STRUCTURE AND PROPERTIES OF DIMETHACRYLATE POLYMERS

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Appendix One

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SUMMARY

In this thesis the chemical, physical and engineering properties of members of the tetrafunctional poly (ethylene glycol) dimethacrylate polymer series were investigated and conclusions drawn about the essentially inhomogeneous nature of these radically cured systems. The molecular structure was probed in a number of ways—both experimentally and theoretically (in the form of a Monte Carlo computer simulation).

Dimethacrylate samples (and in particular tetra (ethylene glycol) dimethacrylate) were examined as a function of cure by thermal methods (scanning calorimetry) and torsion braid analysis, both of which indicated an inhomogeneous, multi-stage curing mechanism in which pools of monomer often persist within highly cured regions, even at high conversions. A dynamic mechanical "post" technique was developed to follow the \( T_g \) of samples over a wide range of cures, whilst also providing sufficient material for other characterization techniques to allow property correlation. One such method involved the use of solid state, proton-enhanced, magic-angle-spinning \(^{13}\text{C} \) NMR—both to characterize the material and perform relaxation experiments on the solid polymer. It was found that, surprisingly, these microscopic, molecular mobilities often correlated well with bulk mechanical properties. A pulse sequence developed in this laboratory was applied to these systems to qualitatively determine the nature and relative amounts of different types of unsaturation in these systems, confirming the inhomogeneous nature of the cured resin. A Monte Carlo computer model which simulated curing of tetrafunctional units on a lattice yielded numerical results describing remaining unsaturation which compared favourably with those obtained experimentally by the pulse sequence above. It also proved useful in providing qualitative insights into the nature of dimethacrylate polymerization.

A tracer method developed in this work used a standard, high resolution NMR spectrometer to quantify the remaining mobilities of unsaturated units, providing information on the homogeneity and free volume of the curing systems.

Members of the homologous poly (ethylene glycol) dimethacrylate series were tested for a variety of properties including mobility (by solid state NMR and torsion pendulum) and also by a variety of fracture techniques. It was found that whilst the ethylene glycol chain flexibility largely determined properties such as \( T_g \) and Young's Modulus, fracture results were influenced by the morphology of the system. The shorter
monomers gave the lowest ultimate cure and largest pools of remaining unsaturation (and hence inhomogeneity).

The inhomogeneous nature of the fully cured homopolymers was also examined and quantified by observing the rate and quantity of solvent absorption. The diffusion process proved to be multi-stage, in agreement with the polymer morphology proposed. The dependence of dynamic mechanical properties on the amount of solvent absorbed gave information on polymer-polymer and polymer-solvent bonds. Sorption sites were examined more directly with a wet deuterio-PMMA sample.

Copolymerization of various mono- and dimethacrylates provided a further technique to vary macromolecular mobility and observe the concomitant change in polymer properties.