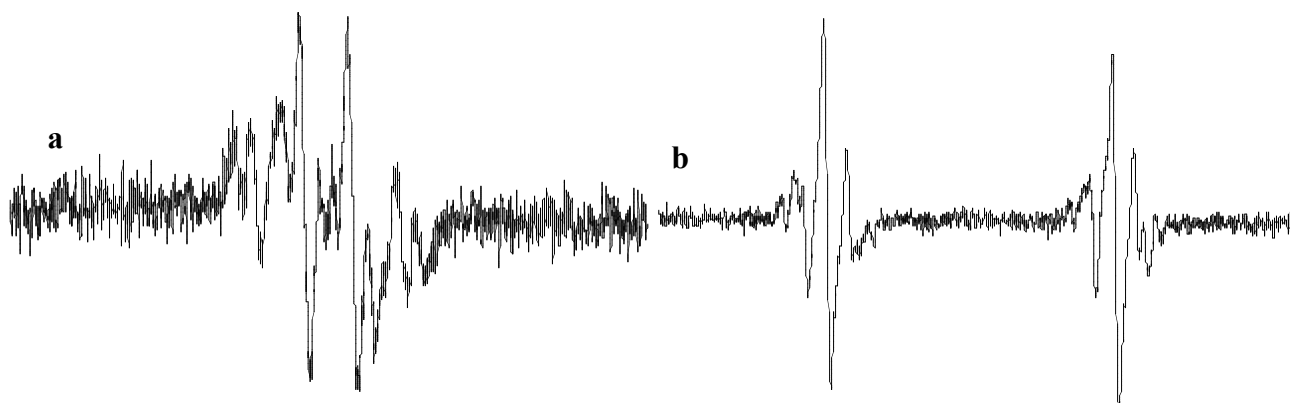


## Styrene RAFT Polymerization. Addition and fragmentation rate constants as estimated by mean of ESR spectroscopy

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Benzyl diethoxyphosphoryldithioformate has proved an efficient chain transfer agent in the RAFT (Reversible Addition Fragmentation Transfer) polymerisation of styrene.<sup>1</sup> This compound is particularly useful for ESR studies as the spin adducts resulting from radical addition to its C=S double bond are characterised by fairly simple spectra with spectral parameters that allow the identification of the different radical species involved in the polymerisation process. Thus, simulation of the ESR spectra observed during polymerisation using the spectral parameters derived for the individual radicals from model studies, allowed the determination of the concentration time profile of three different intermediates in the process.<sup>2</sup> A kinetic model of the polymerisation in which the value of some of the rate constants was varied led to a satisfactory reproduction of the observed concentration profiles and afforded an estimate of the rate constants for the key steps of the RAFT process, *i.e.* addition of the propagating radical to the dithioester and fragmentation of the resulting spin adduct. Calculations have also been carried out to predict the rate constants for the CTA used in the present case and for benzyl dithiobenzoate for which conflicting values are available in the literature.<sup>3-5</sup>



***ESR spectra observed at 90°C during the RAFT polymerisation of styrene using as chain transfer agent cumzyl dithiobenzoate (a) and benzyl diethoxyphosphoryldithioformate (b).***

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