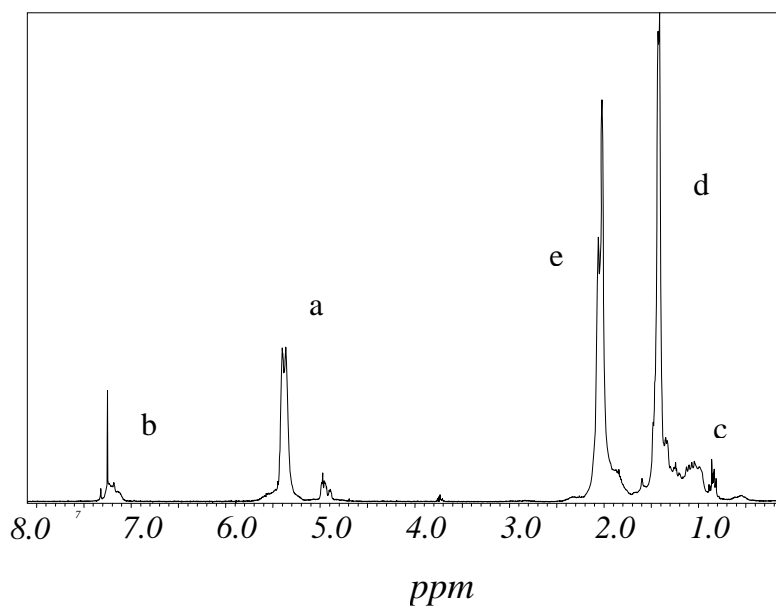


Figure 3 ¹H NMR of PBd-PtBuMA

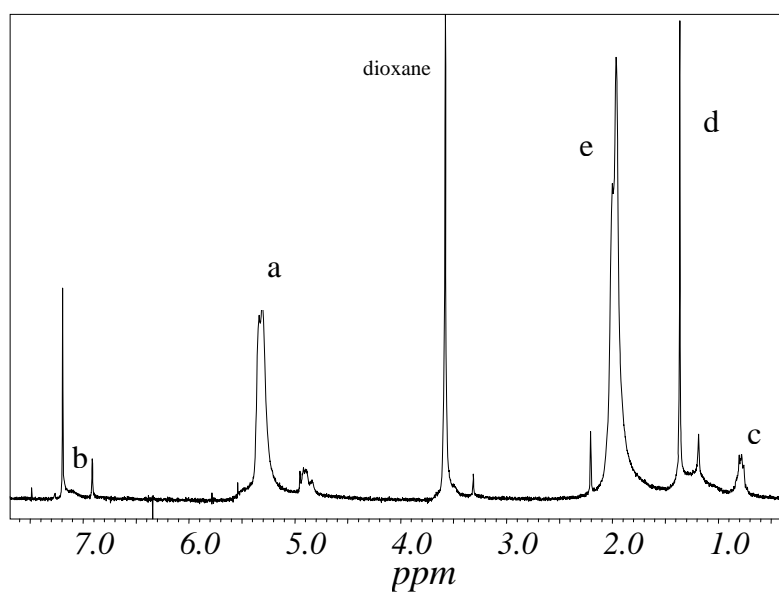
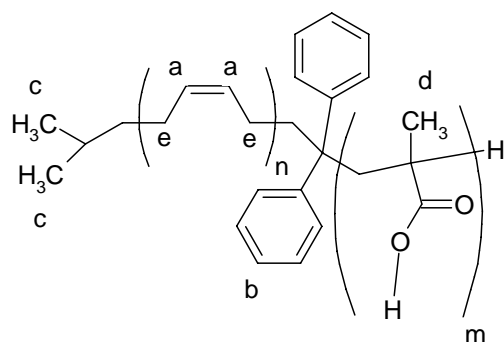


Figure 4 ¹H NMR of PBd-PMAA

Fourier Transform Infra-Red – Attenuated Total Reflectance (FTIR-ATR) was used to confirm that the hydrolysis reaction had been successful. This has the advantage of

the measurement being performed on the solid polymer. With solution measurements problems can arise with regard to solvent selectivity and micellization could affect to results. *t*-Butyl groups absorb at 1366cm^{-1} and a distinctive peak can be seen at this wavenumber in figure 4 which cannot be seen in the product of the hydrolysis reaction in figure 5 indicating the successful hydrolysis of the parent diblock. The shift in the carbonyl peak absorption from 1722 to 1704cm^{-1} also reflects the ester hydrolysis along with the broad absorption from $2500\text{-}3000\text{cm}^{-1}$ signifying an acid O-H stretch.

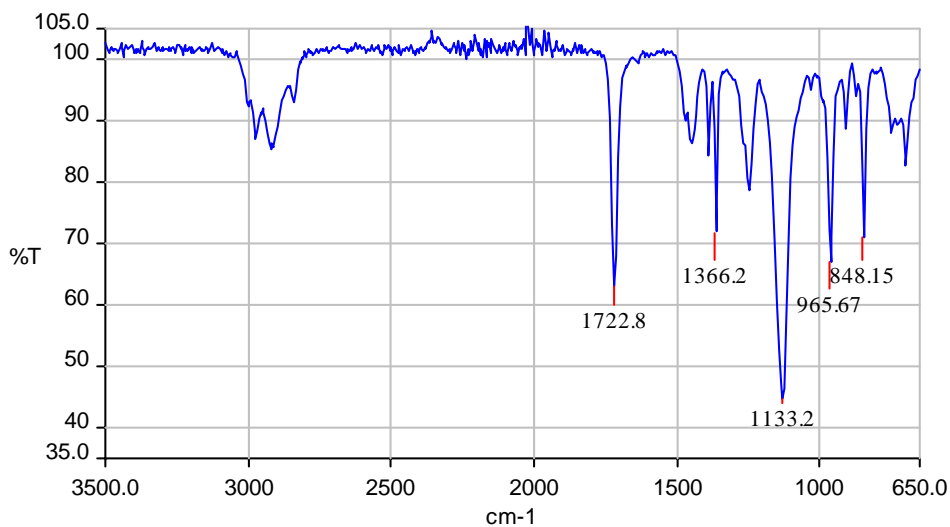


Figure 4; FTIR-ATR of PBd-PtBuMA (prior to hydrolysis)

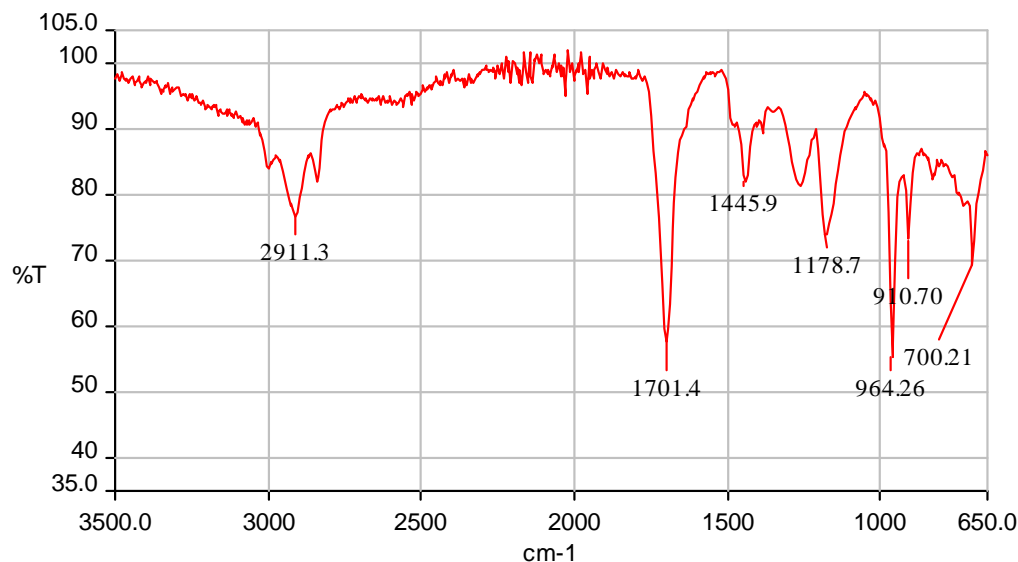


Figure 5 FTIR-ATR of PBd-PMAA