THE UNIQUE FACILITIES OFFERED BY γ RADIOLYIS TO UNDERSTAND POLYMERIZATION KINETICS

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Sydney, NSW 2006.

Polymers literally form the stuff of our everyday lives. Improving the ways of making present polymers in industry, and devising new polymeric materials all require better knowledge of the mechanism of polymer formation. One of the most important means of polymer formation involves initiation by free radicals. A subset of this, especially important in industry, is emulsion polymerization, whereby the polymerization process is dispersed in water: an environmentally-friendly "solvent" [*1*]. γ radiolysis as an initiation method for free-radical polymerization can give unique mechanistic information: it can penetrate opaque media (i.e., produce a uniform flux of radicals) yet can be switched off instantly, thereby enabling radical loss mechanisms to be investigated. It also gives a steady radical flux at any temperature, which is particularly convenient for looking at reactions at low temperatures, thereby giving the means of "tuning out" complications that can occur at elevated temperatures. Data will be presented to show that this has enabled rate coefficients for a variety of free-radical processes to be obtained, often for the first time: for example, radical loss in emulsion polymerization by exit [2] and by termination [*3*]. A new method [*4*] enables termination rate coefficients to be obtained by two completely independent means (one of which requires γ), thereby verifying the results from both. However, care must be taken for certain systems, such as those involving vinyl esters, where evidence has been obtained that unusual species are formed which undergo slow subsequent polymerization but rapid termination, thereby limiting the applications of the technique. The knowledge gained from these studies has been used to develop theories for these free-radical processes [*5-7*] which are being further refined by testing with further experiments. Moreover, this knowledge has also been used to design new materials [*8,9*].

Many collaborations with Professor Don Napper and David Sangster are gratefully acknowledged, as is the support of AINSE.

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