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**Photoreactions in bulk polymers**

Photoreactions in polymers are of great interest for various reasons and particularly in connection with the use of a polymer as a matrix for a photoinduced reaction, e.g. photoimaging processes. However, in most cases considerable deviations from solution are observed if the reaction is carried out in a solid polymer matrix, a phenomenon, which so far was ascribed to the viscoelastic properties of polymers in general. Systematic investigations of the photochromism of aromatic azo compounds and spiropyrans as models for photoactive compounds in a series of polymers revealed that the free volume and the molecular mobility of both the photoactive compound and of the polymer chains arc the reaction controlling parameters. This is demonstrated, e.g., for the case of aromatic azo compounds (cis- Trans isomerization around the azo linkage) in the temperature dependency of at (ratio of the thermal cis-trans relaxation time at temperature T to its value at T g) in the reduced Arrhenius-plot.

The reduced Arrhenius-plot exhibits the existence of two different relaxation mechanisms of the azo chromophore in the glassy polymers, both with temperature independent energies of activation, which are found to be much lower than in solution. These values coincide with the characteristic energies for rotational and translational chain segmental motions in glassy polymers. It is therefore concluded that only chain segmental relaxation processes which depend on the local environment of the chromophore arc the controlling factors for the isomerization.