Analytical Flash Pyrolysis of ATRP-Modified Plant Fibres

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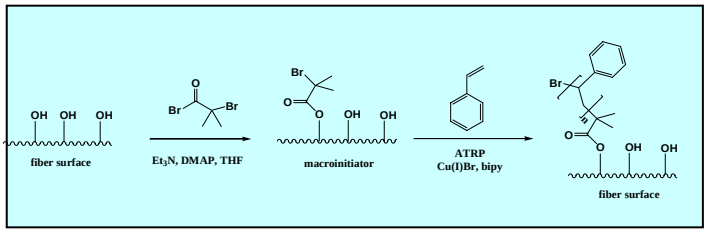
Introduction

Atom Transfer Radical Polymerisation (ATRP) has attracted considerable attention in recent years because of its suitability for synthesis of polymers with strongly controlled macromolecular structures. Plant fibres provide an interesting base for surface-initiated ATRP because the large number of accessible hydroxyl groups may be used as anchoring sites for initiators.

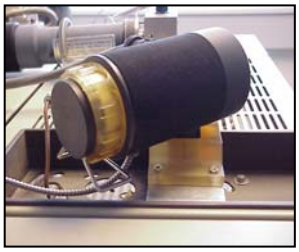


The characterisation of plant fibres modified by ATRP is a challenge due to the highly complex structure and the insolubility of the material. We have used analytical flash pyrolysis and find it highly informative.

Experimental

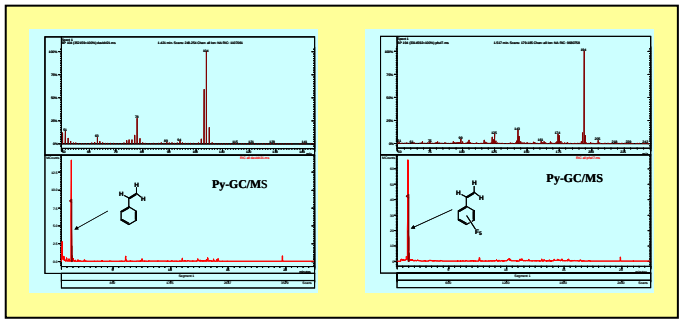
ATRP-modified plant fibres (jute) were prepared as described previously (Plackett *et al*, Biomacromolecules **6** (2005) 2474). Reference compounds were synthesized according to published procedures and characterized by NMR.

Fibres were pyrolyzed at 750 - 850 °C for 2 s using a Pyrola 2000 foil pulse pyrolyzer (Pyrolab, Sweden) in direct combination with an ion trap GCMS system (Varian Saturn). Products were separated on a fused silica column coated with CP-SIL 8CB.

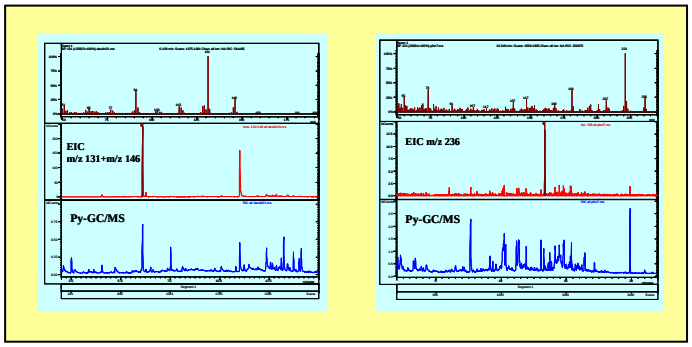


Analytical flash pyrolysis

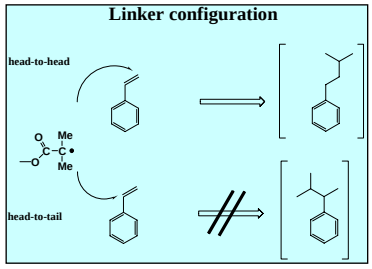
The presence of polystyrene and pentafluoropolystyrene in the synthesized material is demonstrated by abundant signals from the respective monomers accompanied by minor amounts of dimers and trimers.



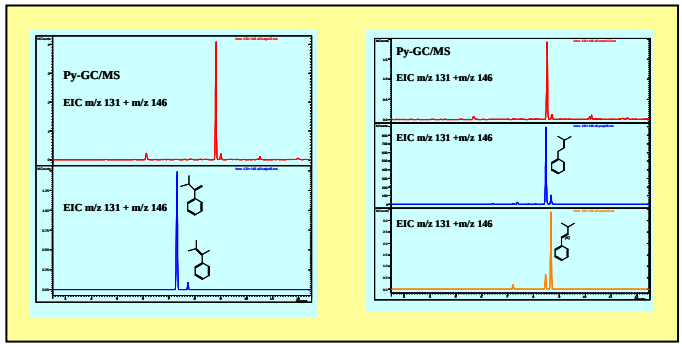
Interestingly, the GC/MS analysis revealed the formation of compounds derived from the monomers plus the initiator part.



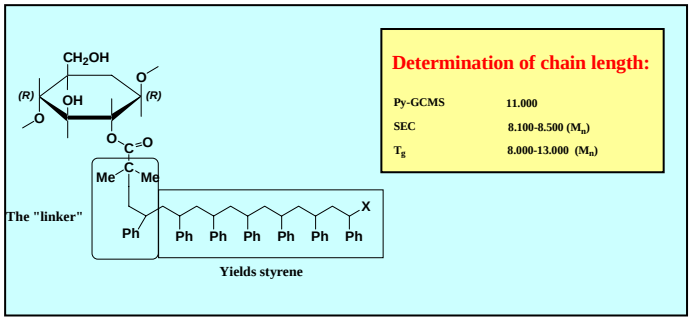
The very first addition of monomer in the ATRP process may be either a head-to-tail or a head-to-head reaction.



This is directly reflected in the distribution of C_5-benzenes generated by the pyrolysis. By comparison with the conceivable isomers a head-to-tail reaction was confirmed for the initiating step.



The ratio of the intensities of the “linker" molecules and the monomer may be used to estimate the chain length. The end group (X) is most likely a CC double bond formed during work-up.



Conclusion

Analytical flash pyrolysis is a powerful method for analysing ATRP-modified plant fibres with respect to polymer identity, linker configuration, chain length, and end group(s).