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

Josef Pola* and Jaroslav Kupčík
Laser Chemistry Group, Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, 16502 Prague, Czech Republic

Sardar M. A. Durani, Ehsan E. Khavaja, and Husain M. Masoudi
Center for Applied Physical Sciences, Research Institute, King Fahd University of Petroleum and Minerals, 31261 Dhahran, Saudi Arabia

Zdeněk Bastl
J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 18223 Prague, Czech Republic

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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 $-\text{CH}_2-$ 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 nonpolymeric residue. The IR laser ablation of poly(ethylene-alt-maleic anhydride) in sodium metasilicate affords deposition of polymeric films containing carboxylate ($-\text{CO}_2^-$) 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 infra-red$^{21-26}$ 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

*Authors to whom correspondence should be addressed. E-mail: pola@cpf.cas.cz or husainmm@kfupm.edu.sa.

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), and IR irradiation of poly(ethylene glycol), and IR irradiation of polycarbosilanes and polyacrylonitrile, and poly(ethylene) films eliminating CN groups upon UV (193 nm) laser ablation and gated polymers were developed via ring closure and elimination of CN groups upon UV (193 nm) laser ablation of polyacrylonitrile, and poly(ethylene) films have been deposited 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 upon laser ablation of 3,4,9,10-peryleneetetracarboxylic dihydride).

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) equipped with a sidearm with rubber septum, a PTFE valve, and a 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 cm² area with a mildly focused beam of TEA CO₂ laser. The TEA CO₂ laser (Polidiv University) operated at the P(20) line of the 0⁰1 → 1⁰0 transition (944 cm⁻¹) at a repetition frequency of 1–10 Hz and 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 focused or mildly focused and impinging on the target (either poly(ethylene-alt-maleic anhydride) or its mixture with sodium metasilicate (the weight polymer/Na2SiO3 ratio 0.25) compressed in a tablet (10-mm diam. and 5–7 mm thick). The TEA CO₂ laser (a Lumonics model TE-820 HP) operated at the P(20) line of the 0⁰1 → 1⁰0 transition (944 cm⁻¹) at a repetition frequency of 1–10 Hz and the films (area ~3 cm² 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.

<table>
<thead>
<tr>
<th>run</th>
<th>configuration</th>
<th>fluence, mJ/cm²</th>
<th>repetition frequency, Hz</th>
<th>target</th>
<th>deposition time, min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>I</td>
<td>1.4</td>
<td>1</td>
<td>PEMA</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>I</td>
<td>2.5</td>
<td>1</td>
<td>PEMA</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>II</td>
<td>1.5</td>
<td>5</td>
<td>PEMA/Na2SiO3</td>
<td>35 or 18</td>
</tr>
<tr>
<td>4</td>
<td>II</td>
<td>2.6</td>
<td>5</td>
<td>PEMA/Na2SiO3</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>II</td>
<td>2.6</td>
<td>10</td>
<td>PEMA/Na2SiO3</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>II</td>
<td>2.6</td>
<td>3</td>
<td>PEMA/Na2SiO3</td>
<td>33</td>
</tr>
<tr>
<td>7</td>
<td>II</td>
<td>2.6</td>
<td>1</td>
<td>PEMA/Na2SiO3</td>
<td>120</td>
</tr>
</tbody>
</table>

*PEMA.*
of atomic concentrations were determined by correcting the photoelectron peak areas for pertinent cross-sections. 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.

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 of C (1s) electrons (Figure 6b) showing the presence of two components attributable to C–O and/or O–C–O moieties, and a weak peak centered at 287.5 eV which can be attributed to C=O and/or 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, $A_{v(C\equiv O)}/A_{v(C\cdots H)}$, in the deposited films is practically equal (Table 3) to that in poly(ethylene-alt-maleic anhydride) ($A_{v(C\equiv O)}/A_{v(C\cdots H)} = 21$). The occurrence of CO, CO$_2$, C$_2$H$_4$, and C$_2$H$_2$ as major volatile decomposition products is thus in line with an equal extrusion of the anhydride and $–(\mathrm{CH}_2)_2–$ moieties.
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\(_2\)H\(_4\), and C\(_2\)H\(_2\) occurs via primary elimination of \(-\text{ethenylanhydride}-\) 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
polymer richer in \(-\text{CH}_2-\) 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 \(-\text{CH}_2-\) 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, \(-10^9\)–\(-10^11\) K\(^{-1}\)·s\(^{-1}\) and \(-10^3\)–\(-10^6\) K\(^{-1}\)·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.\(^4^1\) 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)**

\(\text{Na}_2\text{SiO}_3\). The TEA CO\(_2\) laser irradiation of poly(ethylene-alt-maleic anhydride)–\(\text{Na}_2\text{SiO}_3\) at 1560 and 1404 cm\(^{-1}\) wavenumbers, which assign\(^4^2\) to carbonyl groups in \(-\text{C}(=\text{O})-\)X (X = C, H, units). The absorptivity of these carbonyl bands is significantly diminished, and the relative absorptivity of the most intense \(\text{v}(\text{C}=\text{O})\) band, \((\text{A}(_\text{r}(\text{C}=\text{O})) / \text{A}(_\text{r}(\text{C}=\text{H})) = 0.8-2.5\), 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\(^4^3\) to \(\nu_{\text{asym}}\) and \(\nu_{\text{sym}}\) modes of CO\(_2\)–carbonylate 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\(^4^4\) to \((-\text{CH}_x-\) and \(-\text{CO}-\text{O}\) 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

\(^{35}\) Kupčík, J.; Pola, J. Unpublished results.


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 film 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 (C1.00O0.22Na0.03) is consonant with that assessed from the XP spectra (Table 2). It reveals the absence of silicon (metasilicate) and proves that the CO2- 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 polyethylene polymer incorporating -CO2-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 decarboxylation.

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

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 CO2- group. Such mechanism has been recently suggested46 for cyclic anhydride ring opening during hydrolysis.

Both elimination of the anhydride group and the formation of the carboxylate group as assisted by Na2SiO3 are illustrated in Scheme 2.

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Table 3. Properties of the Deposited Films

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

\(^a\) The value relates to the dominant \(\nu(\text{C}=\text{O})\) band. \(^b\) Correspond to repetition frequencies of 1 and 2 Hz, respectively. \(^c\) 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.

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

4. Conclusion

The IR laser pulsed irradiation 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 unit-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 ($-\text{CO}_2\text{H}$) 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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