8 Photodecomposition of Polymers by Laser Radiation

8.1 Ablative Photodecomposition of Polymers

Pulsed ultraviolet laser radiation (at power densities greater than 1 MW cm$^{-2}$ and a laser pulse of 1 $\mu$s width) from an excimer laser (producing wavelengths of 193, 248, 308 or 351 nm) causes etching of the polymer surface and the explosive ejection of the decomposition products at supersonic velocities (Fig. 8.1). This phenomenon has been termed ablative photodecomposition, and widely reviewed in several publications [57, 208, 432, 433, 709, 711, 712, 715, 719, 720, 726, 729].

Two mechanisms have been considered for the UV laser ablation of polymers [374, 529, 710, 717, 727, 728].

(i) Photochemical decomposition of the initially formed electronically excited states. In any polymeric system excited with photons of energy greater than about 3.6 eV ($\lambda < 340$ nm), the decomposition and ablation is predominantly photochemical, being caused by the excitation of chemical bonds to energy levels that are above the dissociation energy. The result is the scission of bonds and the production of a large number of small, volatile fragments during the absorption of the radiation pulse.

Fig. 8.1. Hypothetical steps in the interaction of a UV laser pulse with a polymer. Top: the laser radiation which is defined by a mask is absorbed. Middle: chemical bonds in the polymer are broken by the photon energy. Bottom: the products ablate at supersonic velocities leaving an etched sample [715]
Since the numerous fragments need a large free volume, an enormous pressure builds up in the small volume within the polymer at the site of irradiation, and they are ejected explosively [214]. Presumably the process is too quick for the fragments to transfer heat to the polymer and the excess energy is carried out. The etching is "clean", without charring or melting, substantially supporting a photochemical mechanism.

(ii) Photochemical decomposition in which the electronically excited state undergoes internal conversion to a vibrationally ("hot") excited ground state. Subsequent thermal decomposition is therefore a pyrolysis of the polymer, not very different from the processes that are observed with the laser radiation at visible or infrared wavelengths [46, 57, 100, 199, 411, 529]. This mechanism becomes increasingly significant at higher wavelength and/or fluence (cf. Sect. 8.3). Two types of thermal processes can occur, the photothermal process (or photopyrolysis) and the thermally activated photoprocess.

In the above two mechanisms, the formation of the electronically excited states of a polymer is a very essential step.

The photon flux from a pulsed UV laser interacts with a number of absorbing species (e.g. atoms, ions, molecules, etc.) in a polymer sample. These absorbing species are excited to the higher excited singlet and/or triplet states. The efficiencies of these transitions and lifetimes of the excited states are characteristic of the polymeric material and the laser photon energy. The higher excited states are generally harder to populate (due to a lower absorption cross section (cf. Sect. 1.3) and shorter lifetimes). This means that, for low intensity, the absorption of radiation only results in the depopulation of the ground state and therefore can be described by a single rate Lambert-Beer equation (Eq. 1.8). In this case, the absorption does not depend on the intensity, but decreases exponentially with the sample thickness. However, by using intense laser pulses, other energy levels are also populated. The absorption and the different population densities thus depend on the intensity. The Lambert-Beer equation is therefore invalid. Unfortunately, the time and spatial dependences of different population densities and the photon flux are unknown since only very few parameters (cross section and lifetime) can be measured experimentally (by using absorption and fluorescence spectroscopy). Because ablation occurs in the solid polymer matrix, the photoreactions are diffusion controlled ("cage reactions") and therefore multimolecular processes must be considered (e.g. annihilation (cf. Sect. 3.18) and collisional re-combination).

A detailed analysis of the mechanism of the UV laser ablation of a given polymer requires a knowledge of:

(i) the energy expended in the material that is ablated;
(ii) an analysis of the products of the reaction;
(iii) the time in which ablation occurs.