Laser Ablative Structural Modification of Poly(ethylene-*alt*-maleic anhydride)

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Pulsed IR laser ablation of poly(ethylene-*alt*-maleic anhydride) results in the deposition of polymeric films possessing the same ratio of anhydride and $-CH_2-$ groups and represents a very rare example of laser ablative deposition of polymeric films that are structurally identical to the ablated polymer. This process differs from the conventional thermolysis of poly(ethylene-*alt*-maleic anhydride) that is controlled by expulsion of CO_2 and CO and yields a nonpolar polymeric residue. The IR laser ablation of poly(ethylene-*alt*-maleic anhydride) in sodium metasilicate affords deposition of polymeric films containing carboxylate ($-CO_2^-$) groups. This process is the first example of reactive ablation in which the deposited polymeric film incorporates constituents of two different species exposed to laser radiation.

1. Introduction

The pulsed laser ablation[1−3] for deposition (PLAD) of thin polymeric films using ultraviolet[4−20] and infrared[21−26] radiation has been continuously attracting much attention. The UV PLAD involves both photochemical and thermal features,[3,19,23] whereas the IR PLAD is a specific thermal process controlled by kinetic rather than thermodynamic polymer degradation. Importance of both techniques has long been considered to stem largely from facile ejection of large macromolecules or of fragments that can efficiently recombine into the original polymer.

An almost clean ejection of macromolecules can be achieved by laser evaporation of polymeric solute in low-temperature solvent matrix,[20] but generation of fragments (selective unzipping of polymer chain) that

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Table 1. Irradiation Experiments with Poly(ethylene-*alt*-maleic anhydride)[a]

run	configuration	fluence, mJ/cm^2	repetition frequency, Hz	target	deposition time, min.
1	I	1.4	1	PEMA	2.5
2	I	2.5	1	PEMA	3.3
3	II	1.5	1 or 2	PEMA	35 or 18
4	II	2	5	PEMA/Na_2SiO_3	10
5	II	2.6	10	PEMA/Na_2SiO_3	10
6	II	2.6	3	PEMA/Na_2SiO_3	33
7	II	2.6	1	PEMA/Na_2SiO_3	120

[a] PEMA.

undergo solely re-polymerization to the initial polymer on a nearby surface is often accompanied by side-reactions of the fragments (decompositions, rearrangements, radical reactions), which finally give rise to structurally modified (cross-linked) polymeric films. These films are of use because of their intractability and high-temperature durability. The importance of these side reactions is affected by the initial polymer structure and irradiation conditions (wavelength and intensity).

Laser ablative deposition of structurally identical films is very uncommon and was demonstrated only with UV irradiation of poly(tetrafluoroethylene),[6,7] IR irradiation of poly(ethylene glycol),[27,28] and IR irradiation of polysilanes and polycarbosilanes composed of $-(CH_3)_2Si-$, $-(CH_3)_2Si(CH_3)_2SiCH_2-$, $-R(CH_3)Si-$, and $-R(CH_3)Si(CH_3)_2SiCH_2CH_2-$ units (R = methyl, adamanthyl, phenyl and H, ref. 25). Negligibly modified films were obtained from poly(*p*-phenylenevinylene),[18] poly(3-octylthiophene),[16] and polycarbonate[4] using UV (VIS) radiation.

More cases reflect significant structural modifications of the polymer and include re-organization of organosilicon polymers and elimination of polar functional group from the carbon-functional polymers. Thus, polymeric films containing Si−C and Si−H bonds were deposited[12] by UV laser ablation of poly(methylphenylsilane), cross-linked polyoxocarbosilane films were obtained[26] upon IR laser irradiation of poly[oxy(tetramethyldisilane-1,2-diyl)], SiO_2 films were deposited by UV laser ablation of dimethylpolysiloxane,[29] π-conjugated polymers were developed[10] via ring closure and elimination of CN groups upon UV (193 nm) laser ablation of polyacrylonitrile, and poly(ethylene) films have been deposited[30] upon UV laser ablation and efficient removal of acetate group from poly(ethylene vinyl acetate). (Elimination of polar (anhydride) group is also known to take place[14,31,32] upon laser ablation of 3,4,9,10-perylenetetracarboxylic dianhydride).

In this work we report on laser ablation of poly(ethylene-*alt*-maleic anhydride) and show this process to differ from conventional polymer decomposition and to represent a unique example of PLAD of structurally identical polymeric films from functional group-containing polymers. We also reveal that PLAD of poly(ethylene-*alt*-maleic anhydride) is remarkably affected by sodium metasilicate, which facilitates removal of anhydride groups and enables fabrication of polymeric films possessing carboxylate groups. The latter process is the first example of reactive ablation that affords polymeric film incorporating constituents of two different species exposed to laser radiation.

2. Experimental Section

The laser irradiation experiments were performed in two different experimental configurations.

In configuration I, a batch Pyrex vessel (of 42 mL in volume)[26] equipped with a sidearm with rubber septum, a PTFE valve, and an NaCl window accommodated the pressed pellet of poly(ethylene-*alt*-maleic anhydride). After evacuation of the reactor to 10^{-2} Torr, the ablation was achieved by irradiating the sample area of ca. 0.6 cm^2 area with a mildly focused beam of TEA CO_2 laser. The TEA CO_2 laser (Plovdiv University) operated at the P(20) line of the 00°1 → 10°0 transition (944 cm^{-1}) with incident fluences 1.5 and 2.4 J·cm^{-2} and at a repetition frequency of 1 Hz. The films were deposited on a KBr plate.

In configuration II, we used a continuously evacuated metal chamber with a rotating substrate holder and the laser beam unfocused or mildly focused and impinging on the target (either (poly(ethylene-*alt*-maleic anhydride) or its mixture with sodium metasilicate (the weight polymer/Na_2SiO_3 ratio 0.25)) compressed in a tablet (10-mm diam. and 5−7 mm thick). The TEA CO_2 laser (a Lumonics model TE-820 HP) operated at the P(20) line of the 00°1 → 10°0 transition (944 cm^{-1}) at a repetition frequency of 1−10 Hz and the films (area ∼3 cm^2 and ca. 0.1−1 μm thick) were deposited on KBr plates positioned 3 cm away from the target.

The list of experiments and irradiation conditions used for the ablation are presented in Table 1.

The gases formed in the Pyrex vessel were transferred under vacuum to an IR spectroscopic cell for FTIR spectroscopic analysis and were also analyzed by GC and GC/MS methods. The analyses of gases were performed on an FTIR Nicolet Impact and 20SXB spectrometers, a Shimadzu QP 1000 quadrupole mass spectrometer (Porapak P), an MS 80 Kratos GC/MS spectrometer (CBP 10-S50-050 capillary column), and a GC 14A Shimadzu gas chromatograph (Porapak P and OV 17 column, programmed temperature 30−150 ° C).

The thin films deposited on KBr (NaCl) and Cu substrates were analyzed by FTIR spectroscopy (Nicolet spectrometers), X-ray photoelectron spectroscopy (XPS), thermal gravimetry, and electron microscopy.

The X-ray photoelectron spectra (XPS) were measured using an ESCA 310 (Gammadata Scienta) electron spectrometer equipped with a high-power rotating anode, wide-angle quartz crystal monochromator, and a hemispherical electron analyzer operated in a fixed transmission mode. All measurements were performed using Al Kα radiation and the analyzer pass energy of 300 eV. The pressure of residual gases in the analyzer chamber during spectra acquisistion was typically 5×10^{-10} mbar. A Scienta flood gun was used for sample static charge compensation. The spectra of C (1s), O (1s), and Na (1s) photoelectrons were measured at high resolution. The ratios

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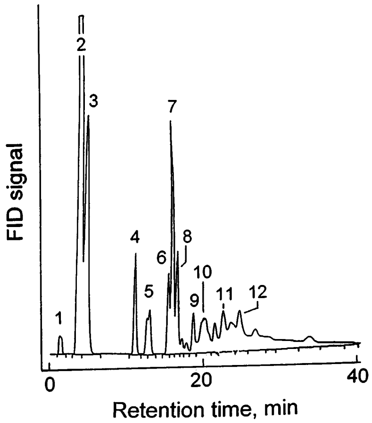


Figure 1. Typical GC trace of volatile products from laser ablation of poly(ethylene-*alt*-maleic anhydride). Porapak P, (30−150 ° C), peak identification: 1, methane; 2, ethene; 3, ethyne and ethane; 4, propene; 5, propadiene and propyne; 6, 2-methylbutene; 7, buta-1,3-diene; 8, 1-buten-3-yne; 9, 2-methyl-buta-1,3-diene; 10, 1,3-dimethyl-propadiene; 11, hexa-1,3,5-triene and hexa-2,4-diene; 12, benzene.

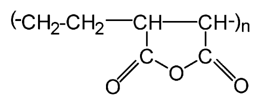
of atomic concentrations were determined by correcting the photoelectron peak areas for pertinent cross-sections.[33] The overlapping spectral features were resolved into individual components of Gaussian−Lorentzian shape using the damped nonlinear squares procedure. For binding energies we estimated the error limit to be ±0.2 eV. The estimated accuracy of the calculated ratios of atomic concentrations amounts to ±10%.

SEM analyses were obtained using a Philips XL30 CP scanning electron microscope.

Gel permeation chromatography measurement of molecular weight distribution in the deposited polymers was carried out in dry tetrahydrofuran (Aldrich, 99.9%, HPLC grade) using tandem HP Plgel columns and polystyrene standards. The original and the deposited polymers were injected as solutions in dry acetone and the wavelength at 215 nm was used for the detection.

Thermal analysis of poly(ethylene-*alt*-maleic anhydride) was carried out by heating the sample (15 mg) in a stream of argon at the rate of 4 °C per minute using Cahn D-200 recording microbalances, and the sample residues remaining on the balance pan were analyzed in a KBr pellet by FTIR spectroscopy.

Poly(ethylene-*alt*-maleic anhydride), average M_W 100 000−500 000, ethylene/maleic anhydride ratio 1, was purchased from Aldrich.



3. Results and Discussion

Laser Irradiation of Poly(ethylene-*alt*-maleic anhydride). The TEA CO_2 laser irradiation of poly(ethylene-*alt*-maleic anhydride) tablets in configurations I and II results in the formation of gaseous products and deposition of thin white films. The gaseous products are carbon monoxide, carbon dioxide, and a variety of hydrocarbons, among which ethene and ethyne are major components (Figure 1). The respective amounts in molar percents of ethene (70 and 48) and ethyne (18 and 22) in runs 1 and 2 indicate more ethyne (a high-temperature product) in the higher pulse energy experiment and suggest that some ethyne arises from decomposition of ethene.

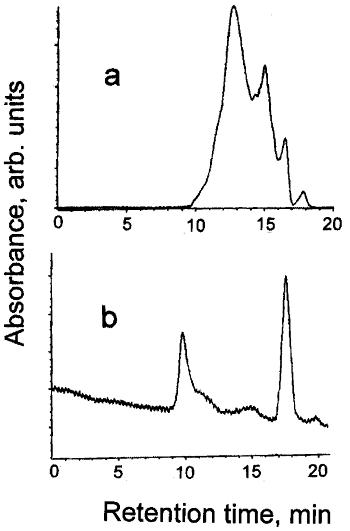


Figure 2. Gel permeation chromatogram of the deposited (a) and original (b) polymer. (HP Plgel columns, mobile phase tetrahydrofuran; the peak at 17.5 min corresponds to acetone.).

The gel permeation analysis of the deposited films (Figure 2) is consistent with M_W 500 000−5000 and this wide molecular weight distribution is indicative of polymer fragmentation during the ablative process.

The films deposited on Cu substrate have a continuous structure and contain merging ca. 3−5-μm islands as demonstrated by SEM analysis (Figure 3a). This morphology is indicative of an aggregation of the once deposited polymer particles. The amounts of carbon and oxygen assessed from EDX analysis are, respectively, 64 and 36 atomic percent, which corresponds to the composition of the initial polymer.

The electron wide-scan survey spectra (Figure 4b) of the deposited films reveal the presence of oxygen, carbon, and trace amounts of silicon. The spectra of C (1s) electrons (Figure 5b, Run 3 in Table 1) are composed of two peaks located at 284.8 and 289.2 eV, respectively, assignable on the basis of comparison with the spectra obtained for poly(ethylene-*alt*-maleic anhydride) to $-(CH_x)-$ and $O{=}C{-}O{-}C{=}O$ moieties, and a weak peak centered at 287.5 eV which can be attributed[34] to $-C{=}O$ and/or to $O{-}C{-}O$ groups. The above assignment is corroborated by corresponding spectra of O (1s) electrons (Figure 6b) showing the presence of two components belonging to $-C{=}O$ and $-C{-}O{-}C-$ functional groups.

FTIR spectra of the films deposited in runs 1−3 show a pattern (Figure 7a) virtually identical to that of the initial polymer (Figure 8a).

Very interestingly, the relative absorptivity of the anhydride (at 1780 cm^{-1}) and C−H stretch (at 2930 cm^{-1}) bands, $A_{\nu(C=O)}/A_{\nu(C-H)}$, in the deposited films is practically equal (Table 3) to that in poly(ethylene-*alt*-maleic anhydride) ($A_{\nu(C=O)}/A_{\nu(C-H)} = 21$). The occurrence of CO, CO_2, C_2H_4, and C_2H_2 as major volatile decomposition products is thus in line with an equal extrusion of the anhydride and $-(CH_2)_2-$ moieties.

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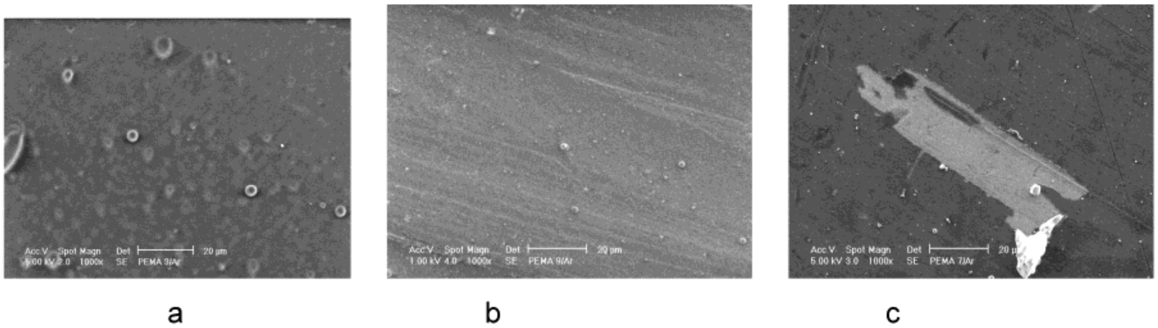

Figure 3. SEM images of the films deposited in run 3 (a), run 7 (b), and run 5 (c). For runs designation see Table 1.

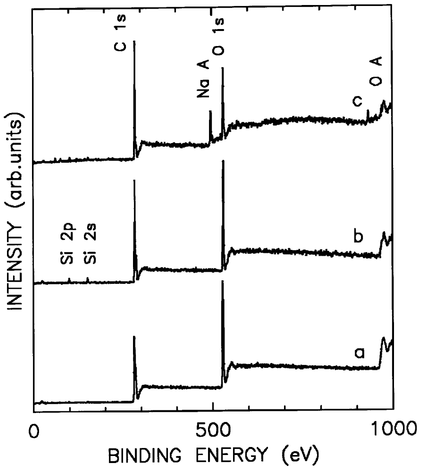

Figure 4. XPS wide-scan survey spectra of (a) poly(ethylene-*alt*-maleic anhydride), (b) sample run 3, and (c) sample run 7.

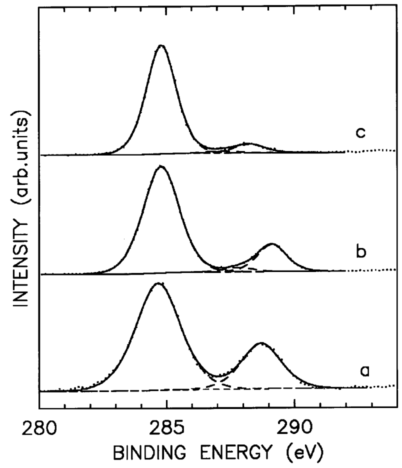

Figure 5. Fitted spectra of C (1s) electrons of (a) poly(ethylene-*alt*-maleic anhydride), (b) sample run 3, and (c) sample run 7.

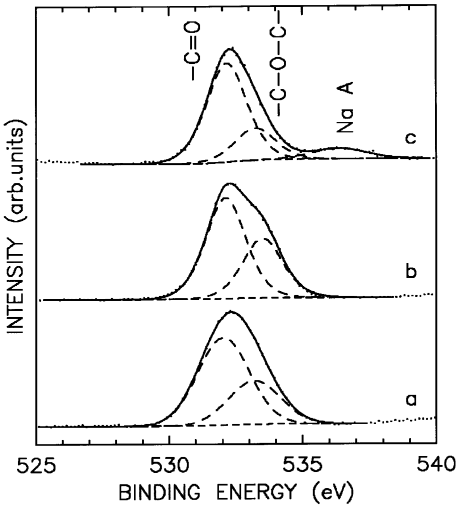

Figure 6. Fitted spectra of O (1s) electrons of (a) poly(ethylene-*alt*-maleic anhydride), (b) sample run 3, and (c) sample run 7.

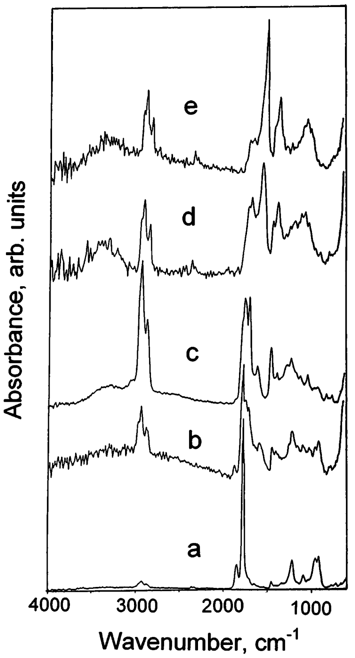

Figure 7. FTIR spectra of deposited films. (a)−(e) relate, in the given order, to runs 3−7.

The unaltered position of the anhydride bands (at 1780 cm^{-1}) is in keeping with the anhydride group remaining in the same environment, and this feature confirms that the formation of CO, CO_2, C_2H_4, and C_2H_2 occurs via primary elimination of -ethenylanhydride-units as depicted in Scheme 1. The observed four major volatile products are then consistent with being formed via decomposition of ethenylanhydride units.

We note that IR PLAD[35] and thermal[36,37] decomposition of maleic anhydride yielding CO, CO_2, and ethyne is consonant with such a view. The assumed (H)C−C(H_2) cleavage in the polymer is in line with the formation of macromolecular diradicals **I** that travel from the irradiated spot to the nearby cold surface where they deposit and spontaneously recombine.

Conventional heating of poly(ethylene-*alt*-maleic anhydride) leads to a very different degradation and yields

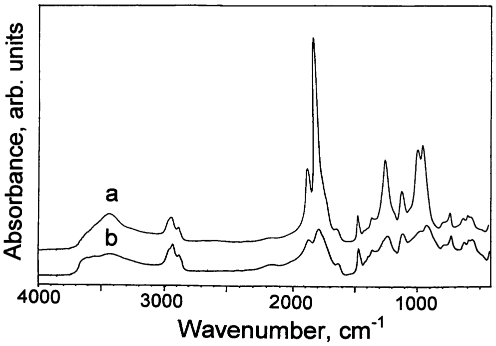

Figure 8. FTIR spectra of poly(ethylene-*alt*-maleic anhydride) (a) and residue after TGA (heating to 180 °C) (b).

Table 2. Core Level Binding Energies (eV) of the C (1s) Spectra Components, Their Assignment, Population of Corresponding Chemical States of Carbon, and Superficial Stoichiometry of the Representative Films Determined from Intensities of Photoelectron Spectra

sample	C (1s) [eV], (population, %)	assignments	stoichiometry
run 3	284.8 (81)	$-(CH_x)-$	
	287.5 (2.6)	$-C{=}O$; $O-C-O$	$C_{1.00}O_{0.41}$
	289.2 (16.4)	$O{=}C-O-C{=}O$	
run 7	284.8 (91)	$-(CH_x)-$	
	287.5 (1.8)	$-C{=}O$; $O-C-O$	$C_{1.00}O_{0.20}Na_{0.05}$
	288.3 (7.2)	$-CO_2^-$ (Na^+)	
PEMA[a]	284.8 (72)	$-(CH_x)-$	$C_{1.00}O_{0.51}$
	288.9 (28)	$O{=}C-O-C{=}O$	

polymer richer in $-CH_2-$ groups. Heating to 180 °C under Ar leads to formation of volatile methane (a very minor product of laser ablation, Figure 1), ethane, CO, and CO_2, and it affords a material whose FTIR spectrum shows almost equally important bands of the anhydride and $-CH_2-$ groups (Figure 8b). This behavior is unequivocal evidence on more efficient removal of the anhydride groups.

Different chemical changes initiated by IR laser pulses (full width at half-maximum <100 ns) and by slow conventional heating reflect different cleavage reactions involved in both processes. It is known that infrared pulsed laser evaporation/deposition of solid polymers is achieved through multiple-photon resonant absorption of energy-poor infrared photons and it leads[38−40] to high vibrational excitation density in the solid and high heating and cooling rates (respectively, $\sim 10^{6-11}$ K·s^{-1} and $\sim 10^{3-6}$ K·s^{-1}) that provide kinetic rather than thermodynamic control of polymer degradation.

The nearly equality of the dissociation energies of the C−C and C−O bonds, however, makes it difficult to rationalize the observed difference in terms of a selective split of one of these bonds. We therefore presume that the specific formation of the macromolecular diradicals containing the anhydride units is possible due to a temperature jump (high heating and cooling rates) in a restricted small volume of the irradiated bulk polymer, wherein decomposition products before and after ejection into gas phase are not interfered with heterogeneous effect of hot wall, as it happens in the conventional heating. It is known that heterogeneous catalysis by metal (platinum) makes decarbonylation/decarboxylation of the anhydride group more feasible.[41] We assume therefore that the absence of such metal−polymer interaction is in favor of the C−C bond scissions taking part in the nonpolar polymer backbone and not in the pendant polar anhydride unit.

Laser Irradiation of Poly(ethylene-*alt*-maleic anhydride)−Na_2SiO_3. The TEA CO_2 laser irradiation of poly(ethylene-*alt*-maleic anhydride)−sodium metasilicate tablets in configuration II leads to deposition of thin, mostly white films (Runs 4−7 in Table 3), but this process is rather slow and can be accomplished only at higher energy densities. This indicates a “cooling effect” of Na_2SiO_3 that directly absorbs[42] and enables laser energy to randomize in thermally stable metasilicate structure.

FTIR spectra of the films deposited in runs 4−7 (Table 3, Figure 7b−d) show patterns different from that of the initial polymer: the characteristic vibrational mode of the anhydride group (at 1780 cm^{-1}) gets lost and some new ν(C=O) bands build up at lower (1750 and 1706 cm^{-1}) wavenumbers, which assign[44] to carbonyl groups in $-C-C(O)-X$ (X = C, H) units. The absorptivity of these carbonyl bands is significantly diminished, and the relative absorptivity of the most intense ν(C=O) band, $(A_{\nu(C=O)}/A_{\nu(C-H)}) = 0.8-2.5$, indicates that concentration of carbonyl groups decreased by an order of magnitude (Table 3). The deposition process becomes more selective when using low repetition frequency of irradiation (run 6 and particularly run 7, Figure 7d and e): the films obtained in run 7 show two major bands at 1560 and 1404 cm^{-1} that are respectively due[44] to ν^{asym} and ν^{sym} modes of CO_2^- carboxylate anion. This interpretation is corroborated by XPS data.

The wide-scan XP spectra of the deposited films reveal the presence of O, C, and Na atoms (Figure 4c). The total oxygen concentration in the topmost layers calculated from the spectra intensities is significantly reduced in comparison with poly(ethylene-*alt*-maleic anhydride) (Table 2). The C (1s) spectra (Figure 5c, Table 2) show two main peaks centered at 284.8 and 288.3 eV, respectively, assignable[34,43] to $-(CH_x)-$ and $-CO_2^-$ moieties. The spectra of O (1s) electrons (Figure 6c) are consistent with this assignment. The occurrence of Na constituent in the XPS spectra makes us infer that the anionic group is linked to Na cation. The measured shift of the high binding energy component in the spectrum of the C (1s) electrons toward lower binding energy compared to the same peak in the spectra of the sample

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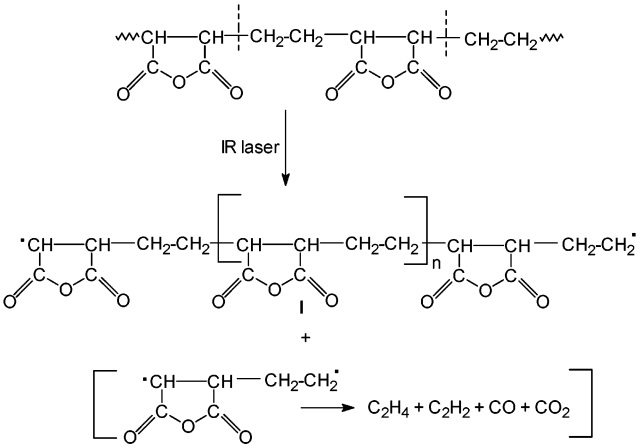
Table 3. Properties of the Deposited Films

	FTIR spectra			
run	ν(C=O), wavenumber, cm^{-1} (relative absorbance)	$A_{\nu(C=O)}/A_{\nu(C-H)}$[a]	note	color
1	1778 (1.0); 1843 (0.15)	21		white
2	1780 (1.0); 1843 (0.14)	19		white
3	1781 (1.0); 1844 (0.14)	26.0[b] and 24.0[c]	Figure 7a	white
4	1775 (1); 1731 (0.24); 1711 (0.24); 1593 (0.33)	2.5	Figure 7b	white
5	1751 (1.0); 1706 (1.0); 1603 (0.25)	0.83	Figure 7c	yellow[d]
6	1706 (0.70); 1578 (1.0); 1444 (0.520	1.45	Figure 7d	white
7	1562 (1.0); 1404 (0.51)	2.3	Figure 7e	white

[a] The value relates to the dominant ν(C=O) band. [b] −[c]Correspond to repetition frequencies of 1 and 2 Hz, respectively. [d] The yellow color reflects a minor extent of carbonization that was verified in independent experiments as growing more feasible at high repetition frequency and fluence.

Scheme 1



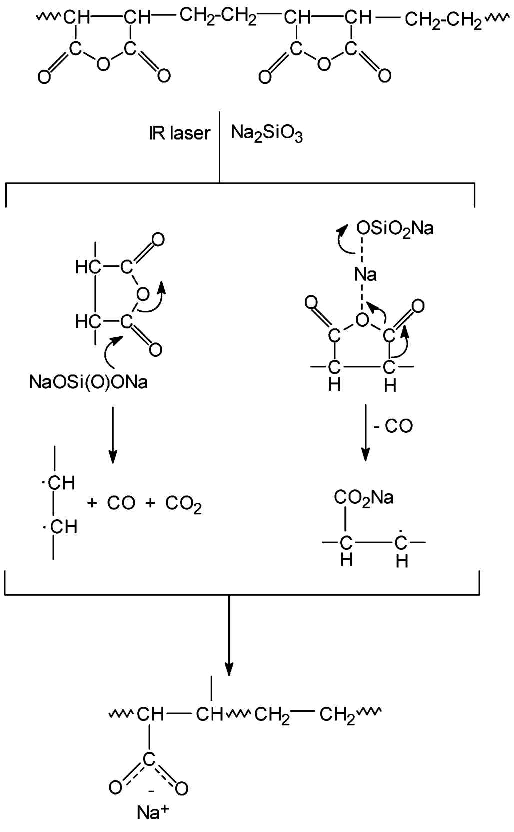
run 3 and poly(ethylene-*alt*-maleic anhydride) (Table 2) is in accord with this interpretation.

SEM analysis confirms that the morphology of the deposited fillm is similar to that of the films deposited by ablation of poly(ethylene-*alt*-maleic anhydride) only. It is shown (Figure 3b) that the films have continuous structure and that they possess some <3-μm round agglomerates stuck to the film surface. The films show good adhesion to KBr plates but not to Cu substrates, from which they can be mechanically removed (Figure 3c). The stoichiometry estimated from EDX analysis ($C_{1.00}O_{0.22}Na_{0.03}$) is consonant with that assessed from the XP spectra (Table 2). It reveals the absence of silicon (metasilicate) and proves that the CO_2^- group is bonded to the Na cation.

The conditions applied in run 7 thus allow efficient conversion of poly(ethylene-*alt*-maleic anhydride) into a polyethene polymer incorporating $-CO_2^-Na^+$ groups. Much lower content of oxygen in the deposited polymer is compatible with the occurrence of two different paths that are (i) the elimination of the whole anhydride groups and (ii) the anhydride ring opening and decarbonylation.

The pronounced elimination of the anhydride group can be, by analogy to base-enhanced decarboxylation of organic compounds,[45] enhanced by nucleophilic metasilicate centers and result in the formation of carbon radical centers that can either form a $-HC=CH-$ bond or recombine in the course of cross-linking polymerization to form C (sp^3) centers. The absence of a ν((Csp^2-H) absorption band above 3000 cm^{-1} in the FTIR spectra of the deposited films gives support to the latter path.

Scheme 2



The formation of the carboxylate group is, on the other hand, in keeping with a specific cleavage of the anhydride group, which is likely 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. Such mechanism has been recently suggested[46] for cyclic anhydride ring opening during hydrolysis.

Both elimination of the anhydride group and the formation of the carboxylate group as assisted by Na_2SiO_3 are illustrated in Scheme 2.

The deposition of polymeric films containing solely a carboxylic group being feasible only at the low repetition frequency indicates that the carboxylate group formation is a lower-energy channel whose importance de-

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creases in excess of heat delivered in the higher repetition frequency experiments.

4. Conclusion

The IR laser pulsed irradiation of of poly(ethylene-*alt*-maleic anhydride) results in the deposition of polymeric films that are structurally almost identical to the initial polymer. The process represents the very rare example of laser ablative deposition of polymeric films that are structurally identical to the ablated polymer and the first example of the laser ablative deposition of polymeric films with virtually undiminished content of polar functional groups.

This process differs from the conventional thermolysis of poly(ethylene-*alt*-maleic anhydride) that is controlled by expulsion of CO_2 and CO and yields a nonpolar polymeric residue.

The specific feature of the laser ablation is attributed to the formation of macromolecular, anhydride units-containing diradicals that are produced by a temperature jump in a restricted small volume of the initial polymer and are expelled to nearby substrate, where they re-polymerize.

The IR laser ablation of poly(ethylene-*alt*-maleic anhydride) in sodium metasilicate affords deposition of polymeric films containing carboxylate ($-CO_2^-$) groups. This process is the first example of reactive ablation in which the deposited polymeric film incorporates constituents of two different species exposed to laser radiation.

Both processes represent an easy and efficient way of fabrication of thin and air moisture sensitive films whose alternative production by conventional (solvent-involved) techniques is a more difficult task.

The films bearing both anhydride and carboxylic groups belong to families of highly reactive films that are of interest in various solution applications such as conversion into polyelectrolyte-type gels, attachment of biological molecules and cells, and have potential use in the drug delivery systems (e.g., refs 47, 48).

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