Laser Ablation of Doped Polymer Systems**

By Thomas Lippert, Akira Yabe, and Alexander Wokaun*

Laser ablation has become a widely recognized tool for materials processing. In the area of polymeric materials, applications of UV lasers for surface modification, microlithography, cutting, and boring have been explored. With the addition of dopants into the bulk, it has become possible to sensitize most known classes of polymers for UV laser ablation at any desired wavelength, including fluoropolymers. Important features of dopant-induced ablation are the reduction of threshold energy fluence required for ablation, and the enhancement of the etching rate by factors higher than ten. In the present review the investigated dopant/polymer systems are summarized and compared. Based on the available information, a general scheme including all relevant pathways is suggested, revealing that in each particular case the dominant mechanism depends on the specific system under study.

1. Introduction

Ablative photo-decomposition was first demonstrated in 1982:[1,2] the surface of a polymer film was etched off upon irradiation with a high intensity UV laser beam. By this technique, polymer films may be structured with submicrometer resolution in a non-contact mode. Since the discovery of the phenomenon, a wide range of applications has been explored, including microfabrication, surface modifications, thin film preparation, and medical applications (e.g., ophthalmic, ceratoplastic, and angioplastic surgery, neuromedicine, and skin therapy).[3-6] As a consequence, laser ablation is one of the most actively pursued subjects in polymer photochemistry.

Investigated materials include standard polymers (e.g., PMMA, PS, PET, and PI), poly(methyl methacrylate), polystyrene, poly(ethylene terephthalate), polyimide, photoresists, conductive polymers, and photoconductive polymers.[7-10] As a general conclusion from the numerous studies, it has been found that both direct *photochemical* bond breaking and *photothermal* polymer degradation/material ejection are important factors influencing the ablation process.

In particular, doped polymer systems have been extensively used in order to explore the new ablation phenomenon, and to elucidate the relevant contributions to the ablation mechanism. Dopants are usually introduced as promoters to confer photosensitivity to intrinsically non-absorbing host materials. Obviously, the range of materials that may be processed by laser ablation is greatly increased by the doping approach. Based on the many possible combinations of polymer materials and dopants, experimental conditions can be easily changed and adjusted. Several types of dopants have been successfully used: subsequent to absorption of energy from the laser pulse, the dopant may undergo ionization, energy and/or electron transfer, radical formation, fragmentation, or intramolecular rearrangements.

The mentioned additives may be doped into base polymers which undergo dissociation, zip depolymerization, or crosslinking upon excitation. As a further parameter to be varied, the dopant and the polymer host may be excited each separately or jointly, depending on the respective absorption spectra and the laser wavelength employed. As a consequence of the large number of degrees of freedom that are accessible to experimentation, doped polymer systems are thought to be well suited for studies aimed at gaining more detailed insight into the ablation mechanism.[11] In the present article, some recent investigations of doped polymer systems are reviewed.

2. Survey of Systems and Parameters Studied

Selected parameters that may potentially influence the ablation characteristics of doped polymer systems are listed in Table 1. Information on these quantities is required for a meaningful comparison of the results from different research groups, who are partly using complementary approaches.

Selected systems of polymers, dopants and irradiation wavelength are listed in Table 2, and have been grouped into classes of systems addressed in Sections 3 and 4 below. Columns have been included to indicate whether the undoped polymer can be ablated at the wavelength alone, and whether the dopant is photolabile or not.

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Table 1. Parameters influencing polymer ablation.

Polymer	Dopant	Film	Irradiation
Absorption spectrum	Absorption spectrum	Content of dopant	Wavelength
Molecular weight	Photolabile/stable	Thickness	Fluence range
Glass temperature		Type of film (free-standing/on substrate)	Repetition rate
Melting temperature	Melting temperature	Preparation technique (stretched foils, poured or spin coated films)	Pulse duration
Decomposition temperature	Decomposition temperature	Surface quality	State of polarization
Source	Source		Homogeneity of beam cross section
Purity	Purity		Atmosphere (air, vacuum, protective or reactive gases)
Morphology (amorphous, crystalline, liquid crystalline)			Method of exposure (contact mask, projection)

Studies have been motivated by a variety of aims, e.g., elucidation of the mechanism, real-time observation of the ablation process, or improvement of the ablation characteristics, as will be mentioned in the following sections.

## 3. Improvement of Polymer Ablation Characteristics

3.1. System Class A: Polymer Blends

Systems in which blending of absorbing and non-absorbing polymers has been used to promote ablation are exemplified in Section A of Table 2. In a first study by Cole et al.,[12] PMMA was doped with 2 and 20 wt.-% of poly(α-methyl-styrene). In agreement with the penetration depths expected from the absorption coefficients of the two polymers, a higher ablation rate at 193 nm resulted for the blend with the lower polystyrene (PS) content. Similar results were obtained for blends of STAA copolymers in a BVMA copolymer[13] (Table 2).

Deviations from the extrapolated concentration dependence that have been observed for pure BVMA[13] and also for pure PMMA[12] may be traced back to the use of a relatively low laser fluence (100 mJ cm^{-2}). The phenomenon may be illustrated in terms of a study (to be mentioned be-

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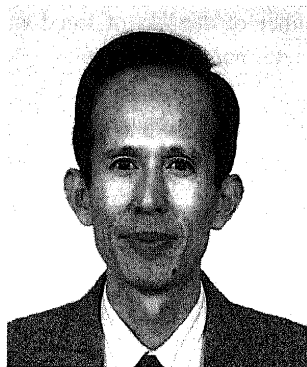
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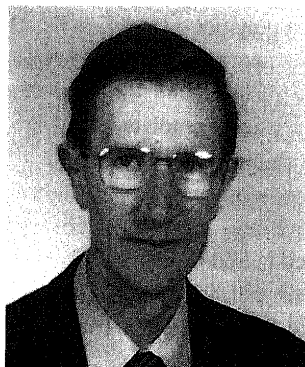
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Table 2. Survey of polymers, dopants, and irradiation wavelengths used, as specified in the literature.

Polymer	Chromophore	λ_{irr} [nm]	Polymer absorption [a]	Photo-lability of dopant [b]	Ref.
Class A					
PMMA	poly(α-methyl-styrene)	193	A	1/2	[12]
butyl-vinyl-ether / maleic anhydride copolymer (BVMA)	styrene-allyl alcohol copolymer (STAA)	193	A	1/2	[13]
Teflon	polyimide	308	B	1/2 ?	[15–19]
Class B.1					
PMMA	benzoin	248	A	1	[1]
PMMA	acridine	248	A	2	[22]
PMMA	pyrene/biphenyl	248	A	2	[23]
PMMA	1,1,3,3-tetraphenylacetone	266	A	1	[24]
polystyrene	diphenyltriazene/DADA [c] azulene/anthracene	308/351	A	1 2	[25]
polystyrene	anthracene/ anthracene-d10	351	B	2	[26,63]
nitrocellulose	stilbene 420, coumarine 120, rhodamine 6G	337	A	2	[27]
cornea	oxybuprocain [d]	308	A	1 ?	[28]
cornea	fluorescein	485	B	1 ?	[28]
Class B.2					
PMMA	benzophenone	308	B	1	[29]
PMMA	pyrene	308	B	2	[29]
PMMA	pyrene/perylene	355	B	2	[30]
PMMA/poly-dimethyl-glutarimide (PMGI)/ chlorinated poly-(α-methyl-styrene) (CMS)	pyrene 4-aminobenzoylhydrazide (ABH)	308	B	2 1	[31,32]
PMMA	tetraphenylporphyrin	351	B	2	[35]
PMMA	tinuvin 328 [e]	308/351	B	2	[37]
PMMA	tinuvin [e]	300–330	B	2	[38–40]
PMMA	diphenyltriazene/DADA [c] azulene/anthracene	308/351	B	1 2	[25]
PMMA	diphenyltriazene (DPT)	308/351	B	1	[14]
PMMA	aryl-dialkyl triazenes (ADAT) pentazadienes, hexazadiene	308	B	1	[42,44]
PMMA	9-anthryl-methyl-methacrylate (AMIB)	351	B	2	[45]
PMMA	triphenylmethanol	351	B	1	[51]
PMMA	6-nitro-BIPS [f]	580	B	1/2	[47]
polyvinylcarbazole (PVCz)	tetraphenylporphyrin	532	B	2	[35]
gelatin	hematoporphyrin	351	B	2	[35]
Teflon	tris-(perfluoroalkyl)-s-triazine [g]	248	B	2	[52,53]
polyimide	rhodamine 6G	532	B	2	[34]
cornea	fluorescein	485	B	1 ?	[28]
polyurethane	rhodamine 6G	532	B	2	[46]
Class B.3					
PS	rhodamine 6G	248	A	2	[54–56]
PS	IR dye S501	193	A	2	[55,56]
PC	rhodamine 6G	248	A	2	[55]
Time-resolved studies					
PMMA	Zn-tetraphenylporphyrin/ tetraphenylporphyrin (TPP)	351	B	2	[36]
PMMA	ethylcarbazole/ poly-N-vinylcarbazole	351	B	2	[67]
PMMA	ethyl-pyrene	308	B	2	[68,69]
PMMA	p-terphenyl	248	A	2	[66]
PMMA	biphenyl	248	A	2	[58,61]
PMMA	pyrene/biphenyl	248	A	2	[23]
PMMA	diazo Meldrum's acid	248	A	1	[62]
PMMA	diazo Meldrum's acid	266	A	1	[64,65]
PMMA	1,1,3,3-tetraphenylacetone	266	A	1	[24]
polystyrene	anthracene/ anthracene-d10	351	B	2	[26,63]
polystyrene	ethylcarbazole/ poly(N-vinylcarbazole)	351	A	2	[67]
polyvinylacetate	hematoporphyrin (HPP)	351	B	2	[11]
PMMA	Cyan-absorb IR-165	1064	B	2	[70,71]
ethyl cellulose	graphite/IR-165	1064	B	2	[75]
EMA/HEMA [h] copolymer	R-165	830	B	2	[76]

[a] A: polymer exhibits absorption at the irradiation wavelength; B: polymer is transparent at this wavelength. [b] 1: sensitizer is labile with respect to photofragmentation; 2: photostable dopant (fragmentation possible at high energies). [c] 9,10-Dihydroanthracene-9,10-dicarboxylic acid anhydride. [d] Local anesthetic. [e] 2-(2′-Hydroxy-3′,3′-diisopentyl-phenyl)benzotriazole. [f] 6-Nitro-1′,3′,3′-trimethyl-spiro-[2H-1-benzopyran-2,2′-indoline]. [g] Perfluoroalkyl = C_9F_{19} or C_7H_{15}. [h] Ethylmethylacrylate/2-hydroxyethylmethacrylate.

low) in which molecular doping with diphenyltriazene was used to sensitize the ablation of PMMA.[14] The ablated depth per pulse is plotted against the logarithm of fluence in Figure 1. Threshold fluence is defined as the intercept of
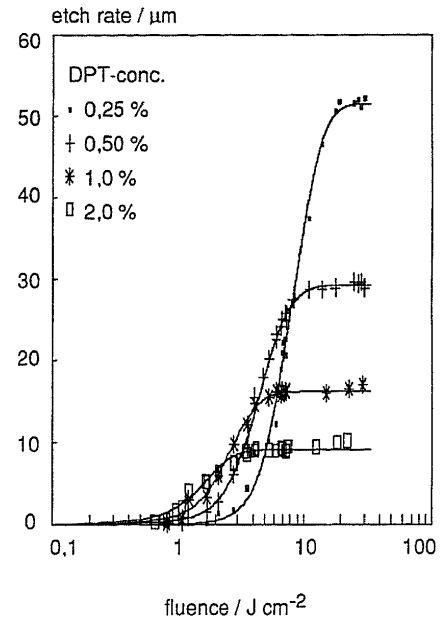

Fig. 1. Fluence dependence of the etch rate (ablated depth per pulse) from PMMA doped with diphenyl-triazene, irradiated at a wavelength of 308 nm [14].

the linear part of the fluence dependence with the abscissa. From Figure 1 we see that the lower the dopant concentration, the higher the threshold fluence; for example, for the lowest dopant content (0.25 wt.-%) of the DPT/PMMA system it is close to 5 $J cm^{-2}$. Referring back to the polymer blends, for the samples with the lowest amounts of the absorbing polymer, the threshold fluence for ablation may be outside the investigated fluence range. This behavior is typical of many polymer systems, hence some of the reported variations may be explained in terms of the narrow fluence range used.

In other studies, polyimide has been used as dopant to sensitize the ablation of Teflon,[15–19] which as a pure material can be ablated only using vacuum ultraviolet wavelengths[20] or femtosecond pulses.[21] It was observed [15–19] that at 248 nm (KrF excimer laser) as well as 308 nm (XeCl excimer laser), the threshold fluence (F_{th}) and the limiting etch rate at high fluences decreased with increasing dopant concentration. An inversely linear dependence of ln F_{th} on the concentration of polyimide was established. The authors found an inverse linear relationship between the fluence F and the optimum dopant absorption (optimum absorption coefficient α_{max}) that resulted in the highest ablation rate at that particular fluence.

A minimum dopant concentration (< 0.2 %) was found below which no ablation is possible. Below this concentration only a roughening and/or swelling of the surface, with formation of various voids and pores, was obtained. Swelling was also observed when using fluences below the abla-

tion threshold. Probing of these surfaces by photoacoustic and attenuated total reflection (ATR) IR spectroscopy (sampling depth, 4 μm) provided clear evidence for a preferential removal of polyimide from a thin surface layer.

The fluence dependence of the etch rate was represented in terms of a purely thermal ablation model, with the two-parameter Equation 1, where d is the etch rate, α_{eff} is the modified absorption coefficient (possibly different from the single photon absorption coefficient), k_0 corresponds to an Arrhenius-type pre-exponential factor, and E^* is given by relation 2, where E is the activation energy, R the gas constant, and C_p the specific heat capacity of the polymer.

$$\ln d = \ln k_0 \frac{E^*}{\alpha_{eff}} \frac{\ln(F/F_{th})}{(F-F_{th})} \qquad (1)$$

$$E^* \propto \frac{E C_p}{R} \qquad (2)$$

Standard deviations of the two parameters were 5–10 % for F_{th} and 7–20 % for E^*/α_{eff}. It has been emphasized that, for a comprehensive theoretical description, multiphoton absorption, saturation, and plume attenuation effects would have to be included. As a yet unexplained observation, it was found that the side wall taper increased with dopant concentration.[16]

3.2. System Class B: Molecular Dopants

3.2.1. Polymer and Dopant Both Absorbing at the Irradiation Wavelength

One of the first investigations of polymer ablation was carried out by Kawamura et al.[1] in 1982, using benzoin-doped PMMA material. The aim of the study was to increase the sensitivity of photolithography at 248 nm. Spin-coated PMMA films were exposed to irradiation from a KrF laser and subsequently developed with a standard developer. An abrupt increase of the etch depth upon increasing the power density of exposure was observed.

Srinivasan et al.[22] demonstrated the possibility of decreasing the threshold of ablation by molecular doping. The threshold of PMMA, which is 400 mJ cm^{-2} at 248 nm for the pure material, decreased to 90 mJ cm^{-2} upon addition of 2 wt.-% of acridine to the polymer. From the ablated mass, it was calculated that the acridine sensitizers absorbed between 13 and 26 photons per molecule, whereas the number of photons absorbed per monomer unit of the PMMA polymer did not change significantly (pure PMMA: 0.31 photons per molecule; PMMA doped with 0.44 M acridine: 0.12 photons per molecule).

Fujiwara et al.[23] studied the ablation of PMMA doped with pyrene and biphenyl, using an irradiation wavelength of 248 nm. Different ablation thresholds were found for the two compounds even though the absorption had been adjusted to the same value. This phenomenon was attributed to transient absorption changes during the excitation.

Arnold and Scaiano[24] studied the ablation of PMMA doped with 1,1,3,3-tetraphenylacetone (TPA) using a frequency-quadrupled Nd:YAG laser at 266 nm. At this wavelength, the intrinsic absorption of PMMA is one order of magnitude lower than at 248 nm. TPA was chosen because of its well known photochemical properties, including the transient species. It was concluded that one-, two-, or three-photon processes played a key role in delivering the energy to the polymer, but that the reaction intermediates occurring during ablation were not strongly altered as compared to photochemical decomposition in solution. CO molecules developed during the photofragmentation are thought to assist bubble formation and ejection of the material. During the ablation, strongly absorbing species are created from either the dopant or the polymer itself, which leads to a dramatic increase in the absorption, in particular close to the surface. It was stated[24] that the intermediacy of absorbing species was the reason for the failure to account for the fluence dependence of the etch depth d in terms of the simple expression Equation 3, where F and F_{th} designate laser fluence and threshold fluence, respectively, and α denotes the *ground state* absorptance of the polymer.

$$d = \frac{1}{\alpha} \log\left(\frac{F}{F_{th}}\right) \qquad (3)$$

In the case of polystyrene,[25] which can be ablated with poor quality only at 308 nm, doping with DPT leads to an improved quality of the ablation contours (Fig. 2). The plateau etch depth for high fluences (see Fig. 1) increased with dopant concentration up to 1 wt.-% and decreased slightly for the higher dopant concentrations at high irradiation fluences. For an irradiation wavelength of 351 nm (XeF excimer laser), doping does not appear to improve the ablation process.

The latter irradiation wavelength was also used by Fukumura et al.[26], who studied the ablation of PS doped with anthracene and anthracene-d$_{10}$ by time-of-flight (TOF) quadrupole spectrometry. Different velocity distributions were recorded for fresh and pre-irradiated surfaces. Below threshold, desorption of anthracene was detected; above threshold, ejection of anthracene together with styrene monomers was recorded. The velocity distribution was analyzed using the Maxwell–Boltzmann equation, and was decomposed into a high (550–600 K) and a low temperature (250–300 K) component . The translational energy changed with the anthracene concentration and the laser fluence used. For deuterated anthracene, surface swelling was found to take place in the initial stages, followed by the ablation process. In addition, the translation energy of the anthracene and styrene molecules was found to be lower. Based on these results a mechanism was suggested in which the photon energy absorbed by the anthracene molecules
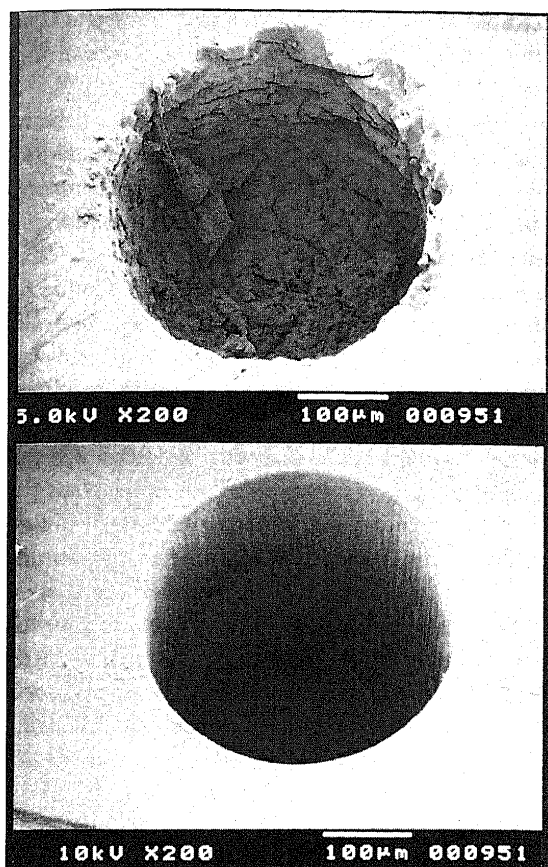
Fig. 2. Scanning electron micrographs of ablation holes etched with 70 pulses of 9 J cm^{-2} at 308 nm. Top: pure PS; bottom: PS doped with 2 % diphenyl-triazene [25].

was transformed into thermal energy via rapid internal conversion and then transferred to the PS matrix, resulting in a thermal decomposition. The variations between protonated and deuterated anthracene dopants were ascribed to differences in the "hotness" of the dopant molecules, the intramolecular decay, the intermolecular energy transfer, or the absorption coefficients of the excited states, which are thought to be involved in the suggested "cyclic multiphotonic absorption process" (up to 30 photons).

In another study,[27] a nitrogen laser (337 nm) has been used for the ablation of nitrocellulose. Stilbene 420, coumarine 120, and rhodamine 6G were used as sensitizers. The etch rate was found to increase significantly with doping, within the investigated fluence range. This increase was found to be proportional to the absorption coefficient and concentration of the dopants. These results are in apparent conflict with standard models of ablation (see Fig. 1); a possible reason for this discrepancy is the small fluence range used in the reported investigation[27] (100 mJ cm^{-2}). The latter may also be the reason for the unsuccessful attempts to ablate nitrocellulose doped with DCM and oxazine 750, using 461 and 660 nm wavelengths. From the low laser fluence used, the authors excluded a thermal mechanism, and a two-step photochemical mechanism was suggested.

Husinsky et al.[28] studied the ablation and dopant-induced ablation of human cornea tissue. A clear influence of the water content of the cornea was found for an irradiation wavelength of 193 nm (ArF excimer laser): higher water contents resulted in higher ablation rates. Upon doping the cornea with oxybuprocain hydrochloride (a commonly used local anesthetic, added at 0.5 wt.-%), ablation rates up to 30 μm per pulse (at 7 J cm^{-2}) have been achieved, using repetition rates of 20 Hz at 308 nm. On doping the cornea with fluorescein a maximum ablation rate of 80 μm was reached for 1 wt.-% of the dopant, at a fluence of 30 J cm^{-2} and a repetition rate of 20 Hz. Lower fluorescein contents resulted in lower ablation rates. For laser spot sizes of less than 0.5 mm diameter, damage zones of about 5 μm were observed around the irradiated area.

An explosive thermal mechanism was suggested as a model for this ablation behavior, with a significant role of the water content and with absence of multiphoton processes. Two plateau values in the dependence of etch depth on concentration, which are found for the doping with oxybuprocain, are thought to be caused by plasma-type avalanche effects and plasma-type plumes. It should be kept in mind that a relatively high repetition rate was used (20 Hz).

3.2.2. Only Dopant Absorbing at the Laser Wavelength

The ablation of PMMA doped with pyrene and benzophenone at 308 nm has been studied by Masuhara et al.[29] For PMMA, doping with comparatively high concentrations of pyrene resulted in sharp ablation contours (Fig. 3b); in the less doped samples, where string-like polymer residuals were deposited in the boundary region between exposed and unexposed areas. For the benzophenone doped films no stringy residues were observed. From the sharp edges of the ablation contours, a significant photochemical contribution to the ablation mechanism is suggested, with a possible involvement of higher excited states, especially in the case of benzophenone.

Misawa et al.[30] have combined the laser trapping technique with ablation. In an aqueous suspension, PMMA latex particles (5–16 μm diameter) doped with pyrene and perylene, were trapped with the fundamental (1064 nm) of an Nd:YAG laser, while the third harmonic output at 355 nm was used to fabricate holes with a diameter of less than 1 μm.

Hiraoka et al.[31] studied the influence of pyrene doping on the ablation of poly(dimethylglutarimide), PMGI, which exhibits only weak intrinsic absorption at 308 nm ($\alpha = 80$ cm^{-1}) at 308 nm. A clear dependence of the etch rate on the absorption coefficient was found. In contrast to the behavior of PMMA mentioned above, redeposition of material around the ablation sites was observed, and was considered to be due to the ejection of big clusters and particles due to the higher glass temperature of PMGI.
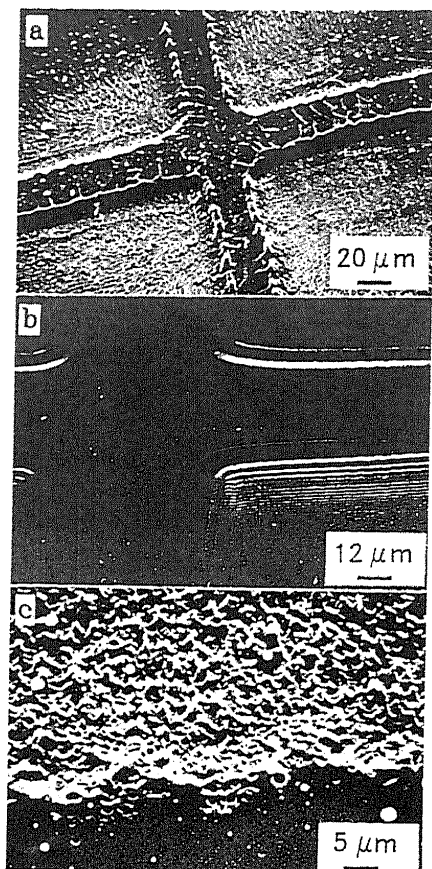
Fig. 3. Scanning electron micrographs of polymer surfaces after laser irradiation: a) tetraphenylporphyrin/PMMA, 351 nm, 674 mJ cm^{-2}; b) pyrene/PMMA, 308 nm, 950 mJ cm^{-2}; c) tetraphenylporphyrin/PMMA, 351 nm, 298 mJ cm^{-2} [29].

For chlorinated poly(α-methyl-styrene), CMS, which can also be ablated without doping ($\alpha = 266$ cm^{-1}), a comparatively smaller dependence of the etch rate on the absorption coefficient was detected. The quality of the ablation contour was poor due to bubbles, holes and craters produced by high local temperatures.

In an extension[32] of this study, PMMA, PMGI, and CMS were doped with pyrene and 4-aminobenzoylhydrazide (ABH). With the PMMA/pyrene system, an optimum dopant concentration for a given fluence was found. A maximum ablation rate of 2.4 μm per pulse was achieved at 1.2 J cm^{-2}. As had been found for PMMA, the threshold fluence for significant etching of PMGI decreased with increasing pyrene concentration. Also for the case of CMS, a reduction of the threshold of ablation upon doping with pyrene was observed. Surface melting, roughening, and deposits inside and outside the ablation craters were detected. In spite of its different photochemical and electronic properties, very similar results were obtained when using ABH as a dopant.

In undoped polymer systems, a constancy of the product of absorption coefficient (α) and threshold fluence (F_{th}) for different irradiation wavelengths has been used as an indication that a photothermal mechanism was active, as shown

for the example of polyimide.[33] Chuang et al.[32] state that this criterion should not be used for doped systems, in view of the complexity of the dynamic processes involved. For the investigated system, the authors conclude that the effective ablation resulted from a transient heating generated by the absorbed photon energy, leading to transient non-equilibrium states, heat-induced decomposition, and ejection of fragments. A similar mechanism was suggested to be active in polyimide systems doped with rhodamine 6G and etched with the second harmonic of a Nd:YAG laser.[34]

Fukumura et al.[35,36] have studied PMMA doped with tetraphenylporphyrin (TPP), gelatin ablation at 351 nm after doping with hematoporphyrin (HPP), and etching of poly-N-vinylcarbazole (PVCz) doped with TPP at 532 nm. For all samples an irreversible swelling of the surface was detected for low fluences. The temperature changes in the polymer matrix were calculated according to Equation 4, where I_0 is the intensity of the incident laser beam, α denotes the absorption coefficient, C designates the specific heat of the polymer, ρ is the density of the polymer matrix, and ΔT is the temperature increase. Temperatures of about 450 K for the swelling, and between 700 and 1080 K for the ablation, were determined. From this experiment the authors inferred that the ablation process does involve a thermal contribution, to a greater or lesser extent.

$$I_0 = \frac{1}{\alpha} C \rho \Delta T \qquad (4)$$

Srinivasan and Braren[37] have used a commercial UV-stabilizer, tinuvin 328, as dopant for the ablation of PMMA at wavelengths of 308 and 351 nm. From the absence of MMA (methylmethacrylate), which is the main *pyrolysis* product, and the large differences in sensitivity with respect to 308 and 351 nm irradiation at a similar absorptivity, the authors concluded that a photochemical decomposition mechanism is active. Tinuvin is excited to higher electronic levels through absorption of two or more photons. Subsequent decomposition of the tinuvin molecules results in many fragments, leading to an explosive decomposition of the polymer matrix.

Srinivasan[38–40] extended the studies of dopant-induced ablation to the region of extremely high "pulse lengths", using a cw Ar$^{\oplus}$ ion laser at its UV emission wavelength of 300–330 nm (output 3.1 W). The laser beam was focused onto the polymer surface, which was mounted on a turntable. The turntable could be rotated at a pre-set speed, resulting in a residence time of the beam diameter on a given area of the sample between 1 and 1000 μs. Etching was found to occur at fluences comparable to the ones required for ablation upon the use of excimer lasers. However, none of the phenomena that are typical for ablation (explosive ejection, acoustic signal) were associated with the removal of the material. This method of etching polymers, without thermal damage around the etched channel, was termed the "photokinetic effect."[41] For a given power density (be-

tween 10 and 100 kW cm^{-2}) and wavelength, an optimum "pulse length" was found in terms of the maximum cutting action. The material is partly removed as vapor, and partly changed into a low-melting polymer, which is soluble in a methyl-isobutylketone/isopropyl-alcohol mixture (3:1). As a consequence of this degradation in molecular mass, the remaining parts of this material could be rinsed out of the etched channel together with the solvent. Differences between the etching behavior of PMMA samples with molecular weights of 140 000 and 10^6 g mol^{-1} were found. The higher M_w polymer showed an optimum etching characteristic at much longer "pulses", but nevertheless with shallower etching features. As a result, a thermal depolymerization process initiated by the incident photons was suggested as the mechanism for the photokinetic etching of the doped PMMA.

Ihlemann et al.[25] examined the ablation of PMMA doped with DPT, DADA, azulene, and anthracene. Maximum etch rates of about 50, 25, 25, and 20 µm/pulse, respectively, could be reached in a fluence range up to 25 J cm^{-2} at 308 nm. For all samples saturation levels were reached at high fluence, suggesting the production of materials with higher absorptances than the primary material. For the two photoreactive compounds (DPT, DADA) the saturation level was found to decrease with an increase of dopant concentration. For the photostable dopants the opposite behavior was obtained; the saturation etch rate slightly increased with increasing concentrations. At low dopant concentrations, the formation of bubbles underneath the surface, and of foamy hills instead of holes, was observed. The authors formulated a complex mechanism including two pathways: both a rise in temperature through thermalization of the excitation energy, and the production of gaseous molecules through dissociation (leading to the formation of the observed bubbles) would give rise to the expansion of the matrix and therefore to ablation. The role of intermediate products, such as radicals, which in turn can give rise to ablation along the same two pathways, was discussed.

In another detailed study,[14] the behavior of PMMA doped with DPT was investigated upon irradiation at 308 and 351 nm. The morphology of the ablation pattern is comparable to the results achieved by use of 248 nm on pure PMMA, but the peak etch rate for the doped samples (50 µm per pulse) is about 10 times higher than for the pure material. From a comparison of the etch rates, which are higher at 351 nm in spite of the fact that the absorption coefficient of DPT is *higher* at this wavelength, an involvement of the photochromic isomerization of DPT was suggested. The cis isomer, which is formed by photoisomerization of the trans ground state, is characterized by a *lower* absorption coefficient at 351 nm. The mentioned mechanism is supported by the observation of an increase in transmission at 351 nm during the first few pulses for low irradiation fluences. The photoproducts of DPT exhibit an absorption at 300 nm, and hence remain unaffected upon irradiation at 351 nm, leading to a high penetration depth of the laser and hence higher ablation rates.

Lippert et al.[42] have studied the ablation at 308 nm of PMMA doped with aryl-dialkyl-triazenes (ADATs). The authors concluded that PMMA can be effectively ablated, and that even below the threshold of ablation the polymer surface is modified, without an observable morphological change. Covalent bonding of triazene chromophores to a methacrylic acid chloride/methylmethacrylate copolymer resulted in similar ablation characteristics as observed with physically doped PMMA.[43]

In a detailed study the same authors investigated[44] the ablation of PMMA doped with DPT, ADAT, pentazadienes, and a hexazadiene, at 308 nm. These photolabile compounds, which release nitrogen upon photolysis following a radical pathway of decomposition, were doped into PMMA at concentrations of 1, 2, and 5 wt.-%. From a comparison with literature data[14,25] on the ablation of PMMA doped with DPT, a clear influence of the preparation technique was derived. Samples with dopant dispersed by dissolution exhibited higher ablation rates compared to the samples where the dopant had been added during the polymerization. In addition, an influence of the molecular weight of the polymer matrix on the etch rate was stated. High M_w polymers exhibited lower etch rates, as a consequence of the higher viscosity of the molten polymer.

For low dopant concentrations (0.25 and 0.5 wt.-%), no defined ablation could be achieved in a fluence range up to 20 J cm^{-2}. However, a swelling of the surface was detected associated with the appearance of bubbles with a height of about 100 µm (Fig. 4). For higher dopant concentrations (2 wt.-%), different ablation depths (20–60 µm per pulse) were recorded for different dopants, depending on the variation of the para-substituent at the phenyl moiety of the triazenes.

A clear dependence of the ablation quality—in terms of contours—on the dopant chosen and on the dopant concentration have been found. Lower concentrations (e.g., 2 wt.-%) resulted in higher ablation rates but lower ablation quality, as shown by a comparison of Figures 5a and 5c. A pronounced influence on the chemical structure of dopant has been detected, demonstrated in Figures 5b and 5d (as compared to Figs. 5a and 5c). The only difference between the dopants was a variation of one substituent in the phenyl system. These results are in contrast to a report in the literature,[32] where no influence of the dopant on the ablation process has been found.

For less heavily doped samples (1 wt.-%), ablation rates up to 80 µm per pulse could be achieved. The etch rates were correlated with the quantum yield of the dopants according to the empirical relation 5, where QY represents the quantum yield, σ is the absorption cross section, and c is the dopant concentration. F and F_{th} represent the laser fluence and ablation threshold fluence, respectively.
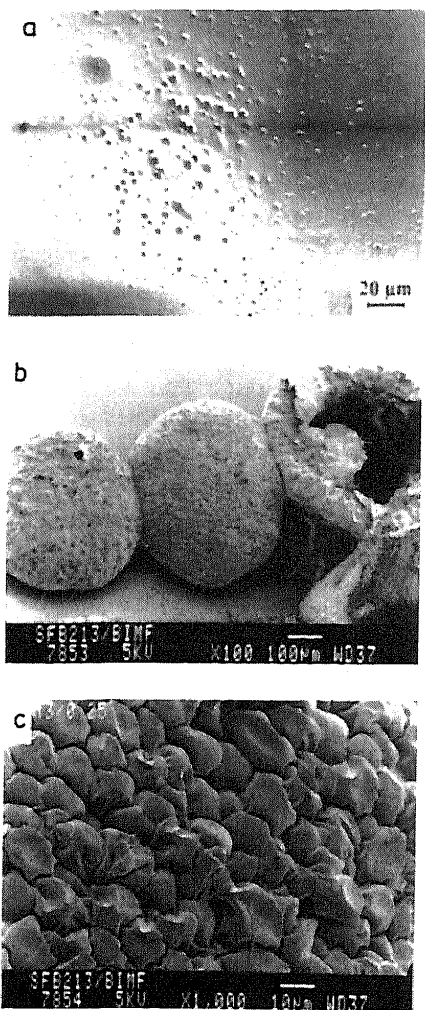
$$d(F) \propto \frac{QY}{\sigma c} \ln\left(\frac{F}{F_{th}}\right) \qquad \text{for } c_{dop} \geq c_{min} \qquad (5)$$

For all compounds a decreasing limiting etch depth at high fluence, and a decreasing threshold fluence were obtained with increasing dopant concentration. Significant variations in the quality of the crater profiles were detected within the series of investigated ADAT dopants. Close inspection of the contour edges showed the appearance of molten material, and hence a clear participation of thermal effects in the ablation process (Fig. 6).

The pentazadienes and hexazadiene compounds resulted in lower maximum etch rates; however, the contours of the ablation profiles were sharper than those obtained with ADAT dopants. With all the mentioned ablation promoters, the unusually high ablation rates were correlated with the production of small molecules, such as N_2, during the photofragmentation of the dopants, which are thought to act as a "driving gas" for the ablation.

Ishii et al.[45] investigated the ablation of PMMA doped with AMIB, and of copolymers of 9-anthryl-methacrylate and MMA at 351 nm. Increasing etch rates with decreasing dopant concentrations were found for both systems, and no remarkable differences of the ablation patterns are stated. Only for low dopant concentrations (0.5 and 0.1 wt.-%) were differences in the threshold reported. The copolymer system exhibited lower threshold values, a higher degradation rate of the ablation fragments (as measured by HPLC), and an increased fraction of crosslinked material. Therefore it was concluded that different mechanisms were active for the two systems, and that a photothermal mechanism involving multiphoton excitation of the anthracene chromophore played an important role in the photocrosslinking of the copolymer.

Brannon and Snyder[46] showed that polyurethane insulation material, which is used in the wire-coating industry, can be effectively ablated after rhodamine 6G doping,

Fig. 4. Surface swelling and bubble formation at low dopant concentration. A medium molecular weight polymer (PMMA, $M_w \approx 77\,000$) was doped with 0.25 wt.-% of an alkyl-diaryl-triazene (ADAT). Scanning electron micrographs were recorded after irradiation as follows: a) single pulse 0.70 J cm^{-2}; b) single pulse with fluence increasing from left to right (3.5 J cm^{-2}, 6.5 J cm^{-2}, and 11 J cm^{-2}). c) The surface of the bubble produced with 6.5 J cm^{-2} fluence imaged at higher magnification [44].
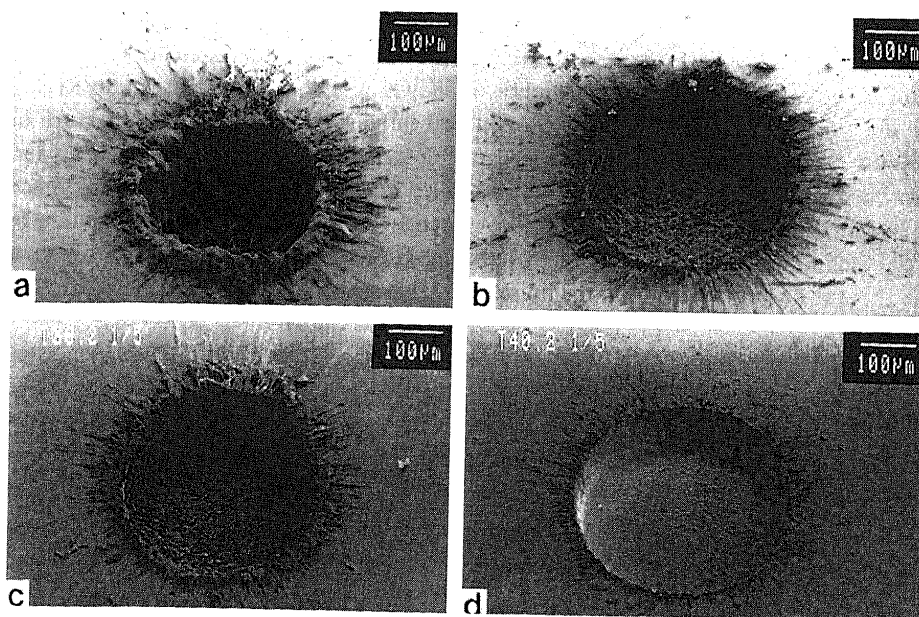

Fig. 5. Scanning electron micrographs of PMMA samples doped with 2 and 5 wt.-% of differently substituted alkyl-diaryl-triazenes, and irradiated with 5 pulses of 5.8 J cm^{-2} fluence [44]. a,b): 2 wt.-% doping, doped with 1-(4-chlorophenyl)-3,3-diethyltriazene (a) and with 1-(4-nitrophenyl)-3,3-diethyltriazene (b). c,d): 5 wt.-% doping, dopants same as in a) and b).
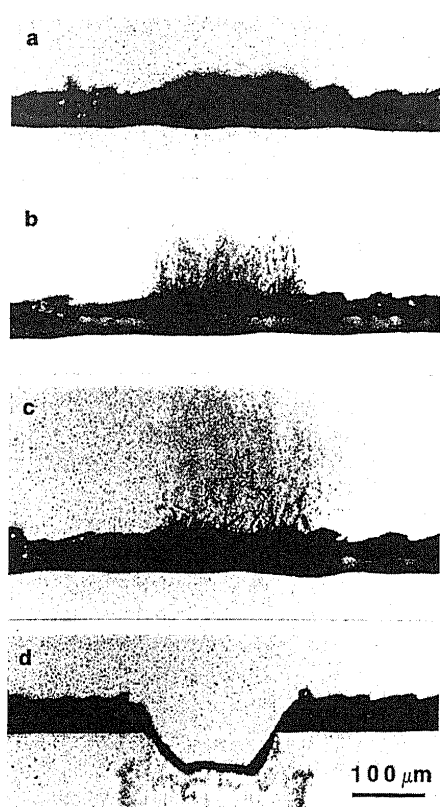
Fig. 6. Images of the surface of a PMMA film doped with biphenyl (2 wt.-%), recorded at different time delays [a) 50 ns, b) 500 ns, c) 5 μs] after irradiation at 248 nm with 600 mJ cm^{-2} pulses. d) The crater after irradiation with 100 pulses (from [57]).

using the second harmonic radiation of an Nd:YAG laser at 532 nm. A dopant concentration of 10 wt.-%, and exposure to 30–50 pulses of 650 mJ cm^{-2} fluence at 10 Hz were found to represent optimum process parameters, leading to excellent edge definition similar to excimer laser stripping. From pulse-by-pulse photorecording of the stripping process, clear evidence for melting and "thermal rollback" of the insulation near the stripped end of the wire was obtained, which indicates a photothermal ablation mechanism.

A novel two-step approach was introduced by Preuss and Stuke,[47] who used a photochromic compound (6-nitro-BIPS) as dopant for PMMA. During the first step (incubation), the doped polymer was irradiated with low energy pulses from an XeCl excimer laser (308 nm), producing visible absorption sites inside the polymer matrix. In the second step the PMMA was ablated with a dye laser at 580 nm. With this technique, which can only be operated with a single ablation pulse, ablation rates of about 2 μm per pulse were realized with a dopant concentration of ~5 wt.-%. A similar two-step method is also applicable for pure PMMA and polyethylene. During the first incubation step, absorption sites were produced with a cw UV lamp or a KrF excimer-laser (248 nm), whereas the ablation of material was carried out with an XeCl excimer laser[48,49] in the case of PMMA. For polyethylene, a few low fluence pulses at 193 nm were used for self-incubation, followed by high fluence pulses for the ablation. This procedure re-

sulted in higher quality ablation contours, as compared to straightforward ablation at 193 nm using high fluence pulses.[50]

Another two-step approach was described by Holtz and Bargon.[51] PMMA was doped with triphenylmethanol, which exhibits absorption bands around 200 and 250 nm. Upon irradiation with an Hg(Xe) lamp the stable triphenylmethyl radical was formed, which features a broad absorption band around 330 nm. In the second step the doped polymer was ablated utilizing an XeF (351 nm) excimer laser. Ablation rates up to 4 μm/pulse could be achieved. In addition bubble formation was observed, which was attributed to gaseous products of the decomposition of the triphenylmethyl radical, via single or multiphoton channels, and to the decomposition of the PMMA matrix.

Hiraoka and Lazare[52] showed that ablation of Teflon AF could be achieved by doping with tris(perfluoroalkyl)-*s*-triazenes and irradiation at 248 and 193 nm, resulting in an etching rate of about 1 μm per pulse. The dopant was removed from the microstructured films by heating the wafers to 200 °C for 5 min, without deformation of the produced images. UV irradiation of the doped film made the dopant persistent in the film at the mentioned temperature, suggesting an imagewise doping possibility.

Using the same dopant/polymer system, Mihailov and Lazare[53] succeeded in producing refractive microlens arrays. The first step in the production of the microlens arrays was the patterning of octagonal lens structures into the doped polymer. During the next step the polymer was thermally de-doped, followed by heating of the polymer up to the melting temperature of 300 °C. The resulting lens arrays are transparent from 190 nm to 2000 nm.

3.2.3. Only Polymer Absorbing at the Laser Wavelength

A totally different approach was taken by Lemoine et al.[54–56] They suggested that the ablation characteristics are influenced not only by the chemical properties of the polymer/dopant, but also by the *physical and mechanical properties* of the matrix. To study the influence of these parameters, the polymer matrix was doped with an additive that did not absorb the laser light but changed some of the physical properties of the matrix, e.g., the free volume. For example, in PS doped with rhodamine 6G[54] the dye markedly enhanced the efficiency of ablation at 248 nm. The absorption coefficient of the doped polymer system was not increased at this wavelength, where neat PS exhibits a strong electronic transition, yet the etch rate was doubled for a 0.04 wt.-% doping. The number of the incubation shots required was also reduced upon doping, but the threshold fluence remained unchanged. These results show that the chemical composition does not play an exclusive role in the ablation process. The fact that the threshold fluence did not change upon doping, while the etch rate increased and the number of incubation shots decreased, was

explained by a decreased minimum density of broken bonds needed to expel the fragments.[55] The additive facilitates the expulsion of the fragments. This supports the view that local volume and pressure changes consecutive to fragmentation are responsible for ablation.

In an extension of this study, [56] the ablation characteristics at 248 nm of polycarbonate (PC) and polystyrene doped with rhodamine 6G have been compared. Here the additive did not alter the number of incubation shots or the etch rate for the doped PC, whereas both had been observed to change for the PS system. In both systems, the additive does not change the electronic configuration of the polymer, but potentially changes its conformation. The ability of the dye to decrease or increase the overall free volume in the film will render the polymer more glassy or more plastic. Rhodamine exhibits a stronger tendency to aggregate in PS, as compared to PC, which can be responsible for a different change of the free volume in the films, and therefore the ablation characteristics. PS doped with IR dye S501,[55,56] a molecule with a long linear structure, changed the etch rate at 193 nm even more significantly than for the rhodamine doped PS.

4. Studies with Time-Resolved Techniques

In time-resolved studies of ablation processes, aromatic compounds have frequently been used as dopants, in view of their favorable strong absorption properties and emission characteristics. Fukumura and Masuhara investigated the mechanism for doped polymer ablation by using nanosecond imaging,[11,57-59] time-resolved creation and detection of interference patterns,[60] time-resolved absorption[24] (see Sec. 3.2.1) and emission spectroscopy, and time-of-flight mass spectroscopy (TOF-MS) (as discussed in detail in the literature,[26] see Sec. 3.2.1). Some of these studies employed irradiation wavelengths coincident with a polymer absorption band.

In the 248 nm ablation of biphenyl-doped PMMA, imaging techniques[57-59] showed that ejection of material became observable after a 50 ns delay, and extended over a time scale longer than 5 μs (Fig. 6). In a detailed study,[61] several intermediate species were identified from a comparison of nanosecond photographs with time-resolved spectroscopic techniques. Below ablation threshold, the spectra were dominated by fluorescence from the excited singlet state of biphenyl. Rising triplet state absorption was observed concomitant with the fluorescence decay. The triplet state was found to become the main transient species prior to the ejection of material. This observation demonstrates the key role of the transient absorption of the triplet state for ablation, which is more important than the shielding of incident radiation by fragmented products. Model simulations of the excited state dynamics provided evidence for the thermal aspects of the ablation process. Only for high fluences (> 3 J cm^{-2}) have biradicals such as C$_2$,

CH, and CN, as well as plasma emission, been observed, which are typical for the ablation of polymers in air. Even for the photolabile diazo Meldrum's acid dopant,[62] which liberates N$_2$ during photofragmentation, a key role was assigned to the cyclic multiphoton process[63] involving the triplet state of the intermediate ketene species. Lippert et al.[64,65] studied the laser irradiation (266 nm) of diazo-Meldrum's acid in PMMA with picosecond IR spectroscopy. They confirmed the formation of the ketene intermediate on a picosecond time scale. From the linear dependence of the absorbance change of the diazo band at 2172 cm^{-1} on the pump power even above the threshold of ablation, it was suggested that material ejection (ablation) was taking place only on a time scale which is much longer than that of the optical measurement (6 ns). The importance of photochemical reactions, which might not be different to the reaction in solution, prior to the ablation event was demonstrated by the fast measurements.

Transient displacement of the surface upon irradiation on a shorter time scale was observed for the first time with a newly developed interferometric method,[60] with a time resolution of 10 ns. The mentioned displacements were detected even for surface modification below the threshold of ablation. The results suggested that the transient surface expansion preceding the ejection of material was an important feature for understanding the laser ablation dynamics.

Time-resolved studies of the absorption of PMMA doped with *p*-terphenyl[66] revealed no transient species other than the excited singlet and triplet states of *p*-terphenyl. On the other hand, the recording of time-resolved emission spectra of PMMA with a Zn-tetraphenyl porphyrin promoter[36] showed a broadening of the fluorescence bands, and an increase in their intensity. The authors concluded that the aromatic sensitizers were rarely decomposed, whereas the observed spectral broadening indicated hot domain formation in the polymer matrix.[57]

PMMA and PS have been doped with ethyl-carbazole (Cz) and poly-*N*-vinylcarbazole, and irradiated at 351 nm. Pronounced differences in the morphological changes for doping with the monomeric and polymeric dopants have been found. At fluences which merely resulted in swelling in the case of the Cz-doped films, clean etching has been obtained for polymer-blend films. From the time-dependent fluorescence spectra, an important role of interchromophore interactions, such as S$_1$–S$_1$ annihilation, has been found for the polymer-sensitized films.[67]

Analysis of TOF mass spectra showed the signals of intact sensitizer molecules.[26] The velocity contribution of these ions indicated that the polymer surface was heated up to around 600 K at the ablation threshold. Only for high fluences (> 2 J cm^{-2}) were also radicals (C$_2$ and CN) ejected for porphyrin-doped PMMA at 351 nm.[59] The light absorption dynamics was explained in terms of repeated excitation and relaxation in electronically excited states of the sensitizer molecule, creating transient hot domains in the polymer that give rise to ablation.[57]

A cyclic multiphoton absorption mechanism has also been proposed for PMMA doped with pyrene and biphenyl. From the time-integrated absorption spectra recorded during irradiation at 248 nm it was calculated that each dopant molecule had absorbed at least 12 photons at the threshold fluence.[23]

Subsequent to the ablation of ethyl-pyrene-doped PMMA at 308 nm,[68,69] changes in the fluorescence properties were detected in a spatial region of ~20 μm width around the ablated area. This was attributed to changes in the distribution (aggregation) of the dopant, as induced by the forces during the volume expansion and the heat dissipation accompanying the ablation process.

Time-dependent experiments on doped polymers have also been performed using 100 ps pump pulses from an Nd:YAG laser (1064 nm) and 532 nm probe pulses of shorter duration. In view of the IR laser irradiation wavelength employed, a purely thermal mechanism is active in these cases.

In a first study,[70,71] PMMA was doped with cyabsorb IR-165 (λ_{max} = 1064 nm) and rhodamine 6G ($\lambda_{max} \approx$ 530 nm). The IR dye was used as an absorber/heater and a thermometer, whereas rhodamine was solely present as a thermometer to perform optical calorimetric measurements. The multiphoton pumping of the molecular heater molecule,[72–74] which can absorb more than one hundred photons during the pump pulse due to the sub-picosecond relaxation back to the ground state, leads to a significant temperature increase. A rapid vibrational cooling rate leads to an ultrafast temperature jump. The authors determined molecular hot spots with T_{peak} of about 1000 °C, a bulk temperature rise ΔT of 140 °C, and a heating rate dT/dt exceeding 10^{12} K s^{-1}.

In the second study,[71] only IR-165 was used as a dopant and thermometer. As a reference, thermogravimetric analysis and differential scanning calorimetry were used to determine the heat capacity C_0, as well as the decomposed fraction χ of the polymer as a function of the heat delivered to the sample. Subsequently, optical calorimetry yielded the decomposed fraction and surface temperature during laser irradiation. The effective heat capacity was approximately equal to C_0 below the ablation threshold, and was observed to increase above threshold fluence. At the threshold, a value χ = 0.02 was calculated. With increasing laser energy, the decomposed fraction, as well as the velocity of the fragments and the intensity of the ablation process, were observed to increase. The maximum surface temperature at the threshold was determined to be T_{abl} = 600 °C, with a heating rate $dT/dt \approx 5 \times 10^9$ K s^{-1}. For a given enthalpy change, the fraction of decomposed material upon fast laser heating was always lower than that determined with slow heating rates, as used in the DSC experiments. At high laser energies the temperature was found to level off at a limiting value of 715 °C.

The same laser system was utilized for a comparison of the influence of the particle size of the dopants on the abla-

tion of ethylcellulose.[75] As dopants a molecular dye sensitizer (IR-165) and nanosized (≤ 220 nm diameter) graphite particles were used. For longer duration pulses (150 ns), which do not produce hot spots, both systems yield the same threshold of ablation. However, for shorter pulses (23 ps) a reduction in threshold by a factor of three is found for the graphite-doped polymer. The authors concluded that an enhanced thermal polymer decomposition in the vicinity of the larger graphite hot spots is responsible for this behavior.

Pinto and Lloyd[76] studied the ablation of EMA/HEMA copolymers doped with IR-165 using 830 nm irradiation. The authors analyzed the ablated material deposited at a receptor surface by means of secondary ion mass spectrometry (SIMS). They detected a change in the co-monomer composition of the resolidified copolymer. This was attributed to a thermal unzipping of the superheated polymer in the ablation plume, followed by a repolymerization of the ejected monomers.

5. Applications in Related Fields

A research area related to dopant-induced ablation is the laser ablation transfer (LAT) imaging process. A transparent substrate with an ablatable coating is used for this technique. The coating consists of a near IR absorber/sensitizer that imparts virtually no color to the coating, a decomposable polymer, and the material to be transferred (e.g., a pigment, ink or dye). A transparent receiver sheet is placed close to or in contact with the air interface of the polymer. An Nd:YAG laser beam (1064 nm) was focused through the transparent substrate onto the LAT film. In this manner, a negative and positive image were generated simultaneously.[77] This process was improved by adding a dynamic release layer (DRL), e.g., Al, between the substrate and the polymer coating. Thereby, the ablation threshold was lowered, as the DRL localizes most of the laser energy at the interface between the coating and the substrate.[78] Another reduction of the threshold fluence by an order of magnitude was achieved by the use of a picosecond Nd:YAG laser.[79]

In similar system described by Novotny and Alexandru[80,81] several dyes (e.g., magenta disperse, disperse blue 60, disperse red 11, yellow 88) were spin-coated on a PET sheet. When an argon ion laser (514.5 nm) was focused onto the surface, the polymer could be marked with submicrometer resolution. From the threshold observed for this technique, and the properties of the used materials, the authors suggested diffusion of the molten dye into the polymer substrate as a mechanism for the laser polymer marking technique. Uchida et al.[82] used laser irradiation of PMMA to incorporate dyes selectively into the polymer, by soaking the irradiated sample in an aqueous dye solution.

For the laser marking of polymers, some special additives have been used for optimizing the marking quality (for ex-

amples see the literature[83,84]). With the combined use of two additives (an inorganic and an organic promoter), even a colored marking and writing of colored symbols has been achieved.[85]

Fukumura et al.[86] have reported the selective incorporation of fluorescent molecules into a receiver polymer sheet. A dye-doped polymer substrate (B) was irradiated through a transparent overlayer A. Upon laser irradiation through polymer A, dye molecules were ejected from B and incorporated into foil A, which was separated from the substrate subsequently. One of the key parameters for the implantation depth was the glass transition temperature of the receiver sheet:[87] low T_g resulted in greater implantation depths.

Bargon and Baumann[88] used laser processing for the production of patterns of conducting polymer areas. One approach was the doping of poly(vinylchloride) with a photosensitive oxidant, e.g., $FeCl_3$. Photoexposure of the composite initially yielded a latent image, which was converted into its electrically conducting form by exposing it to a vapor of a monomer, typically a pyrrole.

Another related application is the use of photobleachable dyes (e.g. xanthene dyes) in a polymer matrix, such as poly(vinylalcohol), for holographic devices.[89-91]

6. Discussion

6.1. Intrinsic Polymers

Numerous descriptions have been given for the interaction of high energy UV laser pulses with polymers that results in ablation. In the low fluence regime, quantitative evaluation has frequently been based on the familiar model Equation 3 for ablation (Eq. 6), where d designates the ablated depth per pulse, α is the absorption coefficient, F is the laser fluence, and F_{th} corresponds to the threshold fluence. Different model concepts have been suggested for the mechanism by which polymer ablation proceeds.

$$\alpha F_{th} = \text{const.} \tag{6}$$

This equation implies an idealized model, assuming absorption according to Beer's law, the existence of a defined ablation threshold, and absence of thermal diffusion and chemical modification. However, as none of these assumptions is strictly valid, various models have been developed, including the effects of a receding surface,[92] plume screening,[92-94] thermal diffusion,[95] Arrhenius-type thermal activation,[96-98] chromophore bleaching,[99,100] and participation of both photochemical and thermal reactions.[101] Even a purely thermal degradation mechanism has been suggested.[102] The dynamics of the ablation plume was analyzed by Kelly et al.[103-105] using gas-dynamic models.

In recent publications, photothermal models for ablation have been favored by several authors.[10,106,107] In the case of polyimide, an Arrhenius-type thermal rate mechanism

was used to model the ablation behavior at 248, 308, and 351 nm. For ablation at 193 nm, the possibility of a photochemical mechanism was stated.[108]

A mathematical model of absorption which includes nonlinear effects, such as chromophore saturation and multiphoton absorption, has been developed by Pettit and Sauerbrey.[109] In two recent publications, Srinivasan[110,111] has drawn attention to the fact that it is necessary to consider the ablation products in model development. From the comparison of pyrolysis products from surface treatment with a cw IR laser with the ablation products generated by an excimer laser, he concluded that photoablation is a truly new *photochemical* process, in which multiphoton excitation may play an important role.

Luk'yanchuk et al.[112,113] used a two-level system in which the excitation energy is dissipated via stimulated emission, thermal relaxation, and activated desorption of excited species. Depending on the thermal relaxation times, moderate surface temperatures (≤ 2000 K) and stable ablation fronts result, leading to smooth surfaces.

6.2. Doped Polymers

As in the case of pure polymers, different suggestions for the mechanism of ablation of doped polymers have been proposed, depending on the system used (polymer/dopant/laser). In the case of Teflon doped with polyimide, an optimum absorption coefficient (α_{max}) was found for a given fluence. The value of α_{max} decreased with increasing fluence.[16] The threshold fluence was found to follow approximately an inverse square root dependence on the polyimide concentration ($\ln F_{th} = \ln K - a \ln c$, with K a constant, c the concentration, and $0.42 \lesssim a \lesssim 0.45$. These observations lead to the suggestion of a purely thermal two-parameter ablation model, described by the Equations 1 and 2. The same authors caution[18] that for a complete theoretical approach, multiphoton absorption, saturation, and plume attenuation effects would have to be included. In the same study, an increasing side wall taper with increasing dopant concentration was observed,[18] which is not accounted for by the model.

The research teams of Hiraoka, Masuhara and Fukumura used a photothermal mechanism for the explanation of the dopant-induced ablation. It was stated[32] that *no major effects on photoetching* were observed by changing the dopant. For porphyrin-doped PMMA, Equation 7 was used to calculate the temperature increase, where I_0 is the intensity of the incident laser, α represents the absorption coefficient, C is the specific heat of the polymer, ρ designates the density of the polymer matrix, and ΔT is the temperature increase to be calculated.[35] Temperatures of about 450 K for the swelling and between 700 and 1080 K for the ablation were determined. From this large temperature rise it was inferred that a thermal part was involved in the ablation process to a greater or lesser extent.

$$I_0 = \frac{1}{\alpha} C \rho \Delta T \qquad (7)$$

In a study of anthracene-doped polystyrene, Fukumura et al.[26] were able to detect intact dopant molecules among the ablation products by using TOF-MS. The velocity distribution was analyzed using a Maxwell–Boltzmann distribution. A fraction of products desorbing with a high temperature of 550–600 K and a second fraction with a lower temperature of 250–300 K were identified from the analysis.

For the mechanism, a *cyclic multiphotonic absorption* process involving up to 30 photons has been suggested. From the highly excited anthracene molecules, the photon energy is transferred to the polystyrene matrix via rapid internal conversion. The associated temperature increase results in a thermal decomposition of the polymer. From the time-dependent absorption studies it was suggested that, in view of their longer lifetimes, excited triplet states should play a key role in this process.

The multiphoton absorption cycle was confirmed by a comparison of the temporal profile of the fluorescence of anthracene-doped polystyrene films with computational results based on the cyclic process. In the computational studies, the ground state, first excited singlet state, and lowest triplet state have been included, as shown in Scheme 1.
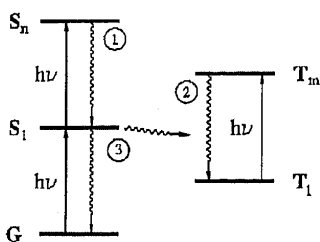
Scheme 1. Possible mechanism for cyclic multiphotonic absorption [63]. (1) $S_n \Rightarrow S_1$ mechanism: $S_1 \Rightarrow S_n$ absorption is followed by rapid internal conversion within the singlet manifold. The sequence can be repeated several times during the laser pulse and can therefore heat up the polymer. (2) $T_m \Rightarrow T_1$ mechanism: The triplet state is the key species in the repetitive absorption and energy dissipation. (3) $S_1 \Rightarrow G$ mechanism: Relaxation to the ground state is not thought to be important in the case of hydrocarbons such as anthracene, due to the relatively slow relaxation process (> ns).

The calculated temperature rise during the laser pulse depends nonlinearly on the laser intensity. Rapid internal conversion within the triplet manifold is the most effective mechanism for depositing heat at the irradiated surface.[63]

Lippert et al.[44] drew attention to the influence of photochemical properties of the photolabile compounds used, in addition to the thermal contributions to dopant-induced ablation. For one class of substances (aryl-dialkyl-triazenes), large variations in the maximum ablated depth per pulse (between 20 and 60 μm for a constant dopant concentration of 2 wt.-%), and in the quality/morphology of the ablation contours were reported as a fundtion of dopant substitution. Molecular nitrogen, which is released during the photolysis of the dopant, is thought to act as a *driving gas* for ablation. Therefore a relation has been suggested

where the ablation depth is proportional to the quantum yield of the dopant molecule, shown in Equation 5.

An influence of the quantum yield on the etched depth was also found for the ablation of photolabile triazene polymers, containing the same structural unit as the dopant molecules, which were designed for the ablation process.[114]

The suggested influence of photochemical properties of the dopants is supported by Ihlemann and co-workers,[114] who reported a participation of trans–cis isomerization of the dopant during the ablation process. Arnold and Scaiano[24] concluded that transient species play a key role during ablation. These authors found no prominent differences between the photolysis of 1,1,3,3-tetraphenyl-acetone in solution and the polymer matrix. From this observation, they concluded that highly excited states (with up to three absorbed photons per molecule) are populated during ablation.
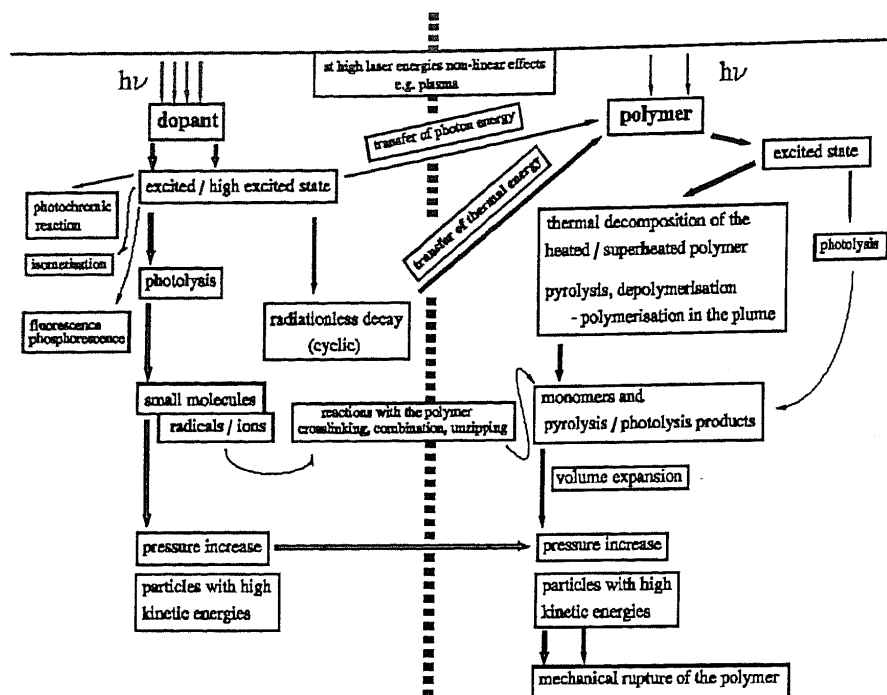
The role of highly excited states is also emphasized by Srinivasan and co-workers, who suggested a photochemical mechanism for acridine and tinuvine dopants.[22,37] It was concluded that ablation started with the fragmentation of highly excited dopant molecules (two or more absorbed photons), which gave rise to mechanical rupture of the polymer.

A completely different reaction pathway was found[38–40] to be followed upon polymer irradiation with a cw $Ar^{\oplus}$ ion laser. This exposure results in a purely thermal depolymerization, and has been termed the *photokinetic effect*, rather than ablative depolymerization.

Taking together the mentioned observations and interpretations, a complex chain of possible (alternative or sequential) reaction pathways emerges, which may be illustrated in a qualitative scheme of dopant induced ablation (Scheme 2). Depending on the properties of the dopant and polymer, the laser wavelength, and the fluence employed, the various possible pathways are involved to a greater or lesser extent.

As shown in the scheme, the dopant can absorb one or several photons (cyclic multiphoton absorption) to reach an excited or highly excited state, from which a variety of different reaction pathways may originate. Photolysis of the dopant can take place to yield small molecules such as N_2 or CO, which act as a *driving gas* for ablation. The resulting pressure increase leads to a mechanical rupture of the polymer. At the same time, radicals or ions are generated, which in turn may induce a multitude of reactions, such as crosslinking of the polymer chains, combination with the polymer or other photolysis products, or "zip" depolymerization of the polymer chain. This depolymerization leads to a pressure increase due to the volume expansion.

Another pathway, which can take place alternatively or concurrently, is the radiationless decay of the excited dopant molecules, from either singlet or triplet states (as shown in more detail in Scheme 1). The relaxation of the

Scheme 2. Qualitative mechanism for the ablation of various dopant/polymer systems

highly excited states leads to heated or superheated polymer chains, resulting in pyrolysis and/or depolymerization. These processes are again accompanied by a volume expansion, leading to a pressure increase, mechanical rupture of the polymer chains, and ejection of particles with high kinetic energies. Upon the use of high laser energies, non-linear effects such as plasma development, avalanche effects, and chromophore saturation have been suggested to occur.

7. Conclusions

The increasing number of studies in the area of dopant-induced ablation reflects the growing interest in this variant of ablative photodecomposition. Doped polymer systems are interesting both in view of potential applications and for fundamental and theoretical studies of the decomposition mechanism.

Investigations aimed at applications showed that, using polymer doping, the threshold of ablation and therefore the costs of machining may be lowered. Dopants open the possibility of using laser wavelengths at which the intrinsic polymer does not exhibit absorption. This provides the process option of using laser wavelengths (such as 308 nm) which may be derived from excimer laser systems with favorable operating costs and safety of gas handling.

For many of the investigations of doped polymer systems reported in the literature, comparatively poor qualities of the produced surface structures have been reported. On the other hand, much higher ablated depths per pulse are obtained as compared to undoped polymer systems, suggesting a possible application in the field of polymer cutting, or in the machining of via holes.

Studies of the mechanism of dopant-induced ablation have revealed many new and fascinating facets of photochemistry for polymers, dyes, and dyes dissolved in a polymer matrix. These experiments have added to our understanding of the interaction of strong laser beams with polymer surfaces. The studies suggest it to be highly unlikely that *a single* mechanism would account for all investigated types of dopant-induced ablation. Rather, it appears necessary to evaluate the mechanism acting for each class of dopant–polymer systems.
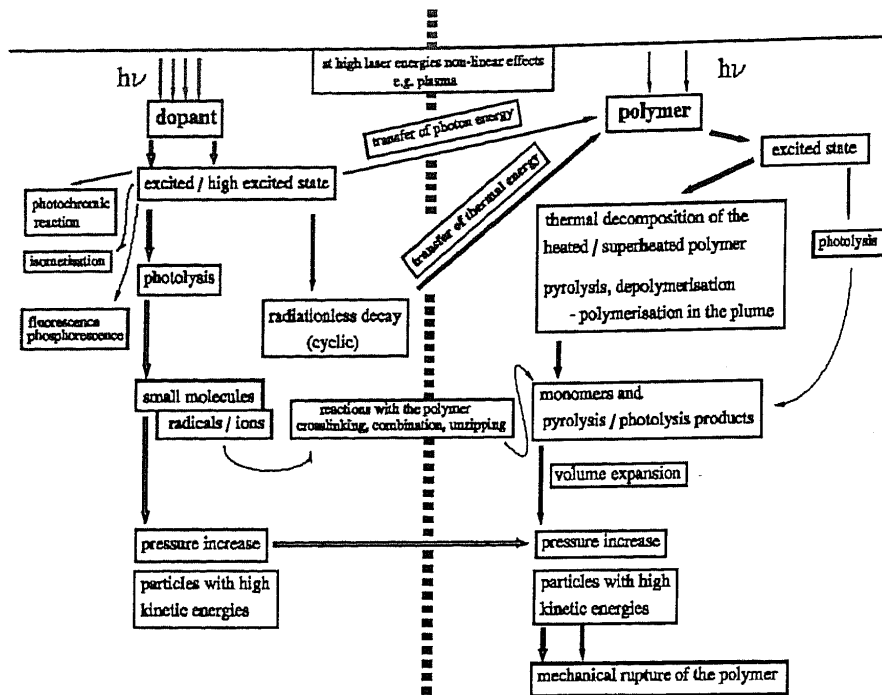
Referring to the complex pathway of reactions shown in Scheme 2, it does not appear to be easy to quantify the relative contributions of the two main routes. For each system, their relative weight also depends on the laser fluence employed.

From the various studies it can be derived that the thermal/photothermal part of dopant-induced ablation plays a key role during the ablation. However, depending on the photochemical properties of the dopant, photolysis may add an additional photochemical contribution, of greater or lesser importance. There is ample room for further studies aimed at obtaining further insight into the mechanism of dopant-induced ablation for the various systems, which are promising candidates for technological applications.

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