

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 CH₂Cl₂ 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

0.5 ms (neat dimethylformamide (DMF)) to 1.1 ms (DMF:C₂H₅OH, 3:2) were found. The difference in values reflects the influence of the solvent quality.

(iii) α,ω -Dianthrylpolystyrene was irradiated in dilute solution with 25 ns flashes of 347 nm light. From triplet-triplet (T-T) absorption measurements, rates of T-T annihilation, corresponding to rates k_{intra} of intramolecular end-to-end collisions, were obtained as functions of chain length N . In benzene at 22 °C $k_{\text{intra}} = \text{constant} \times N^{-1.0}$ with $N = 110$ to $N = 3000$. In cyclohexane at 34 °C $k_{\text{intra}} = \text{constant} \times N^{-1.5}$ for $N \leq 300$ and $k_{\text{intra}} = \text{constant} \times N^{1.0}$ for $N \geq 300$.

Fluorescence and energy transfer of dye-detergent systems in the pre-micellar region

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The fluorescence lifetimes of dyes and also the energy transfer between dyes with closely located S₁ levels were studied in the presence of detergents. These dye-detergent systems can be considered as one of the model membrane systems of chloroplasts and show some peculiar features when the detergent has the opposite charge to that of the dye. A long dimer-like lifetime was observed in the acridine orange-sodium lauryl sulphate (AO-SLS) system in the pre-micellar region, *i.e.* for [SLS] a little less than the critical micelle concentration (CMC). The energy transfer efficiency between rhodamine 6G (Rh-6G) and pinacyanol (PC) in the presence of SLS showed a distinct peak in the pre-micellar region. These findings and the absorption and fluorescence spectra revealed that the dye molecules are associated with dye-rich induced micelles which reduce the average distance (AO-AO or Rh-6G-PC) between dye molecules in the pre-micellar region.

Twisted intramolecular charge transfer state formation and other properties of some triazinyl dyes

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Fluorescence from the dipolar planar intramolecular charge transfer excited singlet state of the dye *N,N*-diethyl-4-(dichloro-1,3,5-triazinyl)aniline (TA) is strongly quenched by solvents of even moderate polarity (at room temperature