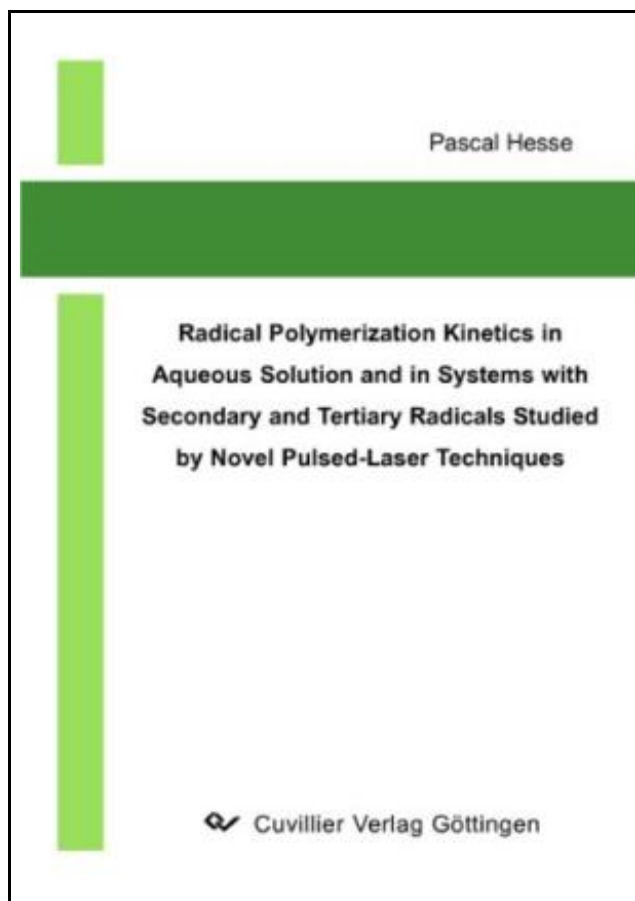


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Cuvillier Verlag Aug 2008, 2008. Taschenbuch. Book Condition: Neu. 208x146x20 mm. Neuware - Abstract Rate coefficients of propagation,  $k_p$ , of termination,  $k_t$ , and of intramolecular transfer-to-polymer,  $k_{bb}$ , have been studied via pulsed-laser polymerization (PLP) methods for systems with strong intermolecular interactions, such as hydrogen bonds, and for polymerizations with two types of distinctly different radicals being present. The propagation kinetics of methacrylic acid (MAA) and N-vinyl pyrrolidone (NVP) in aqueous solution has been investigated by the PLP-SEC technique which combines PLP-initiation with subsequent analysis of the produced polymer by size-exclusion chromatography. The experimental conditions of monomer concentration, temperature, pressure and degree of monomer ionization have been varied in wide ranges. The dependence of  $k_p$  on monomer-to-polymer conversion has been determined from PLP-SEC experiments with pre-mixed polymer. The variation of  $k_p$  may be adequately explained by the interaction of solvent and monomer molecules with the transition state structure for propagation. The termination rate coefficients of MAA and NVP have been studied by the SP PLP NIR method in which the change in monomer concentration after single pulse (SP) initiation is monitored via ms time-resolved near infrared spectroscopy (NIR). The variations of  $k_t$  with conversion for different initial monomer concentrations reflect the diffusion-controlled character of the termination step with  $k_t$  being governed by segmental, translational, and reaction diffusion. In acrylate polymerization backbiting reactions may occur by which chain-end secondary propagating radicals (SPR) are transformed into tertiary midchain radicals (MCR) via 1,5-hydrogen shift. MCRs can react back to SPRs by monomer addition. The basic kinetic scheme has to be extended for additional reactions steps, as SPR and MCR species show widely different  $k_p$  and  $k_t$ , respectively. The impact of MCR formation on the applicability of the experimental techniques for  $k_p$  and  $k_t$  determination, i.e. PLP-SEC and SP-PLP-NIR, was investigated by PREDICI simulations. A...



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