

## Photoreactions of polyvinylcinnamate: laser flash photolysis studies

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Poly-*trans*-vinylcinnamate (PVCin) and *trans*-trimethylenebiscinnamate (TMC) were irradiated with 20 ns flashes of 265 nm light at 25 °C either in dilute CH<sub>2</sub>Cl<sub>2</sub> solution or in a solid polymethylmethacrylate matrix. For PVCin neat polymer films were also irradiated.

Optical absorption measurements and end product analyses led to the following conclusions. For PVCin *trans* → *cis* isomerization and cycloaddition mainly occurred simultaneously during the flash ( $k \geq 3.5 \times 10^7 \text{ s}^{-1}$ ). In these reactions singlet states are involved, presumably. In competition, triplet states were formed to some extent as was inferred from the detection of a relatively long-lived transient absorption between 300 and 400 nm. The decay of the transient absorption was correlated only to some extent with a change in the absorption at 277 nm, indicating the occurrence of a cycloaddition and/or isomerization. In the solid matrix, isomerization was markedly suppressed.

TMC exhibited behaviour quite similar to that of PVCin in liquid solution as well as in the solid matrix.

## Laser flash photolysis studies of the dynamics of polymers in solution

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We report the results of three experiments.

(i) Poly(phenylvinyl ketone) was irradiated in dilute solution with 25 ns flashes of 347 nm light. Light-scattering measurements revealed that the rate of fragment diffusion is controlled by the rate of detachment of intramolecular contact pairs between different segments if certain conditions (*e.g.* high molecular weight or poor solvent quality) prevail.

(ii) A polyamide with backbone azobenzene groups was irradiated in its *cis* form with 20 ns flashes of 530 nm light. The *cis* → *trans* isomerization was completed almost totally by the end of the flash, as revealed from optical absorption measurements. The rate of the conformational change that subsequently occurred was obtained by light-scattering measurements. Relaxation times from