



Thermal reactive modifications of polymer surfaces by infrared laser radiation

J. Pola^{a,b}

^a New Technologies-Research Center, University of West Bohemia, Univerzitní 8, 306 14 Pilsen, Czech Republic

^b Institute of Chemical Process Fundamentals of the Czech Academy of Sciences, Rozvojová 135, 165 02 Prague 6, Czech Republic

ABSTRACT

This review offers an evaluation of research on the thermal reactive modification of polymer surfaces by infrared (IR) laser radiation with a major concern on highlighting and classifying ablative and non-ablative laser irradiations of polymer surfaces. The IR laser-induced reactive changes in polymer structure and composition are compared to those achieved by conventional heating of polymer bulks and films positioned on substrates and dissimilarities of both types of processes are argued to result from specific features of laser-supplied heat and laser-circumvented polymer-substrate interactions. Such complete evaluation is still missing in the literature and has been compiled to demonstrate that IR laser radiation is a potent tool for specific modifications of the chemical structure of polymer surfaces and that its further use is a challenge to achieve new goals in polymer research.

1. Introduction

Polymers find widespread use in various technological applications. Their surface modification by various thermal, mechanical, physical, chemical, and photolytic processes is broadly studied to develop products with specific morphologies, structural compositions, and physico-chemical properties needed in electronics or pharmaceuticals, bioengineering and microsensing industries. Some of these processes make use of laser-induced irradiation and have been explored with VUV, UV, visible and IR lasers. Depending on the amount of laser energy absorbed by polymer, they induce structural changes in the topmost polymer layer or remove this layer by ablation and thereby accomplish structural changes in residual polymer and a layer deposited by ablation onto chosen surfaces.

The technique of laser ablation of various materials has been reviewed (e.g. [1–6]) and studies on laser ablation of polymers have begun more than 40 years ago by utilizing IR pulses to induce multiphoton excitation over the vibrational manifold of ground electronic states to achieve thermal degradation of the irradiated spot [7] and by applying UV pulses for reaching multiphoton excitation to upper electronic states allowing different modes of ionization and decomposition [8,9].

Further research of *UV-induced processes* involved polymer excitation by very short (ns-fs) pulses of high energies, which induced instant local ejection of miniscule volumes of polymer surface and generated varieties of neutral fragments and/or charged species which were emitted in a transient plasma plume and collided onto a chosen substrate to deposit films that are compositionally identical or different to the virgin polymer surface. This research has become favored by many research groups

and is covered by many papers and several reviews and books (e.g. [10–20]). It has broadened knowledge on photothermal and photo-physical modes of UV ablation under different irradiation conditions and in different gaseous environments and also offered congruent deposition variants like matrix-assisted pulsed laser evaporation (MAPLE) [17,18] or molecular transfer through triazene photosensitizing structures [16], the designs for surpassing molecular fragmentation and enabling the stoichiometric transfer of complex molecular structures.

There has also been much activity on an exploration of *IR-induced processes*, but this broad research area has been only partly reviewed by offering a reader a narrow area of the resonant infrared (RIR) pulsed laser ablation of neat targets [21,22] or frozen targets composed of the desired macromolecule dispersed in a matrix selectively absorbing laser radiation [23,24]. The latter variant allows the feasible congruent transfer of degradable polymers and hybrid materials with functional groups from the condensed into the vapor phase and it is highly promising in RIR-MAPLE and emulsion-based RIR-MAPLE deposition of functional films important in electronic and photonic devices. It can also find use in the formation of antimicrobial and bacteria-releasing surfaces. True to a plethora of findings proving that IR laser irradiation causes polymer a certain degree of thermal damage, a lot of effort in polymer ablative depositions has been made to find conditions for effective “stoichiometry and structure transfer”. However, intentional laser-induced modification of polymer surface, through changes in structure and composition of either residual polymer surface or deposited film, has been given less attention.

Here we present the first review of the chemical modification of various polymers by IR laser irradiation and compare IR laser-induced polymer degradation routes with those triggered by conventional heat.

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It is relevant that IR laser-radiative interaction with solid polymers takes place under special conditions, as it occurs within a temperature jump and is controlled by kinetic rather than thermodynamic chemical changes.

In addition, it ensures no interference from a hot surface, which is not unavoidable in standard heated reactors, and gaseous products being transparent to laser radiation remain exposed to high temperatures only within the restricted area of the laser plume. These surface-less reactor conditions thus eliminate heterogeneously catalyzed routes that are feasible in conventional polymer degradations.

2. Polymer excitation by infrared laser radiation

Interaction of intense infrared laser radiation with polyatomic molecules inducing infrared multiphoton absorption (IRMPA) [25,26] and resulting in isotopically selective decomposition [27,28] has given much hope for a successful design of processes enabling to excite a specific vibrational mode of a molecule and induce decomposition or reaction on the excited bond in a channel which differs from thermally driven counterpart. However, the expectations of new synthetic routes for complex molecules have been shown quite unrealistic (e.g. [29–32]). Many examples of laser-induced specific features [33] as laser molecular selectivity, laser-controlled chemical equilibria, laser preference of high energy reaction channels in bifunctional reactants, sensitized organic reactions and reactions in solids and gas-solid interfaces (e.g. [34]) are considered as a result of kinetically controlled reaction channels [35] and not of mode-selective routes.

Polyatomic molecules undergo stepwise vibrational excitation from the ground vibrational state [28] or vibrational overtones [36] to reach the quasicontinuum of vibrational states (Fig. 1), but they cannot become excited solely through a particular vibrational degree of freedom [34,37] leading to energy accommodation in the corresponding nuclear motion.

Vibrational excitation of a particular mode (or a restricted set of modes) competes with intramolecular redistribution of the deposited vibrational and/or rotational energy to translational modes and the laser energy deposited in a specific vibrational mode is rapidly randomized without any use in a specific reaction channel when this V, R/T process is faster than the laser pumping rate. Such randomization of energy has been shown to take place on a picosecond time scale or faster (e.g. [38–40]).

As for the statistical Rice Ramsburger Kassel (RRK) and Rice Ramsburger Kassel Marcus (RRKM) theories of unimolecular decomposition, they preclude any possibility of selectivity because of the very rapid intramolecular vibrational relaxation (IVR) rate, although a restricted IVR model [41] supports the feasibility of selective pathways with extra short and intense pulses.

It is therefore obvious that TEA (Transversely Excited Atmospheric) CO₂ lasers, emitting on over 40 lines in the region of 9–11 μm with ~ μs pulse duration and FWHM of the initial spike around 50 ns can hardly

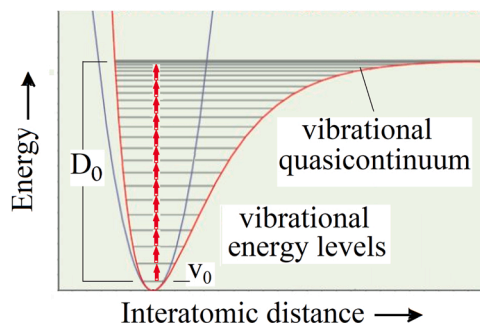


Fig. 1. Scheme of IR laser vibrational excitation in an anharmonic oscillator with dissociation energy D_0 .

stimulate a specific reaction at the laser-activated vibrational site of polyatomic molecules under collision-free conditions unless a vibrating site is insulated within heavy atoms which may retard intramolecular vibrational coupling. However, such an idea of possible promotion of a specific channel in the insulated site has not been examined and needs to be verified through studies of specially designed heterogenic compounds.

The above comment thus provides clear evidence that a selective chemical change on a specific site of polyatomic molecules excited by IRMPA under collision-free conditions is hardly possible and that the weakest bond is the first to break. This view is even more valid for solid macromolecular polymers, wherein vibrationally excited states randomize their energy not only by intramolecular vibrational coupling but also through polymer chains entanglement and interactions between functional groups.

A much better chance for the specific site reaction induced by IR lasers may have been offered by free-electron lasers (FEL) which are tunable within 2–10 μm and have their ~4–6 μs macro pulses comprised of picosecond pulses carrying the energy of tens of μJ. They have been assumed to deliver energy in a time scale comparable to or shorter than vibrational relaxation times [21]. It was surmised that the delivery of the high-intensity picosecond pulses might lead to kinetic enhancement of the chemical change on the excited site [21,22]. Processes that take place in the course of resonant IR laser ablation of polymers with the macro pulse of the free-electron laser are illustrated in Fig. 2, but a confirmation of the kinetic enhancement of chemical change of the excited site is difficult due to the complexity of polymer ablation process which involves a non-linear absorption, energy non-thermal or thermal enhancement of the miniscule volume in depth dependent on absorption coefficient and thermal diffusion coefficient. All these characteristics have an impact on the extent of plasma plume formation, kinetic energy transfer to ejected fragments and consequently on the extent of desorption, evaporation and congruent or noncongruent ablative deposition which can be further complicated by chemical changes in deposited fragments after their collisions with the surface.

3. Heterogeneous routes in thermal degradation of polymers

It is known that the thermal stability of polymer structure is considerably effected by functional groups, molecular weight, branch degree, cross-linking and crystallinity and that thermally induced polymer degradations in conventional reactors can consist of five

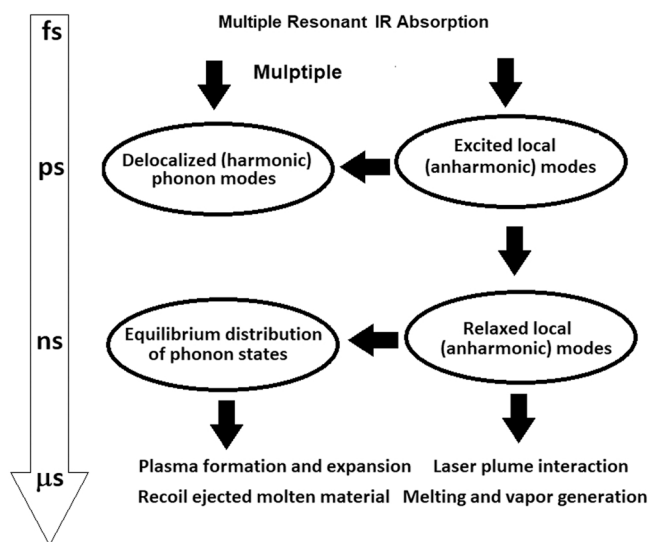


Fig. 2. The temporal sequence of processes that occur during resonant IR laser ablation of polymers using the macro pulse of the free-electron laser [22].

distinct routes [42–45]. These are (i) depolymerization (also called unzipping or end-chain scission) sequentially removing monomers from the chain end, (ii) random chain scission leading to fragmentation of chain to shorter chains, (iii) chain stripping (also called side-group elimination), (iv) radical and molecular recombination processes that lead to cross-linking or cyclization and (v) reactions or decomposition of functional side groups into volatile products. Some of these routes may occur concurrently and the depolymerization route is characteristic for polyaddition polymers (like polystyrene, poly(methyl methacrylate) or polyoxymethylene) but not for polycondensation polymers (e.g. polycarbonates, polyalkeneterephthalates, polyimides) which only decompose into different reactive species which combine to polymers of different structures.

These thermally-induced reactions in conventional reactors may, in principle, take place as homogeneous paths inside bulk polymer volumes and/or as heterogeneous paths on the surface of conventional vessels as a consequence of reactive interactions of pending polar functional groups with (i) polar surface of the glass, (ii) very thin incipient layer of metal oxide rapidly developing on metal in the atmosphere and (iii) any wall surface modified during polymer heating with O- and C-centered or halogen radicals produced from polymer pending groups.

It is however a bit odd that the heterogeneously assisted polymer degradations occurring under thermodynamic equilibrium conditions on the glassy or metal surfaces have not been yet considered, although heterogeneous roles of powdered metals and metal compounds in conventional thermal degradation of polymers have been shown to effect polymer decomposition temperature and to cause remarkable changes in the degradation mechanism and products not observed with neat polymers (Table 1, [46–57]).

Inorganic nanoparticles admixed in polyaddition polymers enhance thermal stability and alter the degradation mechanism of these polymers [58]. Similar effects have also been observed for thermal decomposition of polycondensation polymers containing several inorganic particles including silica [59] and with a copolymer containing gas and water atomized stainless steel powders [60].

4. Infrared laser-induced irradiation of polymers

Using IR laser beam or pulses, a miniscule volume of polymer accommodated in a cold reactor procured with windows transparent to laser radiation is heated to reach very high temperatures within a very short time and undergoes ablation and disintegration ensued by recombination of hot fragments on a cold substrate surface (Fig. 3). This specific thermal process occurring within a temperature jump differs from the slow heat supply in conventional polymer degradation and is therefore controlled by kinetic rather than thermodynamic channels of products formation. Among various IR laser irradiation treatments, such ablation-deposition process has been of prime interest due to specific structural and compositional changes in the deposited thin films, while intentional laser-pyrolyses of polymer surfaces and elucidations of properties of the residual polymer surfaces have attracted less attention.

4.1. Possible effect of heterogeneous reactions

Properties of both products (i.e. of deposited film and residue) may be theoretically effected by two types of heat-induced heterogeneous reactions, one occurring between a thin layer of pristine polymer and a holder and another occurring between hot depositing species and a cold substrate. The former heterogeneous effect can be easily eliminated with enough large polymer lumps or thick films provided that the possible reactive inter-zone between polymer and holder is avoided by a proper choice of balance between irradiation parameters and infrared absorption of polymer.

Whether or not ablated species will reactively interact with a cold substrate remains an open question and will depend on the energy of

Table 1
Thermal degradation of polymers effected by inorganic additives.

Solid additive	Polymer	Heterogeneous effect	Ref.
Metal oxides	Poly(vinylchloride) (PVC)	Cl radicals react with metal oxide to form metal chloride and oxygen radical and then O radicals abstract H from PVC. The formation of metal chloride is the rate-controlling step.	[46]
		Fe ₂ O ₃ , MgO and CuO reduce the release of volatile hydrocarbons, while CaO, ZnO and Al ₂ O ₃ increase the release of volatile hydrocarbons. Some oxides increase the amount of residual hydrocarbon.	[47]
		Metal oxides including rare earth oxides suppress the formation of benzene.	[48]
		Acidic metal oxides accelerate the recombination of Cl atoms with double bonds and enhance the formation of lower aliphatics, toluene, ethylbenzene, o-xylene and chlorobenzenes.	[49]
		Basic metal oxides inhibit Cl – double bond recombination. The formation of unsubstituted aromatics is more suppressed than that of alkyl-aromatics and this is ascribed to the formation of metal chlorides.	[50]
		Some metal oxides retard thermo-oxidative degradation of PC.	[51]
		Degradation of PVAC is mildly affected by metal oxides and degradation of PVC is greatly influenced by metal oxides	[52]
		Polyolefinic chain scission in polymer blend is mildly effected by metal oxides.	[53]
		Transition metal oxides do not affect degradation mechanisms and bismuth oxide strongly promotes dehydrochlorination.	[54]
		Al, Zn, Fe Fe ₂ O ₃ and TiO ₂ decrease the onset dehydrochlorination temperature and HCl formation decreases with Fe, Zn, Ca/Zn carboxylate, CuO and TiO ₂ as they form chlorides with HCl. The promotion of benzene evolution occurs on Al ₂ O ₃ and TiO ₂ .	[55]
Metal oxides and chlorides	Poly(vinyl chloride) -Poly (bisphenol A carbonate) blend	Increased polymer degradation with various metal oxides (ZnO, Fe ₂ O ₃ , Co ₃ O ₄ , TiO ₂) and metal chlorides (AlCl ₃ , ZnCl ₂ , FeCl ₃ , CoCl ₂) in the presence of metal oxides is due to the formation of metal chlorides.	[56]
		Cu and Fe chlorides depress radical transfer reactions in polypropylene and	[56]
	Polypropylene Polystyrene Phenol-formaldehyde		

(continued on next page)

Table 1 (continued)

Solid additive	Polymer	Heterogeneous effect	Ref.
	resin Polycarbonate Epoxy resin	polystyrene, enhance the production of aromatic and polyaromatic compounds from polyethylene, split the Me ester group in poly (methylmethacrylate) and enhance phenol evolution from phenol-formaldehyde resin, polycarbonate and epoxy resin.	
Alumina	Perfluoropolyether, Fomblin Z, Fomblin Y, Krytox	Oxide-to-halide conversion occurring on Al_2O_3 is ensued by a catalytic process induced by Lewis acid AlF_3 .	[57]
Silica	Polyethylene Poly(vinyl alcohol) Polystyrene Poly (methylmethacrylate)	In SiO_2 /polymer composites decomposition rates and thermal stabilities are slightly increased, and the decomposition mechanism is altered by the interaction of SiO_2 with polymer.	[58]
	Poly(ethylene 2,6-naphthalate) Poly(ϵ -caprolactone) Poly(L-lactide) Poly(alkylene succinate)s Polyimide Polyurethanes	Composites show increased thermal decomposition temperature and higher residual yields, but their thermal stability is slightly higher or lower.	[59]
Steel powders	Poly(ethylene-co-vinyl acetate)	Activation energies for copolymer decomposition decrease in the presence of steel powders due to the possible role of a carboxylate anion-Fe transition state complex.	[60]

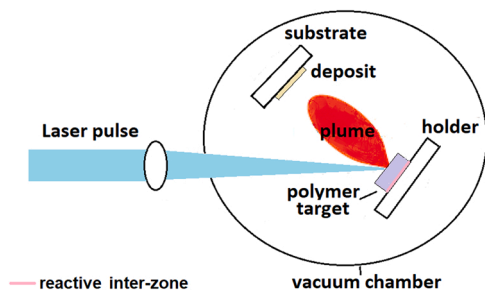


Fig. 3. Scheme of laser-induced ablative deposition.

these species and substrates properties. There are only few examples of such reactions observed in laser deposition of inorganic nanoparticles [61,62] and heterogeneous routes of polymer thermal decomposition, proven only at high temperatures (Section 3), do not allow to discern the importance of heterogeneous reactions of depositing fragments, although heterogeneously catalyzed reactions of organic radicals (e.g. [63–65]) are highly probable.

A completely homogeneous thermal energy-induced degradation/deposition of solid macromolecular organic materials is, in principle, more difficult than the IR laser-induced decomposition of gaseous organic compounds, since collisional multiple-photon excitation of volatile sensitizers or absorbing molecules to high vibrational levels of the ground state occurs far from reactor walls and induces truly homogeneous and specific decomposition pathways illustrated for various classes of organic compounds (e.g. [66–69]).

All these facts thus emphasize that conventional polymer degradation possibly involving catalytically-assisted thermal routes would differ from IR laser ablation-deposition of polymers involving specific initial

bond cleavages and transient steps enabling uncommon polymer modification.

4.2. Infrared laser-induced ablation and deposition

The unique feasibility of achieving localized degradation of several polymers in a segment or prearranged section of a polymer has been demonstrated with continuous wave, TEA CO_2 , and FE laser irradiations, showing that proper energy input within long irradiation exposures leads to de-polymerization, fragmentation, volatilization, ensuing structural and compositional modification of the residual crater and deposition of fragments to a nearby cold surface. The laser radiative energy input cumulated in a minuscule polymer volume leads to lower ablation energies and more efficient polymer degradation relative to energies supplied by conventional heat, and the efficiency of the laser degradation process depends on the absorbance of the polymer at the laser emitted wavelength, thermal diffusivity of polymer, chosen energy flux density and exposure time of incident radiation and finally also on polymer structure.

4.2.1. CW CO_2 laser ablation and deposition

By their behavior in cw laser beam, polymers can be divided into three groups. The first involves polymers (e.g. polyacrylonitriles, polyesters, polyamides) which melt and splatter. The second covers thermosetting aromatic polymers which undergo charring (e.g. polybenzimidazole, polycyanurates, polyphenylenes) and certain thermoplastics which are capable of cross-linking when heated (polyphenylene oxide, polyphenylquinoxaline, polyacrylate). The third encompasses polyaddition polymers ablating without leaving any residue [70]. The way of degradation and the nature of residual and volatile products depends on irradiative energy density which can control the relative extent of selective cleavage of weak bonds and random cleavage of all bonds.

Initial studies of laser irradiation of polymers have been conducted with cw CO_2 lasers in the air or under a nitrogen atmosphere which prevented the ignition of evolving vapors. These studies revealed that the irradiation of some polymers yields products which are identical to those produced by slow isothermal heating of bulk polymer samples. Thus, some polymers undergo efficient thermal degradation to monomers through selective cleavage of their weaker bonds, which is particularly true for poly(chlorotrifluoroethylene), polyoxymethylene, poly(methyl methacrylate) and poly(methyl methacrylate). Optimum laser energy utilization efficiency values of these polymers are in the range of 45–86% [71]. It was anticipated that these and other polyaddition polymers synthesized from 1,1-disubstituted olefins can undergo a residue-free degradation process to monomeric species and may become a class of polymers applicable for the production of functional and decorative plastic devices and objects.

The energy of ablation (given in parentheses) for several linear or crosslinked and aromatic or nonaromatic polymers was measured to assess polymer capability to form cross-linked network structures and thermal stability. The latter increases as follows: polystyrene, polyalkylstyrenes, polytetrafluoroethylene, polyalkylmethacrylates, polybutadiene (3–4 kJ/g), epoxy(bispheno1-A-polyamide) (4.3 kJ/g), polycarbonate and polyimide (13.3 kJ/g), poly(phthalocyanine-C-10 (37 kJ/g) and cyanurate network polymers with different extent of crosslinking (13–18 kJ/g). It appeared [72,73] that a different extent of crosslinking can be induced by different laser ablation energies applied to cyanurate polymers and that the energy utilization efficiency is primarily affected by the absorbance of the polymer at the selected emission wavenumber.

The same irradiation in a vacuum of polytetrafluoroethylene, polytrifluoroethylene, polysulphone, polycarbonate and polyimide at low irradiation energies leads to initial carbonization of crater surface, while no carbonization is observed at higher laser energies when thin films chemically similar to pristine polymers are deposited [74]. Ablation of

amorphous poly(ethylene terephthalate) or poly(etherether ketone) by the passage of the radiation through a high-resolution mask in contact with the polymer surface can produce images having submicron resolution and good edge acuity, but the ablation of two thermosetting poly(cyanurate) polymers required higher irradiation energies and was accompanied by some degree of cross-linking and charring [75].

The feasibility of laser ablation of several polymers has been also examined after their pre-treatment by γ -irradiation to show that the rate of the ablation can be accelerated with polyethylene and ethylene-propylene copolymer [76], polyamide [77], polytetrafluoroethylene [78] and polyketone [79], but reduced with poly(vinyl alcohol) [80] and be dose-dependent with polyvinylidene fluoride [81].

4.2.1.1. Polytetrafluoroethylene. The efficiency of the decomposition (ED) of polytetrafluoroethylene by little absorbing $10.6\ \mu\text{m}$ irradiation increases with higher irradiation energy (IE) and the shape of ED-IE dependence reflects two different slopes suggesting two different decomposition stages, one induced from less vibrationally excited states and another from vibrational quasicontinuum [82]. This degradation yields tetrafluoroethylene (a major gaseous product) together with a solid coat of mixed highly stable micro sized fibers and a less stable amorphous phase, the components which differ by the resistance to the laser beam action as they appear in the ablation crater [82–85]. The process was proposed as an approach to unique fiber-porous polytetrafluoroethylene materials and for polytetrafluoroethylene wastes recycling [82], but it can also result in the deposition of smooth films provided that the substrate is heated at $100\ ^\circ\text{C}$ [86].

A more detailed insight into the chemical mechanism of polytetrafluoroethylene decomposition has been provided in [87] showing that relative amounts of minor gaseous products (tetrafluoroethylene, hexafluoropropylene and octafluorocyclobutane) are not affected by irradiation time, but depend on the density of the incident energy. The yield of deposited PTFE powder ranges from 3% to 15% of all products and that of tetrafluoroethylene increases at the expense of octafluorocyclobutane upon the addition of nitrogen, sulfur hexafluoride or 2-butene. The total amount of gaseous products increases in the presence of SF_6 and decreases in the presence of nitrogen and 2-butene. The latter do not absorb CO_2 laser radiation and cannot directly increase their energy. Sulfur hexafluoride is, however, an excellent absorber of radiation and can be heated [66] within the region of the laser beam to temperatures higher than $1000\ ^\circ\text{C}$. Faster degradation of PTFE in the presence of SF_6 can thus be attributed to a hot gas-phase zone near the polymer surface. Lower amounts of octafluorocyclobutane produced in the presence of all three gases are in line with a decreased ability of energized C_2F_4 molecules propelled from the polymer to cycloadd to $\text{c-C}_4\text{F}_8$ due to dilution by these gases. Tetrafluoroethylene, hexafluoropropylene and solid particles are the primary products of cleavage of PTFE polymer and they do not arise in the gas phase later. The cleavage of PTFE into difluorocarbene does not seem probable; this species is known [88,89] to react with olefins like 2-butene to form three-membered rings, but no products of this reaction were detected. Hexafluoropropylene is apparently formed from $\cdot\text{CF}_2\text{CF}_2\text{CF}_2\cdot$ biradical by 1,2-rearrangement of fluorine. The deposit produced with the energy density of $5\text{--}480\ \text{W}\cdot\text{cm}^{-2}$ consists of non-porous spherical $0.1\text{--}0.5\ \mu\text{m}$ particles having BET specific surface of $8\text{--}12\ \text{m}^2/\text{g}$, which are weakly bonded into movable aggregates. The deposit obtained by using the energy density $610\text{--}1500\ \text{W}\cdot\text{cm}^{-2}$ is formed by compact fibers covered with tiny ($\leq 0.1\ \mu\text{m}$) particles (Fig. 4).

4.2.1.2. Fluoro-polymers. The laser irradiation of poly(perfluoroethene-propene) (FEP) and poly(vinylidene difluoride) (PVDF) follows very different courses [90]. The former process results in the formation of gaseous C_2F_4 dominating over C_3F_6 , C_4F_8 , and ca. 30% of a white and stable aerosol depositing onto nearby glass or Al surface as network structures.

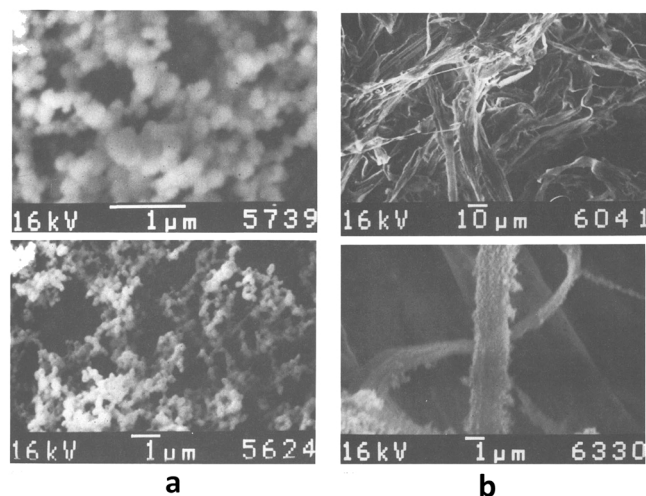


Fig. 4. PTFE deposit obtained with energy density $5\text{--}480\ \text{W}\cdot\text{cm}^{-2}$ (a) and $610\text{--}1500\ \text{W}\cdot\text{cm}^{-2}$. (b) (b) Reproduced from ref. [87], Copyright Elsevier.

The latter process results in a visible glow of the irradiated spot, polymer sintering and a growth of a black area along with the concomitant formation of gaseous compounds ($\text{C}_2\text{H}_2\text{F}_2$, $\text{C}_3\text{F}_3\text{H}_3$, $\text{C}_3\text{F}_5\text{H}$, $\text{C}_2\text{H}_3\text{F}$ and SiF_4), the growth of Na_2SiF_6 on entrance NaCl window and the formation of a white aerosol depositing near the irradiated area. The implied formation of HF and observed gaseous products are in line with the cleavage of the C-C bond, polymer dehydrofluorination and H/F scrambling (cleavage of the C-H and C-F bonds).

The white deposit on the glass is a rather compact layer containing some agglomerates whose size ranged from less than $1\ \mu\text{m}$ up to $4\ \mu\text{m}$. The white coatings on Al turn grey and sometimes even black on prolonged exposure to air and they adopt the structure of turbostratic glassy carbon [91] involving disordered ca. $2\ \text{nm}$ -sized graphitic carbon. These findings were rationalized by assuming that the polymer layers in contact with metal supports undergo catalyzed dehydrofluorination leading to etching of the metals and further decomposition of the polymer (Fig. 5).

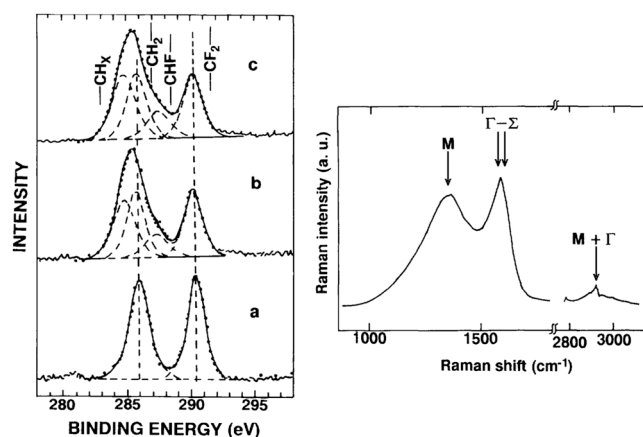


Fig. 5. The curve fitted C(1s) core-level spectra of (a) the non-irradiated PVDF, (b) the PVDF deposit stored in the He atmosphere and (c) the deposit after additional exposure to air; Raman spectrum of the black layer exposed to air, with two bands of highly disordered carbon with marked positions of in-plane E_{2g} vibration (Γ point) of oriented graphite, the Σ line in the Brillouin zone of graphite, disorder-induced phase due to the zone-edge phonons at the M point and a broad continuum due to second-order Raman scattering by phonon $M + \Gamma$ combinations. (b) Reproduced from ref. [90], Copyright Elsevier.

4.2.1.3. Organosilicon polymers. The laser irradiation of poly(1,1,2,2-tetramethyl-1,2-disilabutane) (I), poly(*i*-phenyl-1,2,2-trimethyl-1,2-disilabutane) (II), poly(1,1,2,2-tetramethyl-1,2-disilapropane) (III), poly(dimethylsilane) (IV), and the copolymers poly(1,1,2,2-tetramethyl-1,2-disilabutane-co-dimethylsilane) (V), poly(1,1,2,2-tetramethyl-1,2-disilabutane-co-methylsilane) (VI), poly(1,1,2,2-tetramethyl-1,2-disilabutane-co-methylphenylsilane) (VII) and poly(1,1,2,2-tetramethyl-1,2-disilabutane-co-adamantylmethylsilane) (VIII) results in the formation of very minor gaseous products (organosilanes, disilanes and trisilanes) and solid particles that are propelled from the irradiated surface as a visible aerosol [92]. All these polymers are composed of $-\text{Me}_2\text{Si}-$, $-\text{Me}_2\text{SiMe}_2\text{SiCH}_2-$, $\text{RMeSi}-$ and $\text{RMeSiMe}_2\text{SiCH}_2\text{CH}_2-$ ($\text{R} = \text{methyl, adamantyl, phenyl and hydrogen}$) units and their chemical changes, occurring prior to their ejection to the gas phase, consist essentially of the formation of high molecular biradicals or 1,1-disilacyclobutane monomer which re-polymerize spontaneously upon their deposition onto nearby cold surface. All these polymers are “evaporated” nearly completely except for polymer II, which retains more than 5–10% by weight of carbonized material.

The temperature of these processes can be estimated as being higher than 600 °C, the value at which thermogravimetric analysis of poly(silastylene) and poly(dimethylsilane) reveals that portions of these polymers are driven off as volatile organosilicon compounds [93]. One of the major routes of all the mechanisms discussed in [92] is illustrated in Scheme 1.

These laser solid-gas-solid transfers of polymers allow deposition of thin films having continuous structures as observed with polymers I, IV–VI and VIII (Fig. 6a, d–f and h) and smooth surface of thicker films (with outstanding nodules) as observed with polymers II, III and VII (Fig. 6b, c and g). Such films appear unique and promising in the preparation of thin polymer surfaces that can be used as precursors for β -SiC fibers, impregnating agents for strengthening ceramics and dopable semiconductors.

4.2.2. Pulsed CO₂ laser ablation and deposition

The pulsed laser-induced multiphoton resonant absorption of energy-poor infrared photons in a suitable vibrational mode of polymer can induce high heating rates ($\sim 10^{6-11} \text{ K.s}^{-1}$) and high cooling rates ($\sim 10^{3-6} \text{ K.s}^{-1}$), provide rather kinetic than thermodynamic control of polymer degradation and lead to ablative deposition of materials which cannot be produced by slow conventional heating.

The pulsed CO₂ laser irradiation has been explored with a greater number of polymers and few studies of laser ablations involved analyses of the emission plumes. The emission spectra of the plumes of laser-ablated polyimide (PI), polyethylene terephthalate (PET), and polymethylmethacrylate (PMA) show transition lines of C₂ bands and ionic carbon for all the polymers, oxygen transition lines only for PET and PMA, and CN bands and the ionic N lines only for PI [94]. Furthermore, the gross dynamics of the luminous plume, studied by a streak camera, compares favorably with snowplow model predictions of the time history of the plume expansion for a range of background gas pressures and

laser fluences. Plume expansions induced by pulsed CO₂ laser ablations of poly(methyl methacrylate) (PMMA) and (PI) [95] were imaged by shadowgraphy in He, Ar and also in air wherein plume dynamics may be effected by reactions with O₂, N₂ and air moisture. A shock front detached from the first plume and a later mushroom-shaped plume were observed with PMMA, whereas only a single blob collapsed back to the target was detected with PI (Fig. 7).

4.2.3. Poly(vinyl acetate)

The IR laser-induced modifications of poly(vinyl acetate) (PVAC) carried out as ablative and non-ablative thermal processing of bulk PVAC [96,97] remarkably differ from conventional heating of PVAC, which is dominated (e.g. [98,99]) by elimination of acetic acid and formation of a carbonaceous residue possessing conjugated C=C bonds along with cyclic and aromatic units. The non-ablative treatment at low-fluence irradiations yields volatile vinyl acetate and acetone and leaves the remaining irradiated polymer having an almost identical structure. The ablative treatment at high-fluence irradiations yields a multitude of volatile compounds (methane, ethane, vinyl acetate, acetone, acetic acid, benzene, H₂, CO and CO₂) and affords the deposition of thin polymeric films that contain reactive conjugated C=C bonds and half of the initially present acetate groups (Fig. 8). Residual reactivity of the C=C bonds in deposited films leads to polymer crosslinking displayed by UV spectra (Fig. 8), a substantial decrease in solubility and some increase in thermal stability.

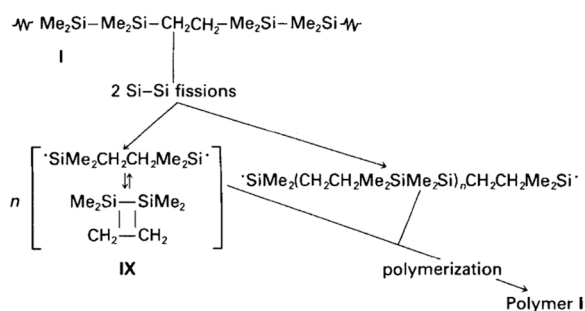
The mechanism of these chemical changes, supported by the identified volatile and solid products, involves three major routes which are the cleavage at near C-C bonds, cleavage at distant C-C bonds and cleavage of/in acetate group and C-H bonds (Scheme 2). Molecular elimination of acetic acid from gaseous alkyl acetates requires ca. 80 kJ mol⁻¹ less energy than the C-C bond homolysis and the preference of vinyl acetate elimination over feasible molecular elimination of acetic acid is related to conformational hindrance against the formation of a 6-membered transition state in the solid state.

4.2.4. Poly(vinyl acetate) loaded with metal particles

The IR laser-induced decomposition of PVAC loaded with nanometer-sized Cu and micrometer-sized Fe particles, discussed below, offers recognition of the role of the heterogeneous effect of metal particles in the ablation-deposition process of PVAC [100]. For both irradiated PVAC/Fe and PVAC/Cu composites, the relative concentrations of gaseous vinyl acetate are remarkably reduced (Fig. 9) and, similarly to conventional thermal degradation [98,99], the main volatile products are hydrocarbons, carbon oxides (CO and CO₂), molecular hydrogen and acetic acid. This dramatic change, with regard to the single polymer, is clearly related to catalytic reactions, but the identification of catalytic steps is difficult due to temperature gradients in plume where both paths a and b in Scheme 2 can be specifically effected by enhanced decomposition of transient vinyl acetate or by cleavage of polymeric fragments traveling through the gas phase.

However, remarkably, the thin films deposited from both PVAC composites exhibit the concentrations of reactive conjugated C=C bonds and acetate groups, which are identical to those of the films deposited from a single PVAC. The metal-containing films also possess residual reactivity and after crosslinking they decrease their solubility. They are, however, less thermally stable than the PVAC films not containing metal particles. The reported process reveals feasible ablation of metal particles when embedded in polymer and makes possible to fabricate films of metal/polymer composites in which metal particles are completely protected by the polymer. The reported laser-induced ablative deposition of thin metal/polymer films may be also of interest in studies of thermally conductive polymer composites [101].

4.2.4.1. Poly(vinyl chloride). A completely different mode of thermal degradation of vinyl polymers has been also achieved with IR laser-



Scheme 1. Major routes occurring in the laser irradiation of polymer I. Reproduced from ref. [92], Copyright Wiley.

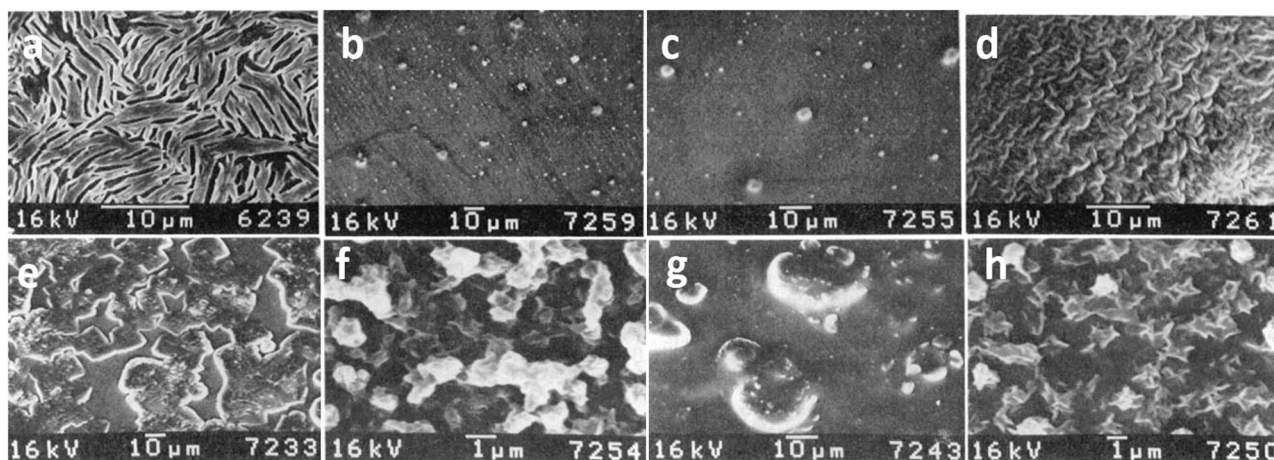


Fig. 6. Morphology of organosilicon films deposited from polymers I-VIII (a-h, respectively). Reproduced from ref. [92], Copyright Wiley.

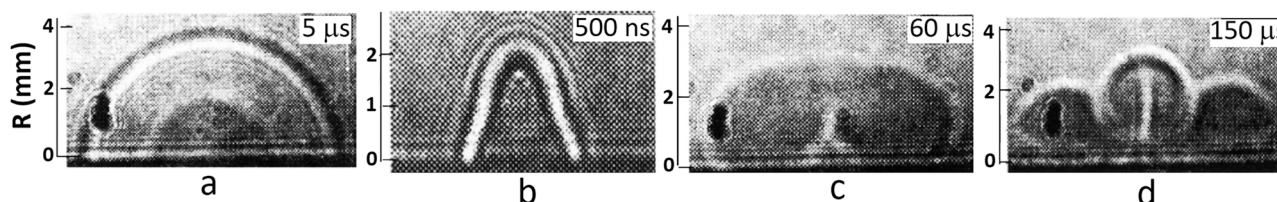


Fig. 7. Shadowgraphy images of plume for PI ablation in Ar: hemispherical plume and a shock front (a), elongated plume structure due to laser absorption (b), plume collapse (c) and re-emission of a plume and the appearance of ejection. (d) Reproduced from ref. [95], Copyright Elsevier.

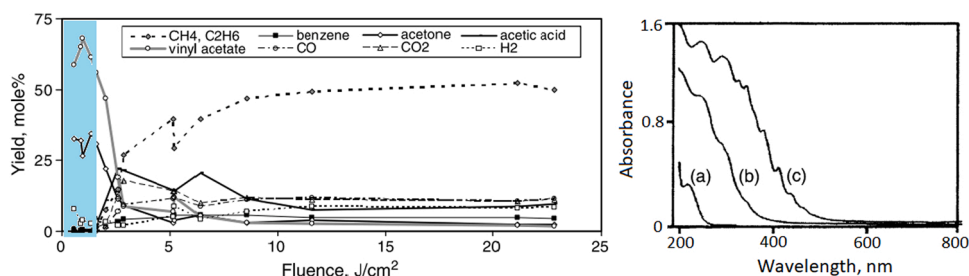


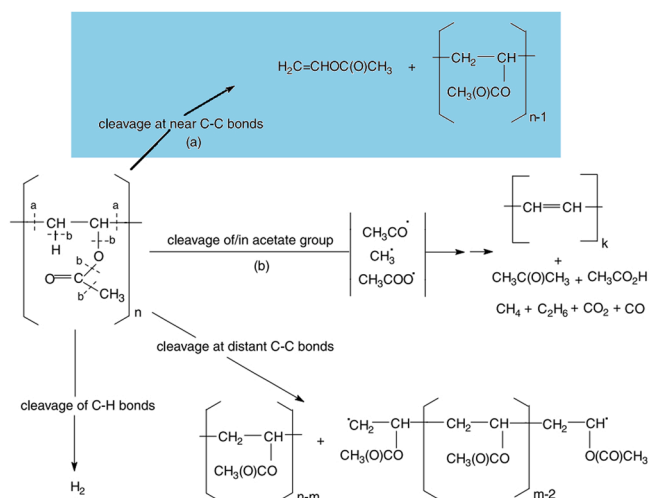
Fig. 8. Distribution of volatile products as dependent on laser fluence with non-ablative irradiation (blue region) and ablative film deposition, and UV spectra of the initial PVAC (a), of the instantly measured deposited films (b) and of the deposited films measured after prolonged staying. (c) Adapted from ref. [97], Copyright Elsevier.

irradiation-induced ablation of immensely useful poly(vinyl chloride) (PVC) [102]. The slow heating of PVC leading to conventional thermal degradation is likely initiated by structural defects, involves polar and radical routes and consists of two equally important decomposition stages which are the initial elimination of HCl (yielding conjugated polyene units) and subsequent formation of aromatic structures and carbonaceous residues (e.g. [103–105]).

The laser-induced process yields vinyl chloride as a major gaseous product, HCl, C₁₋₄ hydrocarbons, benzene, H₂ and toluene, and allows deposition of polymeric films that contain conjugated C=C bonds and less Cl with regard to the initial PVC. The irradiations at higher fluences result in larger portions of solid deposits (and lower amounts of volatile products) and also increase the fraction of vinyl chloride among the volatile products. The formation of vinyl chloride (unobserved with conventional pyrolysis) indicates homolytic cleavage of the monomer from the PVC backbone (Scheme 3) and resembles the mechanism of the laser ablation of PVAC (Scheme 2).

The deposited polymeric films do not contain aromatic fragments and become intractable upon prolonged storage, which is explained by polymerization at the conjugated C=C bonds leading to crosslinking. The films fabricated at medium fluences contain nanosized fibers and necklaces (Fig. 10) whose Cl content becomes lower at higher fluences and their polyene chain length ($n = 13$), assessed from Raman spectra, provides evidence of relatively long conjugated polyene moieties. These features may improve the mechanical properties of the deposited films and the ablative deposition of PVC can be considered a suitable technique for the fabrication of intractable crosslinked polyhydrocarbon films possessing nanofibers with different content of C-Cl bonds.

4.2.4.2. *Poly(vinyl chloride-co-vinyl acetate)*. IR laser-induced ablative decomposition of poly(vinyl chloride-co-vinyl acetate) (PVCAC), compared with that of PVAC and PVC [106], has been shown as a more efficient ablation process leading to gaseous products (H₂, carbon oxides, methane, C₁₋₄ hydrocarbons, vinyl chloride, ethyne, benzene and



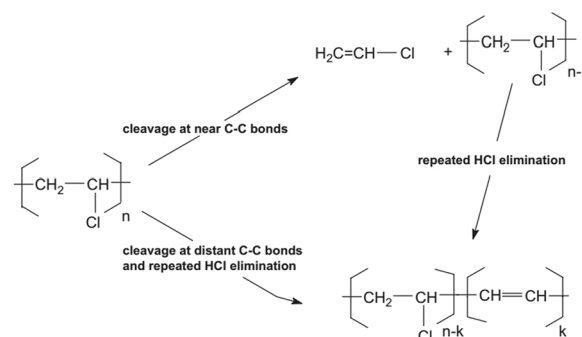
Scheme 2. Mechanism of laser-induced PVAC decomposition. Adapted from ref. [97], Copyright Elsevier.

acetic acid) and solid films with different proportions of Cl- and CH₃C(O)O-groups. These products were explained by cleavage of both pendent groups and copolymer chain (homolysis at the near and distant C-C bonds). The far major volatile product is hydrogen chloride whose amounts are ca. 6–50 times higher than those of vinyl chloride; vinyl chloride is formed in lower quantities than from PVC and vinyl acetate is not formed at all.

While the depletion of PVAC shows a threshold at 2.5 J cm⁻² and increases very little at higher fluence, the depletions of PVCAC and PVC have a substantial threshold at 7 J cm⁻² and are more significant than

that of PVAC. The total yields of gaseous products are the highest with the copolymer, while the relative yields of the volatile and solid products (not shown) are a little dependent on the irradiation conditions at low fluence (up to ca. 7 J cm⁻²) and increase at higher fluence only with PVC. These findings are given in Fig. 11.

Solid products of the copolymer are not homogeneous and contain microfibers that are much poorer in O and Cl than the rest of the deposit and resemble carbonaceous material. The relative loss of O and Cl from the deposited solid depends on the fluence in the opposite ways: with increasing fluence the depletion of chlorine decreases and that of oxygen increases. The more efficient removal of Cl at higher fluence and the less efficient removal of the acetoxy-groups at lower fluence indicate that the removal of Cl is an easier path, which is best explained in terms of a more significant (radical chain) acceleration of the removal reaction by the proximal C=C bonds in a longer -[CH₂-CH(Cl)]_x- segment. The laser-



Scheme 3. Mechanism of IR laser-induced degradation of PVC. Reproduced from ref. [102], Copyright Elsevier.

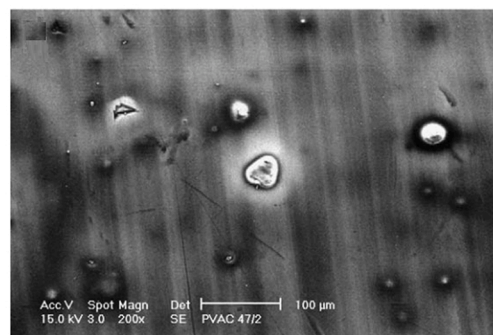
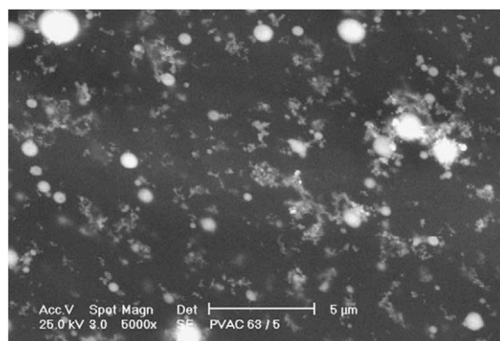
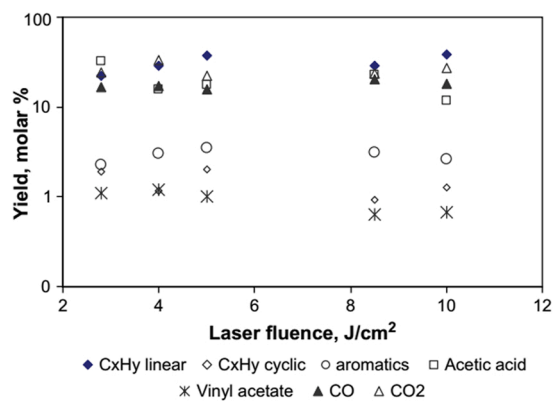
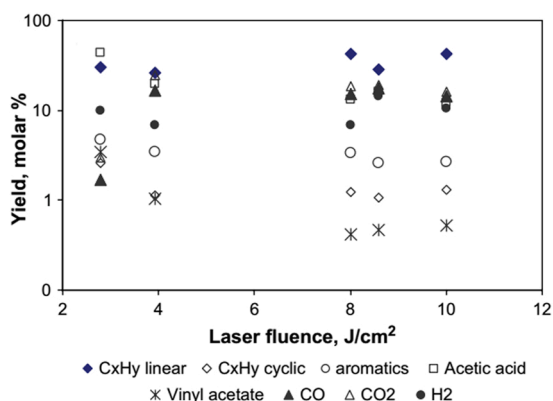


Fig. 9. Distribution of volatile products as dependent on laser flux along with SEM images of deposited films in the IR laser decomposition of PVAC/Fe (a) and PVAC/Cu (b) composites. Reproduced from ref. [100], Copyright Elsevier.

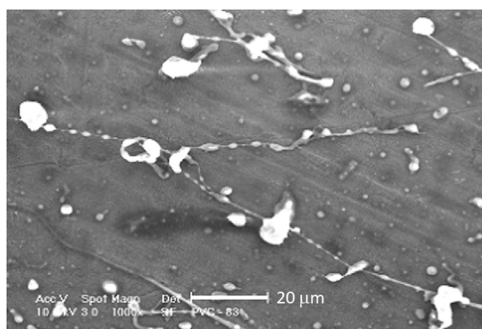


Fig. 10. The SEM image of the film deposited at medium laser fluences. Reproduced from ref. [102], Copyright Elsevier.

induced ablation-deposition PVCAC process is therefore competent to produce solid polar films with the controlled ratio of C-Cl and $\text{CH}_3\text{C}(\text{O})\text{O-C}$ bonds.

The conventional thermal decomposition of PVCAC is also known [107–111] to involve the cleavage of both pendant groups and the formation of acetic acid and HCl as major volatile products. However, further known facts are that (i) the side-group elimination is enhanced at similar content of acetoxy- and Cl-groups, which was assigned [107, 108] to inter-unit facilitation of the initial acid loss, and that (ii) the proportion of acetic acid and hydrogen chloride corresponds to that in the copolymer [110] and remains constant during degradation [108].

The thermal behavior of pristine PVCAC and the laser-deposited polymeric product [112], having about half pendant groups, conjugated $\text{C}=\text{C}$ bonds and partly crosslinked moieties, show different features; their TGA-monitored degradations are three-stage processes, but

the degradation of pristine PVCAC is most significant at 270 °C, while that of the laser-deposited polymer is of similar importance at 180, 310 and 440 °C. Elimination of both pendant groups is more feasible with the laser-deposited product and is ascribed to accelerating effect of neighboring $\text{C}=\text{C}$ bonds.

4.2.4.3. Poly(ethylene-alt-maleic anhydride). The laser ablation of poly(ethylene-alt-maleic anhydride) (PEMA) offers a unique example of the deposition of structurally identical polymeric films having the same functional groups [113]. It results in the formation of gaseous products (CO , CO_2 and a variety of hydrocarbons) and the deposition of thin white films (Fig. 12a) which have their composition equal to that of pristine polymer and possess a wider (M_w 500 000–5000) molecular weight distribution indicative of polymer fragmentation during the ablative process. This laser decomposition differs from conventional thermolysis of PEMA is controlled by the expulsion of CO_2 and CO , yields a nonpolar polymer residue rich in $-\text{CH}_2-$ groups and is likely assisted by the heterogeneous effect of hot surface promoting decarbonylation/decarboxylation of the anhydride groups [114–116]. In the laser-induced process, four major volatile gases (CO , CO_2 , C_2H_2 and C_2H_4) are produced from minor cleavages of the anhydride group and macromolecular diradicals (I, Scheme 4) travel from the irradiated spot to nearby surface where they deposit and spontaneously recombine.

The IR laser ablation of PEMA in sodium metasilicate results in the deposition of polymeric films (Fig. 12b) containing carboxylate ($-\text{CO}_2$) groups. This process is rather slow and can be accomplished only at higher energy densities, which indicates a “cooling effect” of Na_2SiO_3 that directly absorbs IR radiation [117] and enables laser energy to randomize in thermally stable metasilicate structure. The formation of the carboxylate group is in keeping with a specific cleavage of the

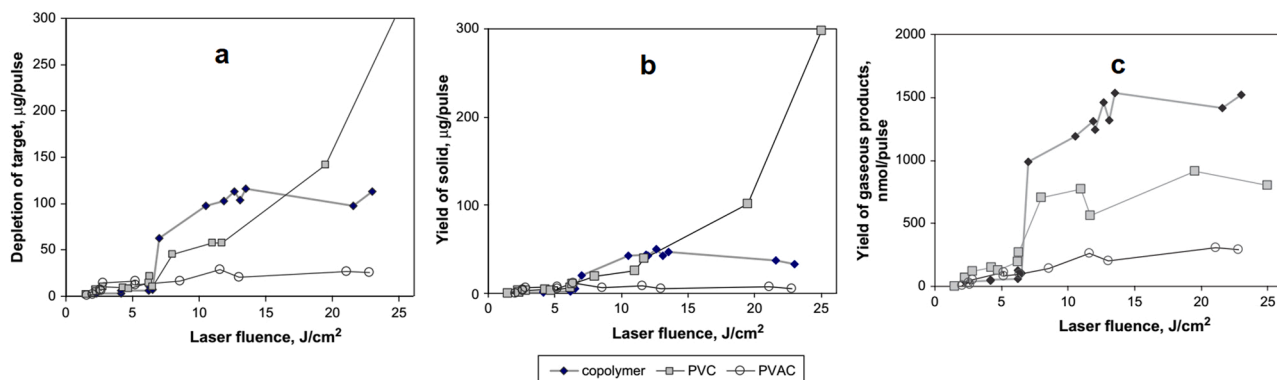


Fig. 11. Depletion (a), the yield of solid material (b), and total yield of gaseous products (c) of PVCAC, PVC and PVAC as dependent on laser flux. Reproduced from ref. [106], Copyright Elsevier.

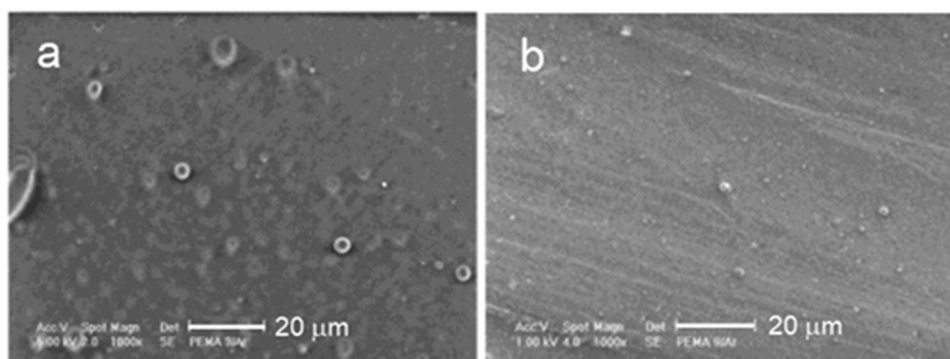
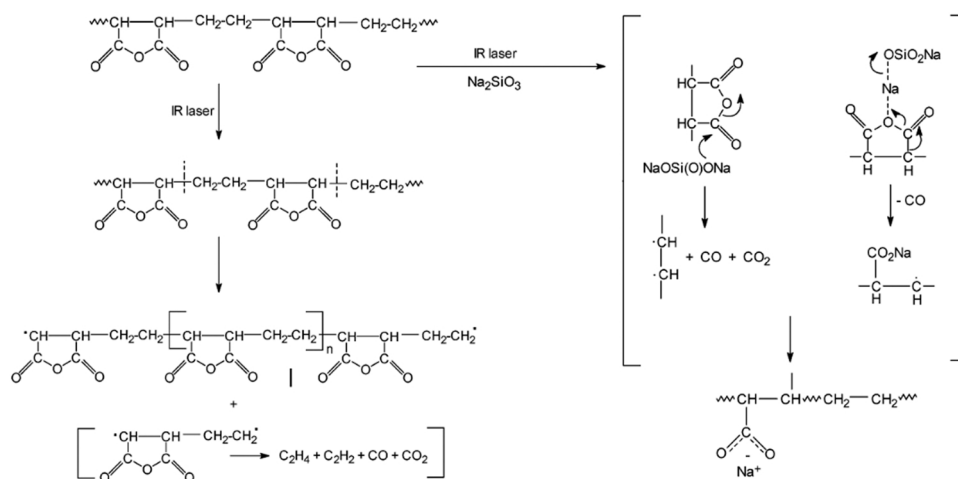


Fig. 12. SEM images of deposited PEMA (a) and PEMA- Na_2SiO_3 (b) films. Reproduced from ref. [113], Copyright Elsevier.



Scheme 4. Mechanism of IR laser-induced ablation-deposition of PEMA and PEMA- Na_2SiO_3 films. Adapted from ref. [113], Copyright Elsevier.

anhydride group, which is assisted via interaction of the sodium cation of metasilicate with the C-O-C oxygen and by stabilizing interaction of sodium cation with generated CO_2 group. Both elimination of the anhydride group and formation of the carboxylate group assisted by Na_2SiO_3 (Scheme 4) appear to be represent a unique example of reactive ablation in which the deposited polymeric film incorporates constituents of two different species exposed to laser radiation.

4.2.4.4. Poly(1,4-phenylene sulfide). Poly(1,4-phenylene sulfide) (PPS) is an important polymer with many potential applications due to its.

exceptional thermal and mechanical durability and chemical resistance [118]. It was proposed [119] that heating of PPS to over 300°C induces polymer branching, heating to ca. $300\text{--}500^\circ\text{C}$ results in the formation of cyclic oligomers $[1,4\text{-C}_6\text{H}_4\text{-S}]_n$ ($n = 4\text{--}7$) [120–122] and further heating to still higher temperatures (up to 900°C) yields benzene, aromatic compounds with $\text{C}_6\text{H}_n\text{-S}$ units ($n = 4, 5$) and dibenzothiophenes along with H_2S and CS_2 and other minor products [119,122,123].

The comparison of the IR laser-irradiated and TGA-derived materials [124] reveals significant differences in their compositions. While the slow conventional heating of PPS is a surface-assisted reaction and can be described as eliminations of cyclooligomers and S-containing aromatic compounds [119–123] resulting in a solid with S content and bonding similar to PPS, the laser ablation produces thin films poor in sulfur due to extrusion of S atoms (a two-fold C–S bond fission) yielding the identified elemental sulfur (S8 allotrope) which is removed from the S-polymer composite under high vacuum. The S content in the deposited films is significantly decreased at higher laser fluence and higher repetition frequency, which indicates that more sulfur extrusion is favored under these conditions.

Hence, the laser irradiations of PPS resulting in the extrusion of sulfur represents a novel type of desulfurization of S-containing polyaromatic materials.

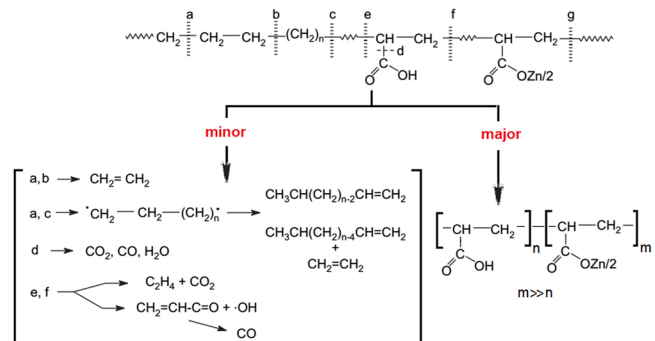
4.2.4.5. Poly(ethylene-co-acrylic acid) zinc salt. Ionomers based on polyethylene chains containing low levels of zinc acrylate or maleate groups are of interest due to their unique mechanical properties, ionomer-silica hybrids, reactive compatibilization of polymer blends and better physical properties of ionomeric polyblends when compared to non-ionomeric counterparts. Conventional degradation of poly(ethylene-co-methacrylic acid) zinc salt yields carbon oxides, $\text{C}_2\text{--}\text{C}_4$ olefins as major volatile products, cold ring fraction produced at heating to 440°C containing only CO_2H group, and the residue (mainly ZnO) which, formed at heating to 500°C , contains zinc methacrylate groups

and much less of $\text{-CO}_2\text{H}$ and anhydride groups [125]. The mechanism of conventional degradation is rather complex and was suggested to begin by side group scission in a carboxylate unit and to involve CO expulsion and backbone scission to dimethylketene [126].

The IR laser-induced ablative degradation of poly(ethylene-co-acrylic acid) (PEAZn) [127] leads to cleavage of both polyethylene backbone and CO_2H group and yields minor amounts of carbon oxides and volatile hydrocarbons (ethene as a major product). It also affords ablative deposition of solid whitish ionomeric films in which the initial ratio $\text{-CO}_2\text{H}/\text{-CO}_2\text{Zn}$ is decreased due to higher thermal stability of the $\text{-CO}_2\text{Zn}$ group (Scheme 5). The cleavage of the polyethylene backbone in the laser-induced degradation becomes more important at higher fluences, when the extent of scission of a polyethylene chain is increased compared to the cleavage of the pendant CO_2H groups. The different fluences have also a pronounced effect on the morphology of the deposited films (Fig. 13). The laser-induced process thus differs remarkably from conventional degradation of similar polyethylene chain-based metal methacrylate ionomers that are known to yield cold ring fraction containing only $\text{-CO}_2\text{H}$ group.

The IR laser ablation of PEAZn in laser radiation-absorbing sodium metasilicate (Na_2SiO_3) enhances the decomposition of the $\text{-CO}_2\text{H}$ group and leads to the deposition of films containing an inorganic fraction (Na_2SiO_3 , Na_2CO_3) along with a small portion of the polymer.

4.2.4.6. Poly(ethylene succinate). The IR laser ablation of poly(ethylene succinate) (PESC) [128] belongs to rare cases of laser ablative deposition of polymeric films having morphology, stoichiometry, NMR, UV and FTIR spectra and molecular weight distribution (1500–10,000) of the



Scheme 5. Mechanism of IR laser-induced ablation-deposition of poly(ethylene-co-acrylic acid) zinc salt. Adapted from ref. [127], Copyright Elsevier.

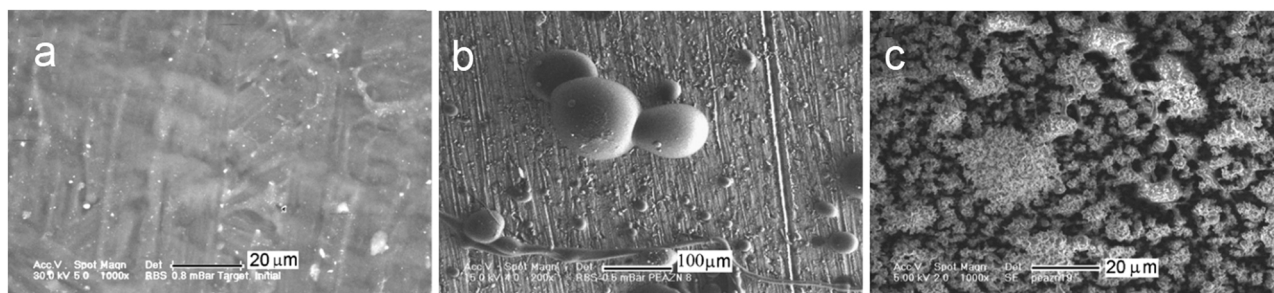


Fig. 13. SEM images of initial PEAzn (a) and the films deposited at 10 J.cm^{-2} (b) and 40 J.cm^{-2} (c). (c) Reproduced from ref. [127], Copyright Elsevier.

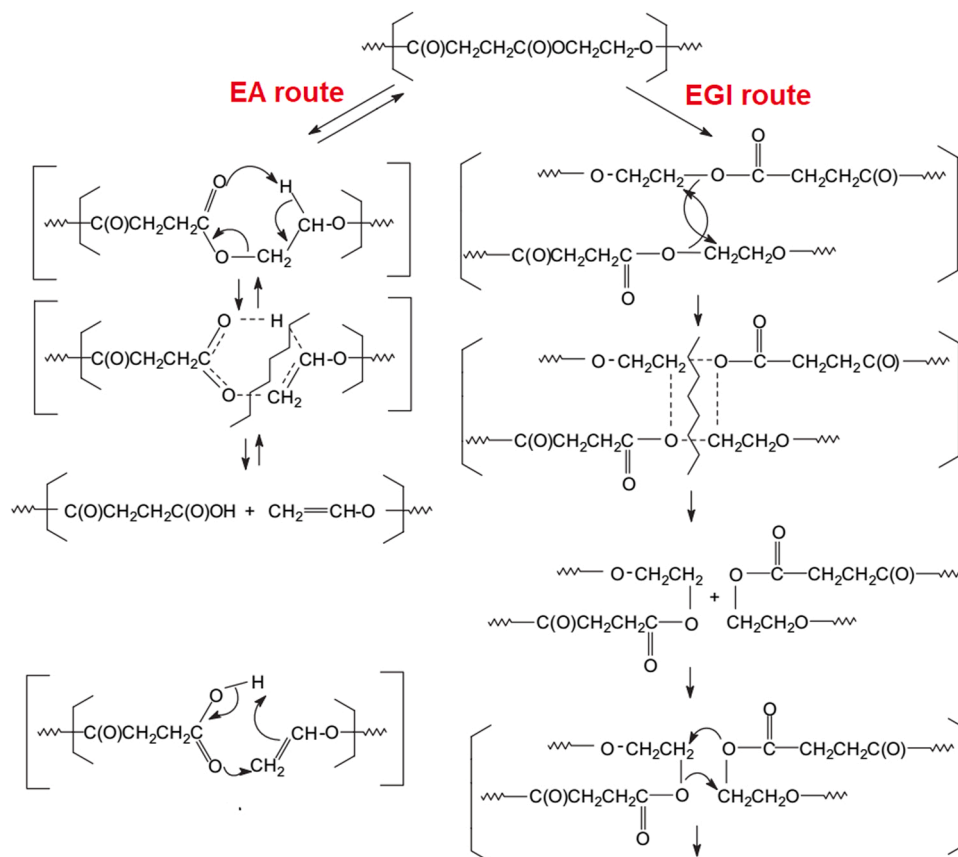
initial polymer. The solid products dominate over the minor volatile products (carbon oxides, hydrogen, C₁-C₄ hydrocarbons, aldehydes and vinyl esters), but their dominance decreases at higher laser fluence.

The laser ablative degradation in excess of D₂ does not result in the formation of D-isotopomers of the volatile products or incorporation of D into the deposited solid and these facts were discussed in terms of two different mechanisms. The volatile products arise from random cleavages of the polymer backbone, while restoration of the initial polymer structure occurs through (i) C-C bond homolysis and coupling of two produced $\text{-(O)COH}_2\text{C}^\cdot$ radicals, (ii) the earlier proposed ester groups interchange (EGI, [129,130]) and (iii) a sequence of formation of carboxylic acid and vinyl group through a 6-membered transition state, followed by addition of carboxylic acid to vinyl group (elimination and addition (EA)). **Scheme 6.**

The films have a continuous structure (**Fig. 14**) and do not contain μm-sized isolated bodies that are typical for ablative ejection/deposition

of large particles.

4.2.4.7. Poly(ethylene terephthalate). The IR laser-induced ablation of poly(ethylene terephthalate) (PET) has been studied with bulk samples in a vacuum [131] and with 50 μm thick films in the air [132]. The formed room-temperature-volatile products are similar to those observed in conventional pyrolysis and low incident energies lead to ablation of mainly high-molecular involatile species which undergo more fragmentation to carbon oxides and other small molecules at high incident energies. The films etching in the air [132] exhibits a relationship between etch depth and fluence, which is broadly similar to that observed for excimer laser etching but with a less well-defined threshold. Time-resolved photoacoustic measurements of stress waves generated in the etching show that at a fluence of 1.8 J.cm^{-2} ablation occurs 100–200 ns after the start of the laser pulse, a time which is consistent with the rate of thermal decomposition of PET.



Scheme 6. Mechanism of IR laser ablation deposition of poly(ethylene succinate) films. Adapted from ref. [128], Copyright Elsevier.

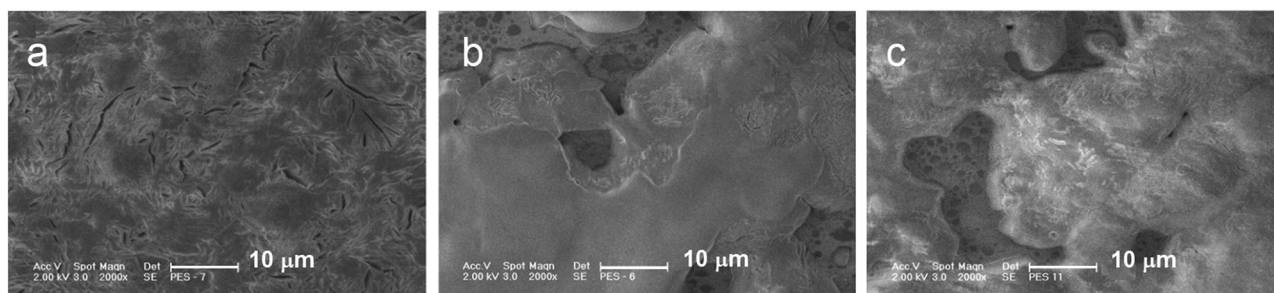


Fig. 14. SEM images of PES films deposited at 5 (a), 13 (b) and 30 (c) J. cm⁻². Reproduced from ref. [128], Copyright Elsevier.

As for the IR laser process conducted in a vacuum [131], a detailed analysis of volatile products reveals.

carbon oxides, H₂, C₁₋₂ hydrocarbons, acetaldehyde, benzene and toluene (major products), styrene,

benzaldehyde, propenylbenzene, 4-methyl-3-penten-2-one, cyclooctatetraene, acetophenone, benzoic acid and diphenylethanedione (minor products) which are in line with a complex mechanism involving a plethora of reactions in the hot zone. The solid deposits produced by ablation at higher laser fluences are poor in oxygen due to the efficient expulsion of oxygen-containing products from ablated agglomerates. These solid deposits are composed of soluble oligomers having the C=O bond in the same environment as PET and of an insoluble polymer having the C=O group bonded in the initial ester and -COOH groups. The major steps controlling the formation of solid oligomeric and polymeric particles were deduced (Scheme 7) to be a random scission of the polymeric chain ensued by the recombination of produced fragments (A), formation and recombination of fragments carrying -CO₂H groups (B) and expulsion of -OCH₂CH₂- linkages, leading to the creation of biphenylene units (C).

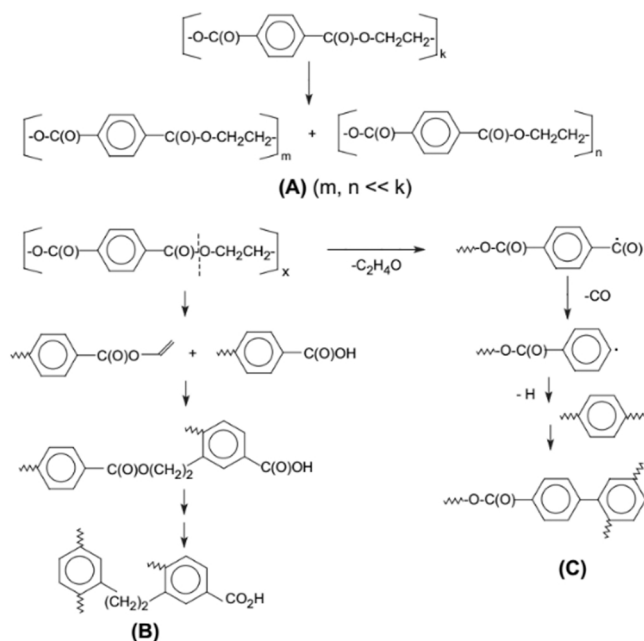
4.2.4.8. Poly(vinyl phenyl ketone). Pulsed IR laser ablation of poly(vinyl phenyl ketone) (PVPK) [133] results in the formation of volatile products (carbon monoxide, C₁-C₄ hydrocarbons, benzene, styrene and phenylacetylene) and leads to the deposition of polymeric films which

have molecular weight distribution matching pristine PVK, but contain less O and some of their C=O groups linked to C=C bonds. The elemental composition of the laser-formed craters is identical to that of pristine PVPK and this indicates that the oxygen loss takes place only in ablatively ejected agglomerated species. The simplified illustration of the decomposition steps (Scheme 8) involves paths leading to the observed products and route h (leading to the -C(O)· radical that, together with the ensuing steps (>C(O)· and >C· radical combination and C-H bond cleavages in the formed product) explains the formation of H-poor structures containing C=O bonds conjugated with C=C bonds.

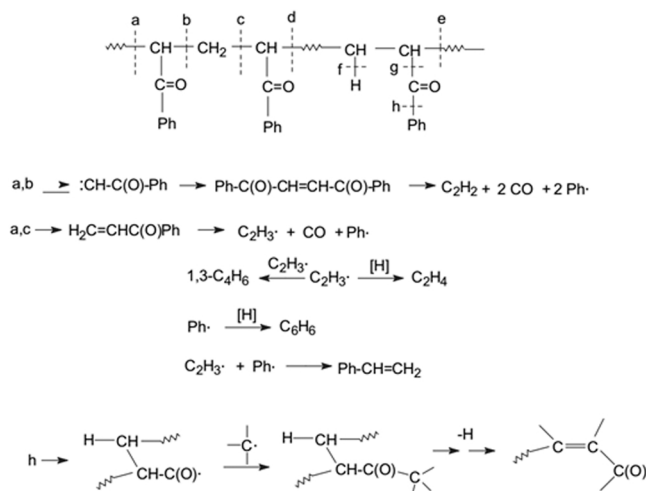
The morphology of the deposited films differs depending on the fluence used. Thus, ca. 10–100 μm large oval-shaped bodies, irregular ca. 200 μm features or very large ca. 100 μm to several hundred micrometer-sized globules merge into larger agglomerates (Fig. 15). These features are different from the smooth surface of the initial polymer and the ablated crater area.

Thermal decomposition of (PVPK) at 300 °C conducted in a hot-wall reactor [133] yields different gaseous products, white sublimed solid droplets, and a yellow residue. These gaseous products are CO, formaldehyde, methanol (CO/CH₃OH ~3) and hydrocarbons (in relative molar per cent) - methane (7), ethene (77), propene (3), butadiene (3), benzene (5), toluene and styrene (both <1) - among which benzene is a dominating component. The different degradation products from both processes are ascribed to different modes of heating and surface effect.

4.2.4.9. Polyether sulphone and polyether ether ketone. Polyether sulphone (PES) and polyether ether ketone (PEEK) films undergo ablation at chosen irradiation wavelengths to create different morphologies of



Scheme 7. Major steps in laser-induced degradation of PET. Adapted from ref. [131], Copyright Elsevier.



Scheme 8. Plausible reactions taking place during laser degradation of PVPK. Adapted from ref. [133], Copyright Elsevier.

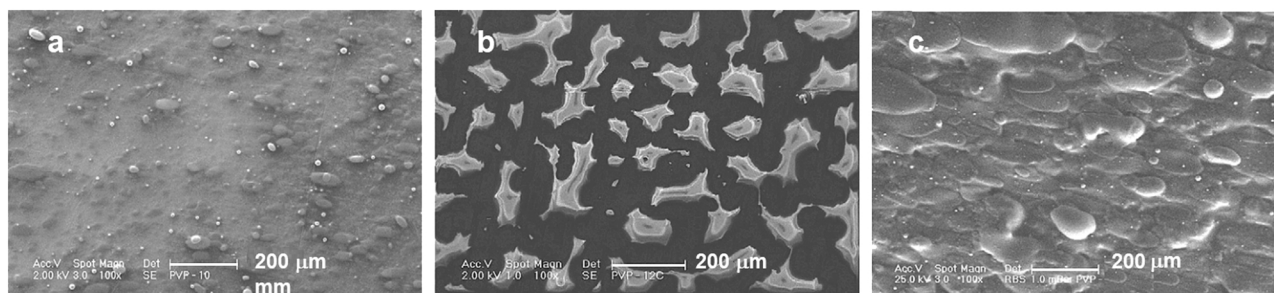


Fig. 15. SEM images of the films deposited at 30 J.cm^{-2} (a), 12 J.cm^{-2} (b), 5 J.cm^{-2} (c). Reproduced from ref. [133], Copyright Elsevier.

the irradiated spots and the ablation process is dependent on the incident laser intensity and ambient gas [134]. With the irradiation of films in a vacuum, for PES film (of $150 \mu\text{m}$ thickness) the fluence averaged over the ablated area was 15 J.cm^{-2} , while for PEEK film (of $200 \mu\text{m}$ thickness) it was only 6 J.cm^{-2} . Such differences in the sufficient fluences reflect different IR absorption coefficients and laser absorption densities and also possible re-absorption of the laser energy by ablated polymer within the pulse duration. The gas constituents in the air may accelerate the ablation process and so can do water vapor or other molecules in the air, which were considered to enhance observed perforation of the PEEK surface.

4.2.4.10. Poly(1,4-phenylene ether-sulfone). Poly(arylene ether-sulfone)s (PPES) containing arylenes linked with ether and sulfone groups as well as those with reactive end groups are well-known high-performance thermoplastic polymers that have excellent mechanical properties and high resistance to high temperatures, chemical corrosion and ignition. There has been much interest in their conventional thermal behavior, mechanism of thermal decomposition and elucidation of their backbone structure. The simplest member of these polymers is poly(1,4-(phenylene ether-sulfone) (PPES) which evolves diphenyl ether and diphenyl below 400°C and at higher temperatures undergoes one-stage main-chain random scission and carbonization to form SO_2 , phenol (major products), diphenyl sulfone, diphenyl ether, and a cross-linked structure (e.g. [135–137]).

A very different mode of thermal decomposition achieved by IR laser pulses [138] results in the extrusion of SO_2 , CO and hydrocarbon molecules and allows the deposition of dark solid paramagnetic carbonaceous films that are poor in S and contain CO, >SO_2 , --SO-- and C--S--C units. The films show absorption above 300 nm due to pronounced conjugation of $\text{sp}^2\text{-C}$ atoms and their EPR spectra are a sensitive function of the presence of molecular oxygen (Fig. 16). The gaseous products (SO_2 , CO, ethyne, benzene and carbon sulfide) of the laser degradation and the identified >S=O and C--S--C groups in the deposited films are

compatible with (i) feasible elimination of both SO_2 and CO bridges, (ii) reduction of $\text{C--(SO}_2\text{)--C}$ bridges to C--(S=O)--C and C--S--C units by H_2 and/or H atoms, and (iii) cleavage of the phenylene unit. It was assumed that the reduction path indicates the presence of phenylene dehydrogenation.

4.2.4.11. Poly[oxy(tetramethyldisilane-1,2-diy)]. Thin intractable films produced by pulsed UV or IR laser ablation/deposition of organosilicon polymers and particularly of peralkylsiloxanes would find many applications in materials science and microelectronics, but UV photolysis of these polymers occurs very reluctantly at the Si-C bonds, conventional pyrolysis of peralkylsiloxanes results in extrusion of stable low-molecular cyclic oligomers [139–141] and pulsed IR laser irradiation of peralkylsiloxanes leads to the formation of gaseous hydrocarbons through extensive cleavage of the Si-C bonds [142]. These facts thus indicate that fabrication of thin intractable peralkylsilicone films accomplished through reorganization of the Si-O-Si backbone by laser methods is an impossible task.

There is, however, an important need for processes that do not yield the native, but modified polymers with improved properties and fabrication of novel-type intractable and highly thermally stable silicones in a controllable way from a synthetically available precursor is of ongoing interest. Hence, the pulsed IR laser irradiation of poly[oxy(tetramethyldisilane-1,2-diy)] (POMDSD) [143] serves the above goal because its $\text{--}[(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{SiO}]_n\text{--}$ structure is cleaved with pulsed IR laser radiation at weak Si-Si bonds, producing macromolecular biradicals which spontaneously rearrange and repolymerize during their ejection onto a cold nearby substrate and this process makes possible fabrication of intractable and thermally superior cross-linked polymeric films (Fig. 17).

In this process, gaseous compounds ($\text{C}_1\text{--C}_4$ hydrocarbons, methylsilanes, methylsiloxanes, methyltrisiloxanes and methylcyclotri/tetrasiloxanes) are very minor products and the preponderance (95%) of the ejected mass is changed into solid films which possess very good

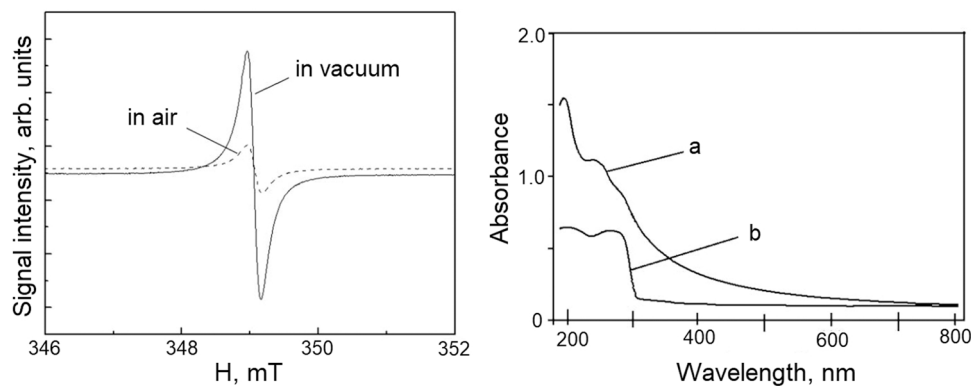


Fig. 16. EPR spectrum of deposited film and UV-vis spectrum of the deposited film (a) compared to pristine (b) PPES. Reproduced from ref. [138], Copyright Elsevier.

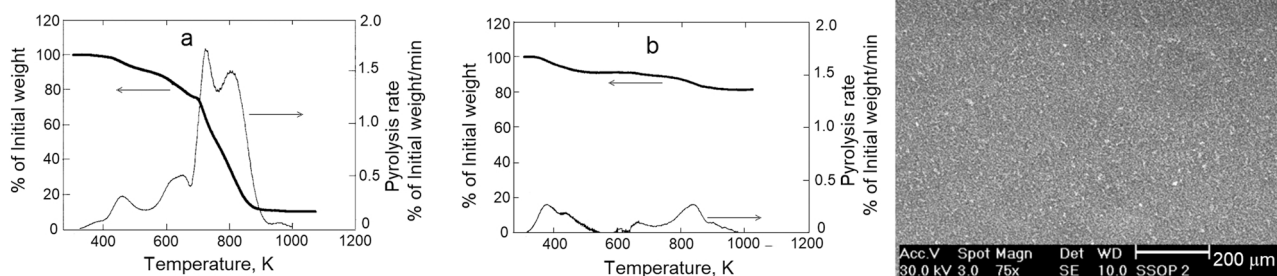


Fig. 17. TGA of poly[oxy(tetramethyldisilane-1,2-diyl)] (a) and the laser-crosslinked polymer (b) and SEM of the laser-crosslinked polymer. Reproduced from ref. [143], Copyright Elsevier.

adhesion to KBr and glass. These films are polyoxocarbosilanes and consist of a backbone composed of $-(\text{CH}_3)_2\text{Si}(\text{CH}_3)_2\text{SiO}-$ and $-\text{O}(\text{CH}_3)_2\text{SiO}-$ units, which are cross-linked via SiSiC_2O , C_3SiO , C_2SiHO , CSiHO_2 , and CSiO_3 moieties.

The feasible cross-linking steps (Scheme 9), derived from detailed analyses of their structure, can be envisaged as the coupling of Si-centered and $\geq\text{SiCH}_2$ radicals to form Si-Si and $\text{Si}-(\text{CH}_2)_n\text{Si}$ ($n = 0-2$) linkages, wherein the radical centers are generated via homolysis of the Si-CH₃ bond and H-abstraction from the CH₃(Si) group. The Si-CH₂-Si bridges can be also formed by the Yajima rearrangement [144] (YR) of the $-(\text{CH}_3)_2\text{Si}-\text{Si}(\text{CH}_3)_2-$ mobile and/or cross-linking units.

These laser-fabricated hybrids of siloxanes and polysilylenes are insoluble in common organic solvents and are thermally superior to siloxanes and polysilylenes, which makes them intriguing for applications in thermally exposed devices.

4.2.4.12. Polyimides. The pulsed CO₂ laser ablation of thin films has been conducted with polyimides (Kapton, Upilex) which exhibit outstanding mechanical strength, low water absorption and very high chemical and thermal stability and have been extensively applied as insulating films in microelectronic devices. The ablation processes carried out in air were aimed at etching precisely defined regions [145], recognition of the fluence dependence on the irradiation wavelength [146], getting excellent quality of etched through-holes (vias) with properly tuned radiation [147,148], and achieving effective removal of debris generated near laser-drilled vias in polyimide-based flex circuits [149].

A more detailed examination of the surface of Upilex-S polyimide (PI) film irradiated by the pulsed CO₂ laser in the air [150] reveals a halo-surrounded hole covered with sub-μm particles (Fig. 18) which contain more carbon and less oxygen and nitrogen as compared to the untreated area. The XPS analyses confirming fewer C=O groups and a

new N=C=O unit on the surface are in line with the decomposition of the imide ring, which is in accordance with the presence of CO₂, H₂O, and CO in vapors generated during laser etching [145]. Nonetheless, no analyses of ablated particles given do not allow to formulate a complete scheme of the ablation-deposition process and one can only admit that the produced volatile compounds are similar to those formed during conventional thermal pyrolysis of PI polymers.

It is known that conventional pyrolysis of PI films induces changes in weight, shrinkage of the film and evolution of CO and CO₂ at 500–650 °C, and involves an evolution of small amounts of CH₄, H₂, N₂ at 800–1000 °C (e.g. [151,152]) and bond cleavages around PI ring and H-transfer generating various intermediates on aromatic segments in polymer chains [153], finally allowing carbonization.

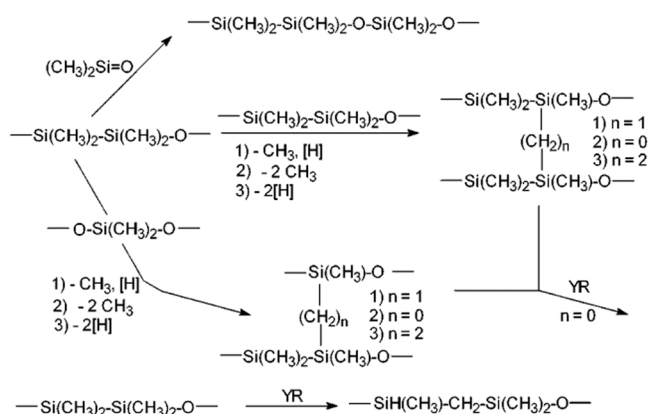
4.2.5. FEL ablation and deposition

The resonant IR laser ablation of polymers in vacuum induced by free-electron laser irradiation selectively absorbed in polymers leads to target to substrate transfer of polymeric entities which deposit as films having stoichiometry and structure almost identical to the pristine polymer. The major motivation of this research was to reveal whether FEL irradiation can eject intact macromolecular polymers into the gas phase and deposit them without any structural damage. Such laser action would therefore dramatically differ from that of UV-pulsed laser ablation/deposition which enables transient cleavage into monomers and subsequent reconstruction of macromolecular structures, which is feasible with only polyaddition polymers [16].

The FEL ablation-deposition of poly(ethylene glycol) [154,155], polystyrene [156,157], fluoropolyol [158], poly(DL-lactide-co-glycolide) (PLGA [159] has been reported to be capable to produce films with structure and composition almost identical to native polymers, which has been corroborated by IR spectra and molecular weight distribution assessed from gel permeation chromatography of native and deposited films. Minor deviations from the ideal congruent deposition are, however, observed, especially with regard to different extent of polymer chain fragmentation.

4.2.5.1. Poly(ethylene glycol). The films deposited by irradiating pristine PEG polymer at wavelengths resonant with vibrational modes of $\nu_{\text{C-H}}$ (~3.40 and 3.45 μm), $\nu_{\text{C-O}}$ (~8.96 μm) and $\nu_{\text{O-H}}$ (~2.90 μm) are superior to those deposited with non-resonant radiation with regard to both chemical structure and molecular weight distribution. Nonetheless, a low extent of polymer fragmentation leading to reduced polymer chain has also been confirmed with $\nu_{\text{C-H}}$ excitation (Fig. 19a).

4.2.5.2. Polystyrene. The films were successfully deposited with excitation into both aliphatic and aromatic $\nu_{\text{C-H}}$ modes and show IR spectra nearly identical to that of native polymer, whereas non-resonant irradiation results only in the target damage and no ablation. The average molecular weight of both deposited films is markedly lower and corresponds to about 5 scissions of the polymer chain. Different results have been, however, obtained with the same irradiations of low molecular



Scheme 9. Reactions involved in the formation of the laser-crosslinked polymer.

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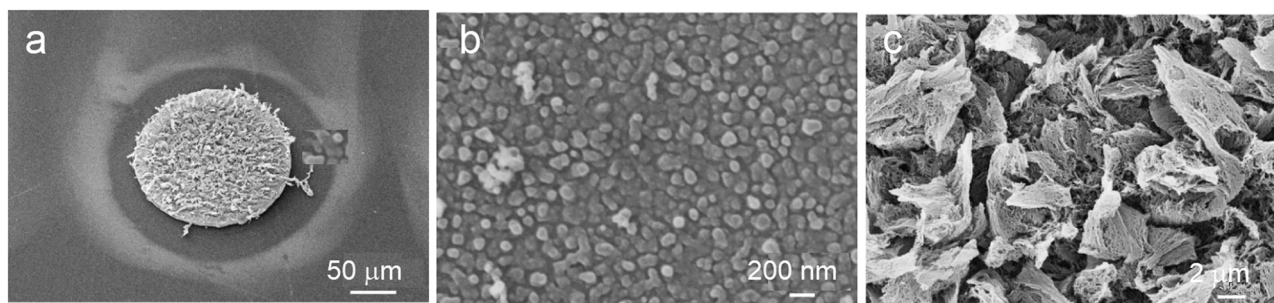


Fig. 18. A crater (a), halo (b), and debris in SEM images of the etched PI surface. Reproduced from ref. [150] Copyright Elsevier.

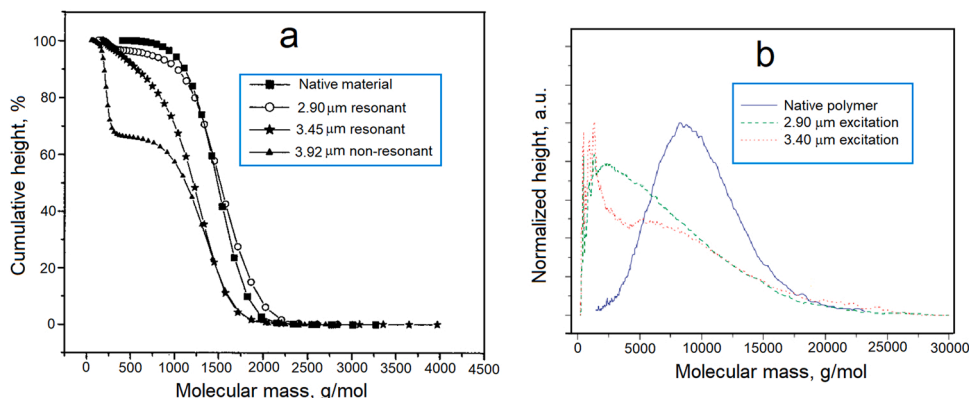


Fig. 19. Comparison of gel permeation chromatograms of FEL-deposited and native poly(ethylene glycol) (a) and poly(DL-lactide-co-glycolide) (b). Figs. a and b were respectively reproduced from ref. [155] and ref. [159], (Copyright AIP Publishing).

weight polystyrene due to minor bond scissions allowing to deposit films with an average molecular weight similar to that of pristine material.

4.2.5.3. Fluoropolyol. Thin films of nearly identical IR spectra and molecular weight distribution have been deposited from only ~1.5 mg of fluoropolyol which is a chemoselective polymer, by IR laser irradiation tuned to hydroxyl stretch at 2.90 μm. This has been concluded along with admitting some uncertainty of molecular weight distribution.

4.2.5.4. Poly(DL-lactide-co-glycolide). The IR irradiation resonant with O-H stretch (2.90 μm) or C-H stretch (3.40 μm) focused on this biodegradable polymer allows deposition of relatively thick (0.5 μm) films which possess IR spectral pattern nearly identical to that of pristine polymer but have the average molecular weight a little less than half that of the starting material (Fig. 19b).

4.2.5.5. Poly(tetrafluoroethylene). Films of poly(tetrafluoroethylene) were deposited by resonant (4.2 and 8.26 μm) irradiation of either a pressed powder or a commercial bulk target and they retained the chemical properties of the starting material, which is supported by IR and XP spectra and is also in line with a steady flow of undamaged polymeric entities from ablated target to the substrate [160]. Conversely, a non-resonant (7.1 μm) irradiation produces large particles.

Although not admitted, the prevalence of these ablations conducted under a high vacuum may be strongly influenced by three overlooked phenomena. The first is a formation of low-molecular volatile entities (monomers, dimers, low-mass oligomers) which were not observed and escaped detection owing to being sucked from the gas phase and substrate by vacuum and not frozen in a proper low-temperature condensation unit. The second is the likelihood of an efficient re-polymerization of transiently formed monomers and n-mers on the substrate surface,

particularly with unzipped units of polyaddition polymer chains, which undergo solely re-polymerization. The third is the possibility of heterogeneously enhanced re-polymerization of these transient oligomers due to catalytic surface effects. It should be therefore useful to check these three effects to be sure that the FEL irradiation induces solely ejection of high mass polymer entities.

4.3. Infrared laser degradation

A recent critical review of laser pyrolysis of various materials and compounds [161] appears to give very little attention to laser degradation of polymers, which gives the sense to review the topic of IR laser polymer degradation here and include only reactive changes undertaken by laser radiation on polymer surfaces. Such degradations become obvious when ablation processes are hindered or minimized owing to the reluctance of polymer structure or conditions of laser irradiation.

The ns pulsed CO₂ laser degradation of polymers causing thermal damage to polymer surface has been little explored. An investigation of the rules controlling the formation of a crater having a high "keyhole-penetration" parameter has been reported for poly(methylmethacrylate) under the action of pulse periodic CO₂ laser radiation, which revealed that the crater formation depends on the absorption of the incident radiation in the gaseous phase and also by the excitation of forced acoustic standing vibrations within the forming crater cavity [162]. The acoustic flow patterns increasing the heat flux to the walls of the cavity and producing locally broadened regions restrict the feasibility of attaining high values of the depth-to-diameter ratio of the crater.

Many degradations (pyrolyses) were accomplished by using cw and long-pulsed CO₂ lasers. The surface heat treatment of poly(ethylene terephthalate) and nylon, which have strong absorption bands near 6 μm, have been irradiated by μs pulses of a frequency selected Q-switched e-beam controlled-discharge CO-laser [163] and resulted in

microstructure changes and darkening of the polymer surface.

4.3.1. CW CO₂ laser degradation

An initial stage of degradation by CO₂ laser radiation in the absence of air has been examined with thermoplastic (polyethylene and polysulfone) and thermosetting (epoxy resin) polymer films coated on infrared transparent AgBrCl optical fibers [164]. It was found out that, after reaching the threshold energy of laser radiation, the IR absorption bands of rocking and stretching vibrations of CH₂ groups deplete, while,

new absorption bands related to vinyl tail -CH=CH₂ units increase and confirm the early degradation stage of these polymers.

The laser pyrolysis of polyphenylene- and polyamidocarboranes has been recognized as a novel versatile approach to the creation of new polymeric materials called secondary polymer structures (SPS) which possess high strength, thermal resistance and also specific properties [165]. Such elementoorganic and carborane-containing materials were used to be developed by traditional procedures involving two stages of conventional thermal treatments (e.g. [166]), the first reaching the crosslinking temperature and the second modifying the crosslinked structure into SPS. The laser heating of polymer I results in decarbonylation of end units, formation of dicarbaundecarborane anion and partial decomposition of benzene rings, while that of polymer II yields three-dimensional structures with triply substituted benzene rings, indicating that polymer II is better suited to form SPS structures. Scheme 10.

The laser-induced degradation of polystyrene has been studied using a low power cw CO₂ laser radiation for sample pyrolysis and a time-of-flight mass spectrometer for rapid analysis of degradation products. This enabled monitoring of selected time-resolved degradation products (polystyrene monomer and the monomer derived benzene and ethylene fragments) during the lifetime of the thermal event [167]. The observed dimer and trimer of styrene were consistent with the thermal chain scission of polystyrene, the mechanism proposed in early studies [168].

4.3.2. Degradation with long pulses of CO₂ laser

Much effort has been made to use μ s and ms pulsed radiation to induce degradation of polymers in a one-step approach towards porous laser-induced graphene (LIG). This turned out successful through laser heating of polyimide (PI) in the ambient atmosphere [169]. The high energy density radiation results in extremely high localized temperatures (>2500 °C) permitting to split the C-O, C=O and N-C bonds, expell oxygen and nitrogen contents and form residual graphene films. This discovery of transforming PI film into porous graphene structure with ultra-polycrystalline domains of pentagon-heptagon rings has become of great interest due to possibilities of further research of advanced applications of LIG in many fields, like microfluidics, sensors, and electrocatalysts [170]. Another effort related to the fabrication of graphene-based flexible and stackable solid-state supercapacitors with enhanced capacitive performance [171] or to direct laser carbonization writing (DLCW) of flexible and highly conductive graphitic porous patterns or arrays utilized as multifunctional [172,173] or piezoresistive [174] sensors. These graphene and graphitic structures are illustrated in Fig. 20. It was also shown that the repeated high fluence pyrolysis of the starting graphene foam can induce the production of carbon nanotubes [175]. Most recently, laser-induced N-self-doped graphite nanofibers

exhibiting stability up to 470 °C in the air have been fabricated by DLCW treatment of cyanate ester monomer-coated PI film [176] and their resistance overtakes that of LIG, transition metal carbide layers and Ti₃C₂ Xenes.

Chemical changes in poly(l-lactide) (PLLA) accomplished at fluences above the ablation threshold [177] revealed bimodal (reduced and pristine) molecular weights, a negligible depletion of the main chain (C-O-C=O) and ester (O=C-O) units due to evolution of carbon oxides and also the obvious occurrence of vinyl (RCH=CH₂), ketone (RCOCH=CH₂), vinyl ethers (ROCH=CH₂) and mostly vinyl groups, the last ascribed to cis-elimination reactions. It thus appears that the laser-induced process somewhat differs from conventional thermal degradation (Scheme 11) which takes place as a multi-stage process involving PLLA transesterification (macrocyclization) [178] and affords simple dimers, acetaldehyde, ketene, ethylene, methane, carbon oxides and cyclic poly(lactide) (-[CH(CH₃)COO]_n-) oligomers which reproduce the polymer structure [178–180].

4.3.3. Degradation with high-power CO₂ lasers

Unavoidable thermal degradations of polymers also take place during cutting, drilling or welding of plastics and polymer composites using irradiations of industrial cw CO₂ lasers, which were found to produce volatile and particulate organic substances as side products. The nature of these pollutants has been identified with many polymers [181–185] and shown to be complex mixtures of monomers, their decomposition products, aromatics and polycyclic aromatic compounds. These routine processes operating under strict safety measures thus produce small quantities of high molecular organic products via complex degradation and rearrangement reactions which necessitate temperatures considerably higher than those employed in usual laboratory studies.

4.4. Infrared laser reactive treatments

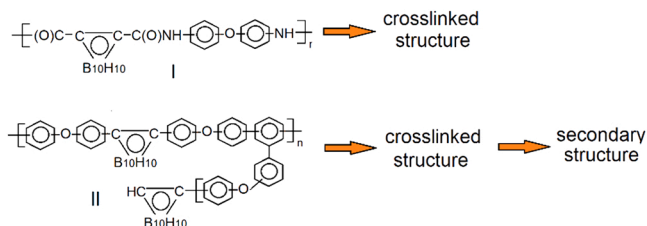
Many studies reaching for advanced properties of polymer surfaces through modifications of pristine (synthesized) polymers employing physical, chemical, thermal and optical methods have been reported (e.g. [186]), but IR laser irradiations leading to reactive structural changes of polymer surfaces due to the interaction between laser-thermally induced polymer surface and another potential reactant have been little studied and relate only to irradiations by pulsed and cw CO₂ lasers in ambient atmosphere.

The pulsed irradiation of thin low-density polyethylene (LDPE) films in air results in oxidation of polymer surface and formation of peroxidic species, keto-, carboxylic and alcoholic functional groups whose concentration depends on the number of pulses [187]. These chemical changes were explained by homolysis of the C-H bond and interception of O₂ which were considered responsible for changes in surface morphology and higher surface hydrophilicity (Fig. 21).

The pulsed irradiation of 70 μ m thick films of poly(ethylene terephthalate) in the air [188] reveals that few initial pulses modify the PET surface by development of long-lasting peroxidic bonds whose density decreases with further pulses. The -OOH bonds were ascribed to the reaction of transiently formed C-centered radicals with O₂. It was also observed that different morphologies of the irradiated PET films were accomplished with different irradiation wavelengths (Fig. 22) and they were thought to be associated with stress release on the melted surface layer.

The O-enrichment of polymer surface achieved by cw [189] or pulsed [190] laser irradiation in the air has been also achieved with poly(ether ether ketone). In the former case, HO-groups are formed on the polymer surface, as verified through reaction with trifluoroacetic anhydride, while in the latter case, increased content of C-O and decreased content of C=O groups, assigned by C1s and O1s XP spectra, is indicative of a change of carbonyl units into O-H groups.

An increase of O content on the surface of poly(methyl methacrylate), identified by XP spectra, was also observed with irradiations by cw



Scheme 10. Laser heating towards cross-linked and secondary polymers.

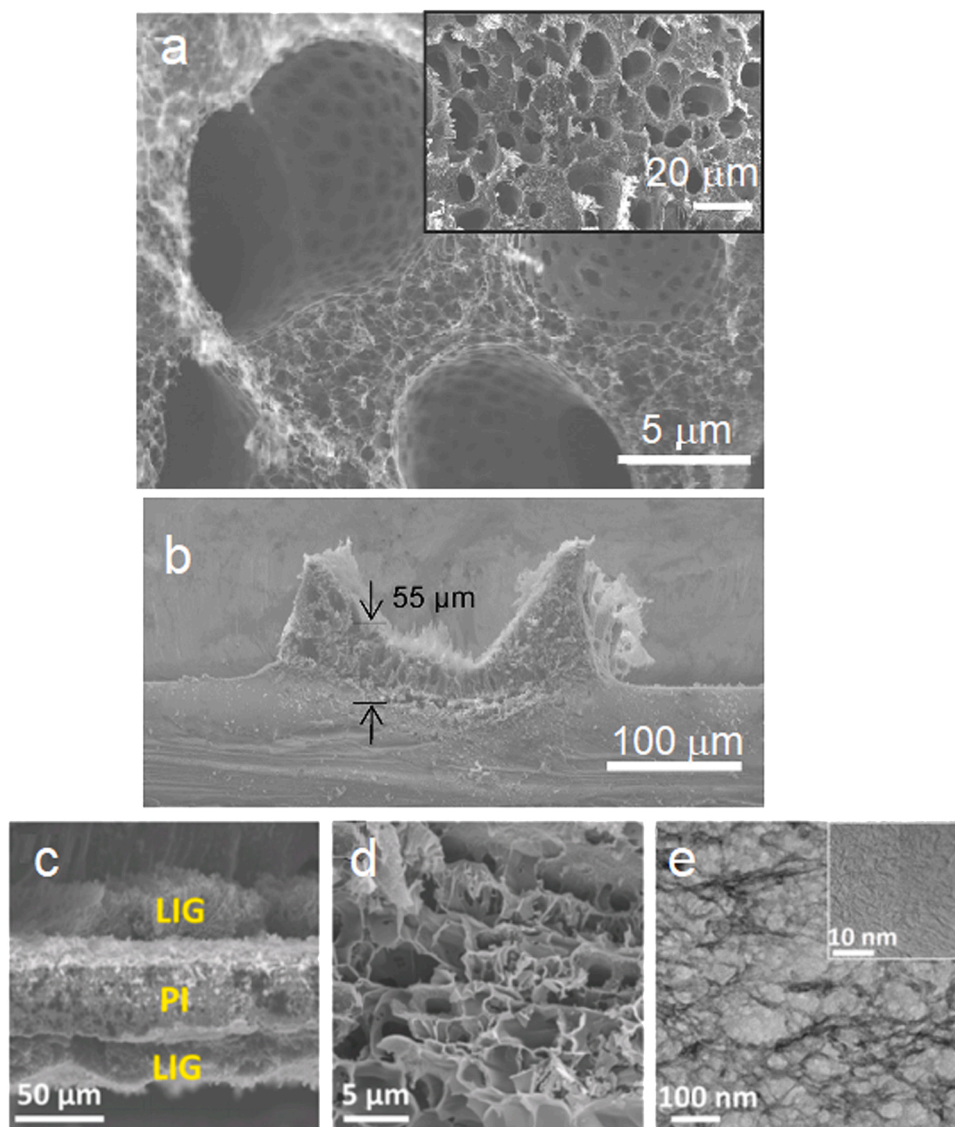
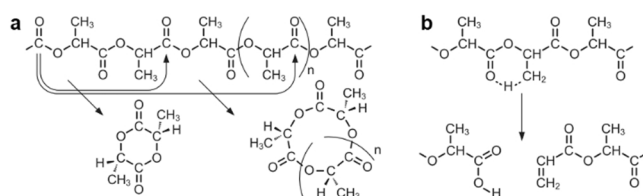


Fig. 20. Porous structure (a) and cross-section morphology (b) of graphitic lines produced by DLCW [172], cross-sectional image of PI substrate with LIG sides (c), SEM image of the porous 3D network (d), and TEM image of LIG films with nanosized wrinkles, ripples and graphene edges (insert). (e) Ref [171]. Copyright Elsevier and American Chemical Society, respectively.



Scheme 11. Radical-free thermal degradation of PLLA: macrocyclization [180] and cis-elimination [178].

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laser and ascribed to higher hydrophilicity of the surface. The assessment of different water drop contact angles with different samples thickness was, however, explained by the operation of two effects, wettability and surface roughness [191].

Polydimethylsiloxane

An interesting reactive modification of polymer surface in the air has become available through pulsed CO₂ laser irradiation tuned to ν(Si-O-

Si) band of polydimethylsiloxane [192]. This process affords rather hydrophobic and porous residues with higher O/Si ratios, fewer methyl groups and some content of carbonate group which was intercepted by residue surface from ambient CO₂. It was argued that the fragmentation of Si-O-Si units and CH₃-Si bonds may occur via transient formation of hydroperoxide species, but such a view and the detection of the carbonate group remain to be open for further discussion.

It is known that permethylsiloxanes exposed to less intense pulsed CO₂ laser radiation are cleaved just at Si-C but not at highly resistant Si-O bonds [142], whereas Si-O-Si cleavage can be induced only with highly intense TEA CO₂ [193,194] or UV [195] laser irradiation of permethyl or methyl hydrosiloxanes via transient Si-centered radicals formed after preceding Si-C and Si-H bond fissions. The residue produced in [192] thus appears to reflect an evolution of escaping C₁-C₂ hydrocarbons and methylsilanes (observed in [193]) and association steps [196] of presumed [193] transient silenes, silanones, silylenes and silyl radicals to grow agglomerates of the observed solid silicone material.

The silicon bonded to carbonate group remains to be a rather elusive species and their highly unstable forms require stabilizations by bulky

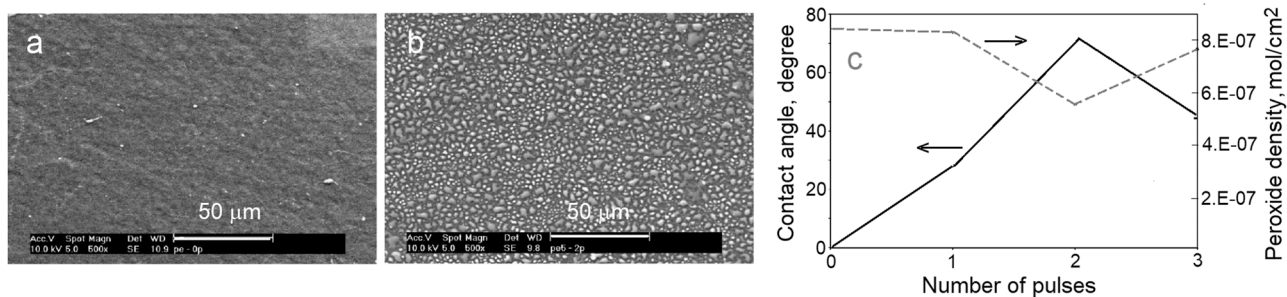


Fig. 21. SEM images of LDPE surface before (a) and after (b) irradiation with 2 pulses, and the plots of contact angle and peroxide density on the number of pulses. Adapted from ref. [187], Copyright Elsevier.

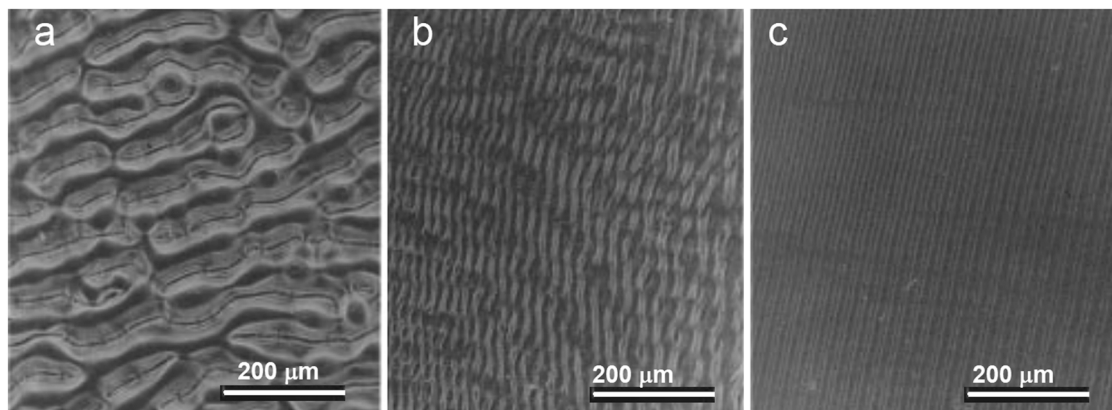


Fig. 22. SEM images of PET films irradiated with (a) 9.25 μm , (b) 9.58 μm and (c) 10.28 μm wavelength. Adapted from ref. [188], Copyright Elsevier.

substituents or complexation with carbenes. Hence, the only known examples of such structures are (i) bis(silyl)carbonate obtained by reaction of CO_2 with dialkylsilylene [197] and (ii) monomeric SiO_2 dicarbonate complex stabilized by bis-N-heterocyclic carbene [198], the latter having been proposed to develop via a sequence of zero-valent silicon atom \rightarrow monomeric silicon monoxide \rightarrow monomeric silicon dioxide conversions as proved by quantum chemical calculations.

All these facts thus suggest that CO_2 interception by the silicon residue is due to CO_2 reaction with transient silenes, silanones or silylenes and that the persistence of a low amount of silicon carbonate on the laser treated surface is caused by yet unspecified stabilizing interactions within the nanostructured surface.

5. Conclusions and perspectives

This review has dealt with the field of infrared laser irradiations of polymer surfaces, which now happens to be somewhat overlooked due to more attention later and currently given to UV lasers-irradiations of polymers and other macromolecules to achieve mostly stoichiometric transfer through the ablation-deposition process and surpass polymer and macromolecule fragmentation.

The specific IR energy input is demonstrated to create many uncommon surfaces on a variety of polymers. It is shown that IR laser irradiations modify polymer surfaces in ways different from those induced by conventional heating, which is due to selective laser energy supply to vibrational degrees of freedom and laser hindrance of polymer-substrate interactions.

The irradiations of polymers by cw CO_2 , TEA CO_2 and free-electron lasers to induce ablation-deposition processes have been evaluated together with the irradiations by CO_2 lasers to accomplish mere polymer degradation in vacuum and air.

The specific laser-derived changes in the chemical structure of

ablated, deposited and degraded polymer surfaces have been compared to those of conventionally heated polymers and attributed to distinct phenomena and chemical reactions taking place in IR laser-induced processes.

The compiled data and advantages of IR laser irradiations are of use for future topical research, particularly for new proposals for construction of novel polymer surfaces. These can be accomplished through the easier possibility to control changes in polymer structure during multi-step processes requiring initial work in a vacuum and subsequent irradiation in the presence of an additive. Other new types of surfaces can be made by targeted polymer crosslinking or by ablative deposition of novel polymer-inorganic composite films.

Additional potential benefits of IR laser polymer treatments may be possibilities to capture intermediary stable (deposited) entities which are difficult to observe in conventional pyrolysis, ablative deposition of charge-carrying polymeric films, protective stabilization of reactive nanoparticles and fabrication of reactive films. These can find application in material science and bio-engineering and are also of interest in various solution applications such as the conversion of polymers into polyelectrolyte-type gels.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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