POLYMERS WITH TRIAZENE UNITS IN THE MAIN CHAIN

Application for Laser-Lithography

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ABSTRACT

Several monomeric and polymeric triazenes have been synthesized and characterized by common methods such as ¹H NMR-, IR-, Raman-, UV-spectroscopy, DSC, and GPC. Their thermolysis, photosensitivity, and the effect of H₃O⁺ on their stability have been studied in detail, since those characteristics are very important for an application of these compounds in microlithography.

In laser ablation experiments, polymers containing triazene units in the main chain (TP1 - TP9) exhibited several advantages over systems in which common polymers (e.g. PMMA) are doped with low molecular triazenes (T1 - T14), especially the fact that their ablation craters have clean contours and sharp edges is of great interest for this type of microstructering.

1. INTRODUCTION

“Triazenes” (R₁-N=N-N(R₂)(R₃)) are rather “old” compounds from the organic chemists viewpoint. It was as early as 1862 that Griess described a suitable way for the synthesis of 1,3-diphenyltriazene [1]. Since one could not find any application for triazenes at that time, these compounds have been ignored for many decades. Moreover, they have been considered an undesired sideproduct in the azo-dye synthesis.

Unsubstituted triazenes are unstable under normal conditions. Substituted triazenes, however, can be rather thermally stable. In newer time, some attention was paid to substituted...
triazenes, especially to 1-aryl-3,3-dialkyl-triazenes, which were synthesized for the first time in 1875 [2] because some of them show activity as insecticides and anti-tumor properties [3]. This is also the main reason for more than 1200 references on triazenes in the last 20 years.

A rather modern aspect, and the main reason for our interest in triazenes, is their potential in the information storage technology, mainly due to their high photosensitivity [4,5]. Therefore we have studied the ground state and excited state properties of selected 1-aryl-3,3-dialkyl-triazenes but also of polymers containing triazene groups as part of the main chain in some detail.

2. SYNTHESIS AND GROUND STATE PROPERTIES OF TRIAZENES

The most suitable route for the synthesis of triazenes is given in the following scheme:

\[
\begin{align*}
\text{R}_{1}^{+} \text{N} = \text{N} \text{Cl}^{-} + \text{H} - \text{N} \text{R}_{2} \text{N} \text{R}_{3} & \rightarrow & \text{R}_{1}^{+} \text{N} = \text{N} \text{N} \text{R}_{2} \text{N} \text{R}_{3} \\
\end{align*}
\]

Triaazenes are photosensitive, thermosensitive, and sensitive against protons. Furthermore, their stability is strongly influenced by their substitution pattern. Thermolysis and photolysis yield radicals as intermediates, meanwhile the retrosynthetic route to diazonium ions and amines is forced by protons.

From X-ray it is known that the most stable isomer has a trans-conformation at the N=N-bond [6].

The 1,3-dipolar structures become increasingly important when the aromat is substituted with electron acceptor groups such as NO₂ or CN. In this case the rotation barrier around the N²-N³ bond increases [7].

To support the existence of this rotation barrier we carried out ¹H NMR experiments for selected triazenes in d₄-methanol at different temperatures. As shown in Table 1, the highest coalescence temperatures were determined for compounds with electron withdrawing substituents on the aromatic ring(T₁,T₂). A typical NMR pattern in these experiments is given in Fig.1:

The Hammett-plot (Fig.2) of the rate constants of the rotation around the N²-N³ bond at 273 K, obtained from the NMR experiments, results in \( \rho = -1.95 \pm 0.21 \) which is in good agreement with literature values [8,9]. The negative value is a clear indication for a rotation barrier due to the \( \pi \)-overlapping of azo and amine orbitals. Furthermore it supports the postulated 1,3-dipolar structure.
Table 1. Coalescence temperature for model triazenes of the structure $R_1$-Ph-N=N-N(R_2)(R_3) ($R_2 = R_3 = C_2H_5$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_1$</th>
<th>T (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>4-NO$_2$</td>
<td>308</td>
</tr>
<tr>
<td>T2</td>
<td>4-CN</td>
<td>302</td>
</tr>
<tr>
<td>T3</td>
<td>4-COOH</td>
<td>283</td>
</tr>
<tr>
<td>T5</td>
<td>H</td>
<td>255</td>
</tr>
<tr>
<td>T7</td>
<td>4-OCH$_3$</td>
<td>238</td>
</tr>
<tr>
<td>T9</td>
<td>3,5-di(COOH)</td>
<td>280</td>
</tr>
<tr>
<td>T11</td>
<td>3-COOH</td>
<td>284</td>
</tr>
<tr>
<td>T13</td>
<td>3-COOH*</td>
<td>274</td>
</tr>
<tr>
<td>T14</td>
<td>3-COOH**</td>
<td>285</td>
</tr>
</tbody>
</table>

* $R_{2,3} = n$-propyl; ** $R_{2,3} = isopropyl

3. THERMOANALYSIS OF TRIAZENES

From thermolysis data one can get information about the thermostability, which is important not only from the academic viewpoint but also from the viewpoint of safety and application. Therefore selected triazenes have been studied by DSC (differential scanning calorimetry) to determine the decomposition temperatures and the decomposition rate constants [compare ref. 10].

Figure 1. $^1$H NMR of methyl protons (T11, T7) and methin protons (T14) of triazenes at different temperatures.
A typical result (arrhenius plot of the rate constants at different temperatures, determined by DSC) for triazines is shown in Fig. 3 for T9.

The thermolysis experiments quite clearly showed, that triazines having electron withdrawing substituents in para-position of the aromatic ring stabilize the compound. Some of the models do not decompose at T<200°.

The thermolysis of triazines has been studied several times [11-13]. Aromatic triazines (1,3-diaryl)triazenes) decompose thermally via radicalic intermediates under rupture of the N2-N3-bond.

The products depend strongly on the solvent used, e.g. decomposition in benzene yields diaryls, decomposition in alcohols yields ethers [14]. The intermediate radicals were

Table 2. Decomposition temperatures $T_{\text{max}}$ and $E_a$ for different triazines (measured by DSC in bulk), structures $R_1$-$\text{Ph}$-$\text{N}$$=$$\text{N}$(R$_2$)(R$_3$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>$R_1$</th>
<th>$R_2$, $R_3$</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$E_a$ (kJmol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T3</td>
<td>4-COOH</td>
<td>di-C$_2$H$_5$</td>
<td>148</td>
<td>242</td>
</tr>
<tr>
<td>T9</td>
<td>3,5-di(COOH)</td>
<td>di-C$_2$H$_5$</td>
<td>151</td>
<td>282</td>
</tr>
<tr>
<td>T11</td>
<td>3-COOH</td>
<td>di-C$_2$H$_5$</td>
<td>113</td>
<td>282</td>
</tr>
<tr>
<td>T13</td>
<td>3-COOH</td>
<td>di-n-propyl</td>
<td>128</td>
<td>221</td>
</tr>
<tr>
<td>T14</td>
<td>3-COOH</td>
<td>di-isopropyl</td>
<td>136</td>
<td>---</td>
</tr>
<tr>
<td>T15</td>
<td>4-OC$_3$H$_3$</td>
<td>CH$_3$, (CH$_2$)$_2$CH$_3$</td>
<td>270</td>
<td>---</td>
</tr>
<tr>
<td>T16</td>
<td>4-CN</td>
<td>CH$_3$, (CH$_2$)$_2$CH$_3$</td>
<td>308</td>
<td>---</td>
</tr>
</tbody>
</table>

* not determined
found to be able to initiate a free radical polymerization, e.g. of butadiene, a copolymerization of acrylonitrile with vinylpyridine, and others [11-13, 15].

An interesting observation was that addition of acids reduce the decomposition temperatures of triazenes [16]. Therefore we found it necessary to study the effect of protons on the decomposition of triazenes in some detail.

4. PROTOLYSIS OF TRIAZENES

It is known from earlier work that triazenes decompose in the presence of acids. Di- and trialkyltriazenes [17], 3-alkyl-1-aryltriazenes [18,19], and 3-alkyl-1,3-diaryltriazenes [20,21] are studied in detail. Surprisingly little is known, however, for the protolysis of 1-aryl-3,3-dialkyltriazene [22-24].

\[
\begin{align*}
\text{R}_1\text{N}=\text{N}=\text{N}\text{R}_2 + \text{H}^+ & \xrightarrow{k_a^1} \text{R}_1\text{N}=\text{N}\text{R}_2 + \text{H}^+ \\
\text{R}_1\text{N}=\text{N}=\text{N}\text{R}_2 & \xrightarrow{k_a^2} \text{R}_1\text{N}=\text{N}\text{R}_2 + \text{H}^+ \\
\text{products} & \text{products}
\end{align*}
\]

Typical experiments were carried out in buffer-methanol mixtures in the presence of a 5 fold concentration of NaCl compared to the triazene ($8\cdot10^{-5}$ mol l$^{-1}$). The decrease of
Figure 4. Protolysis of $R_1$-Ph-N= N-N($C_2H_5)_2$ ($R_1 = \text{Cl}$), followed by UV-spectroscopy, pH = 4.7, RT, intervals: 60 min.

triazene concentration with time was measured at room temperature in different buffer solutions. A characteristic example for a protolysis experiment followed by UV-measurements is presented in Fig 4.

The effective rate constants as a function of pH values results in straight lines for all triazenes investigated in this work (Fig. 5). Meanwhile $T_8$ ($R_1 = 4-N(CH_3)_2$) decomposes already at pH = 10 with a half life time of only 100s, $T_1$ ($R_1 = 4-NO_2$) is very resistant against the retrosynthetic decomposition.

From the decomposition scheme for the protolysis of triazenes results (E1):

Figure 5. Dependence of the effective first order rate constants of triazene decomposition on solution pH. For each curve the slope of the corresponding linear regression is included in the figure. Structures according to Table 1, $R_1$=H (■), $CH_3$ (+), $OCH_3$ (♀), Cl (□), CN (x), NO$_2$ (Θ), N($CH_3)_2$ (Δ), m-NO$_2$ (Ε).
\[ k_a^i = \frac{[TH^*]}{[T][H_3O^*]} \]  

(E1)

\( K_a \) equilibrium constant of protonation  
\([T]\) concentration of the triazene in equilibrium  
\([TH^*]\) concentration of the protonated triazene in equilibrium

If unimolecular decomposition of \([TH^*]\) is rate determined then (E2) is valid:

\[ \frac{d[T]}{dt} = k_1 [TH^*] = k_1 k_a^i [T][H_3O^*] \]  

(E2)

In this case the effective rate constant depends on \(H_3O^*\) concentration and the decomposition reaction has the characteristics of a specific acid catalysis.

Systematic variation of the buffer concentration and of the buffer type (pH = 2 for glycine or citrate buffer) shows that “specific acid catalysis” is a suitable description for the protolysis of triazene, since the reaction depends not on the chemical nature of the buffer but on the actual \(H_3O^*\) concentration only. This view is also supported by deuterolysis: \(D_2O\) was used for protolysis instead of \(H_2O\). The isotope effect (differences in the rate constants) was determined to be \(k_H/k_D = 0.432\). Since \(D_2O^+\) is a stronger acid than \(H_3O^+\) the reaction is faster in \(D_2O\) than in \(H_2O\).

As already mentioned above, the protolytic stability is dramatically influenced by the substituents at the aromatic ring of the triazenes. A comparison of the rate constants for the decomposition of triazenes at pH=7 is given in Table 3. The Hammett-plot for these results (Fig. 6) is a straight line, resulting in \(\rho = -4.70\) which is quite similar to a value given in the literature for 1-aryl-3,3-dimethyltriazene (\(\rho = -4.03\)) [24].

The linear dependency of the triazene decomposition on the \(H_3O^+\) concentration opens the chance to control the rate by variation of the pH-value. An additional possibility to produce protons is given by irradiation of photo acids e.g. sulfonium salts. Those investigations are in progress.

![Graph showing Hammett-plot for the protolysis of triazenes](image)

**Figure 6.** Hammett-plot for the protolysis of triazenes T1 - T9 at room temperature, pH=7; 1=T1, 2=T2, 3=T4, 4=T7, 5=T6, 6=T5, 7=T8, 8=T12.
Table 3. Extrapolated rate constants \( k_{\text{exp}} \) at pH = 7 for different triazenes \( R_1\text{-Ph-N=N-N(C}_2\text{H}_5\text{)}_2 \)

<table>
<thead>
<tr>
<th>Triazene</th>
<th>Substituents</th>
<th>- log ( k_{\text{exp}} )</th>
<th>( t_{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>4-NO(_2)</td>
<td>- 7.470</td>
<td>39 years</td>
</tr>
<tr>
<td>T12</td>
<td>3-NO(_2)</td>
<td>- 7.430</td>
<td>36 years</td>
</tr>
<tr>
<td>T2</td>
<td>4-CN</td>
<td>- 6.068</td>
<td>2 years</td>
</tr>
<tr>
<td>T4</td>
<td>4-Cl</td>
<td>- 4.676</td>
<td>23 days</td>
</tr>
<tr>
<td>T10</td>
<td>3-OCH(_3)</td>
<td>- 3.629</td>
<td>2 days</td>
</tr>
<tr>
<td>T5</td>
<td>H</td>
<td>- 3.197</td>
<td>18 h</td>
</tr>
<tr>
<td>T6</td>
<td>4-CH(_3)</td>
<td>- 2.522</td>
<td>4 h</td>
</tr>
<tr>
<td>T7</td>
<td>4-OCH(_3)</td>
<td>- 1.697</td>
<td>35 min</td>
</tr>
<tr>
<td>T8</td>
<td>4-N(CH(_3))(_2)</td>
<td>0.170</td>
<td>28 s</td>
</tr>
</tbody>
</table>

5. PHOTOLYSIS OF TRIAZENES

Among the 1200 papers published on triazene chemistry in recent years there are only few dealing with the photochemistry of these compounds and those mostly are related to 1,3-diaryltriazenes and their application as doping material for laser ablation of polymethylmethacrylate [25-27].

Irradiation of triazenes with UV-light in general yields radicals and nitrogen:

\[
\begin{align*}
\text{N} & \text{N} \quad \text{N} \\
R_2 & \quad R_3 \\
\text{hv} & \rightarrow \\
\circ & \quad \cdot + N_2 + \bullet N_{R_2}^{R_3} \rightarrow \text{products}
\end{align*}
\]

The radical intermediates have been detected by ESR-spectroscopy [28]. A typical photolysis experiment is shown in Fig. 7.

The observed isosbestic points (1-3) are a clear indication for a well-defined decomposition mechanism, which is suitable described by a first order kinetics [29,30]. The uniformity of the decomposition is strongly supported by evaluation in Mauser plots according to (E3) (Fig.9) [31-34] in which straight lines were observed for most triazenes.

![Figure 7. Photolysis of T7 in THF, RT, followed by UV-spectroscopy, 0.2s intervals; lamp: Xe-high pressure.](image-url)
\[ \Delta A_i = f(\Delta A) \]  
(E3)

\( \Delta A_i \) = difference between absorption at \( t = 0 \) (\( A_0 \)) and absorption at \( t=t \) for a certain wavelength  
\( \Delta A_r \) = difference between \( A_0 \) and \( A_r \) for a reference wavelength.

Since the uniformity of the photolysis is confirmed one can determine the actual rate constants. A Hammett-plot of these rate constants results in a straight line, from which it was possible to determine \( \rho = -2.13 \). The advantage of the availability of Hammett-plots is that with known \( \sigma \)-values one can predict values of \( \delta \) for substituents which were not measured.

In order to get information about the excited state of triazenes some experiments were carried out in the presence of oxygen which is known to function as triplet quencher [35]. However, no change was observed in these experiments compared with those carried out in an argon atmosphere. Therefore the triplet excited state was considered to be unlikely. In contrast, experiments in the presence of pyrene, which is known to be an effective singulett quencher, have shown strong effects, e.g. decrease of the quantum yield by a factor of 5 to 10.

UV-spectra taken from selected triazene support the view, that the 1,3-dipole character is favored when the aromatic ring is substituted with electron withdrawing functions such as NO₂ or CN (T1, T2), indicated by absorption at high wavelength with high absorption coefficient (Table 4).

6. IR- AND RAMAN SPECTROSCOPY

A combination of IR and Raman spectra was used for the assignment of the \( \text{N=N} \) frequency. A survey on the position of the \( \text{N=N} \) signals of different triazenes is given in Table 5.

For para-substituted triazenes the frequency \( v (\text{N¹=N²}) \) decreases with increasing electron withdrawing character of the substituent. Meanwhile, the frequency of the \( \text{N²-N³} \) single bond increases, however, to a smaller extent. This behavior is expected for a 1,3 dipolar resonance structure.
Table 4. UV-absorptions of selected triazenes 4-R₁-Ph-N=N-N(C₅H₄)₂

<table>
<thead>
<tr>
<th>Triazene</th>
<th>R₁</th>
<th>λ₁ (nm)</th>
<th>ε₁ (l mol⁻¹ cm⁻¹)</th>
<th>λ₂ (nm)</th>
<th>ε₂ (l mol⁻¹ cm⁻¹)</th>
<th>λ₃ (nm)</th>
<th>ε₃ (l mol⁻¹ cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>NO₂</td>
<td>242</td>
<td>8400</td>
<td>—</td>
<td>—</td>
<td>371</td>
<td>23700</td>
</tr>
<tr>
<td>T2</td>
<td>CN</td>
<td>231</td>
<td>9500</td>
<td>—</td>
<td>—</td>
<td>328</td>
<td>22400</td>
</tr>
<tr>
<td>T4</td>
<td>Cl</td>
<td>227</td>
<td>10200</td>
<td>289</td>
<td>17900</td>
<td>320</td>
<td>15500</td>
</tr>
<tr>
<td>T5</td>
<td>H</td>
<td>227</td>
<td>8400</td>
<td>285</td>
<td>13900</td>
<td>308</td>
<td>13100</td>
</tr>
<tr>
<td>T6</td>
<td>CH₃</td>
<td>228</td>
<td>9300</td>
<td>287</td>
<td>14500</td>
<td>316</td>
<td>13400</td>
</tr>
<tr>
<td>T7</td>
<td>OCH₃</td>
<td>222</td>
<td>10300</td>
<td>291</td>
<td>15900</td>
<td>328</td>
<td>14000</td>
</tr>
</tbody>
</table>

Ab initio and semiempirical calculations (AM1, PM3, SCAMP [36]) also support the 1,3 dipolar structure of the triazenes: the highest degree of N¹=N²-double bond character is calculated for R₁ = OCH₃ and the lowest for R₁ = NO₂, and corresponding with those results the single bond character for N²-N³ increases from R₁ = NO₂ to R₁ = OCH₃.

7. DOPANT INDUCED LASER ABLATION OF PMMA AT 308 NM

Since the early reports in 1982 [39,40] ablative photodecomposition of polymers became a field of intense investigation. Recently promising results have been published for the ablation of PMMA by a 308 nm excimer laser, using diphenyltriazene as dopant [41].

The following figures show undoped PMMA after irradiation with 308 nm excimer laser (fluence F > 6.5 J cm⁻²). In this case PMMA is damaged but not structured (Fig. 10). Better results were received by doping of PMMA with triazenes (Fig. 12): the film surface is now clearly structured. For these experiments films were cast from THF solution of PMMA doped with different amounts of 4-NC-Ph-N=N-N(C₅H₄)₂ (T2) of 200μm thickness. These films were irradiated with a 308 nm excimer laser with a repetition rate of 2 Hz and a pulse length of 30 ns (fluence between 0.5 and 11.2 J cm⁻²). Results of the ablation experiments performed on two doped PMMA samples of different molar masses are presented in Fig. 11. The triazene (T2) concentration was varied between 1 and 2 wt %.

Doubling the triazene concentration roughly halves the limiting etch depth per pulse. Fig. 11 shows also a dependence of the etch depth on the molar mass, indicating that the etch depth is always lower for higher molar masses under comparable conditions.

The ablation quality is also a function of the triazene concentration - sharper, higher quality structures are received when higher triazene concentrations are applied (Fig. 12).

Table 5. Effect of the substituents R₁ in 4-R₁-Ph-N=N-N(C₅H₄)₂ on the vibrational frequencies of the triazene group in cm⁻¹

<table>
<thead>
<tr>
<th>Compound</th>
<th>R₁</th>
<th>v (N¹=N²)</th>
<th>v (N²-N³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raman</td>
<td>IR</td>
<td>Raman</td>
</tr>
<tr>
<td>T8</td>
<td>N(CH₃)₂</td>
<td>1417/1407</td>
<td>1416/1406</td>
</tr>
<tr>
<td>T5</td>
<td>H</td>
<td>1414</td>
<td>1414</td>
</tr>
<tr>
<td>T7</td>
<td>OCH₃</td>
<td>1408</td>
<td>1407</td>
</tr>
<tr>
<td>T6</td>
<td>CH₃</td>
<td>1403</td>
<td>1403</td>
</tr>
<tr>
<td>T3</td>
<td>COOH</td>
<td>1397</td>
<td>1401</td>
</tr>
<tr>
<td>T2</td>
<td>CN</td>
<td>1386</td>
<td>1384</td>
</tr>
<tr>
<td>T1</td>
<td>NO₂</td>
<td>1391</td>
<td>1383</td>
</tr>
</tbody>
</table>
The much better ablation results on the doped material might be best explained on the basis of a "driving gas" effect of the nitrogen formed during irradiation. However, a large quantity of ejected material is seen around the edges of the crater. Furthermore, both the walls and the bottom of the crater exhibit an irregular structure.

These studies demonstrate that non-absorbing polymers can be efficiently doped for 308 nm eximer laser ablation by adding small amounts of substituted 1-phenyl-3,3-dialkyl triazenes. Crater formation is induced by a photochemical ablation mechanism on the basis of photolytic fragmentation of the dopant. Nitrogen acts as driving gas for the ejection of the polymer material. Ablated depth per pulse as high as 80μm have been observed.

The dependence of the etch rate on laser fluence exhibits two regimes, i.e. a linear dependence on the logarithm of fluence \{ln (F/F_0)\} followed by a plateau region. In the linear

**Figure 9.** Raman spectra of para-substituted triazenes.

**Figure 10.** Electron micrograph of PMMA film, irradiated with a 308 nm excimer laser, 1 and 2 pulses (F = 6.5 and 11.7 Jcm\(^{-2}\)).
regime, the ablated depth per pulse is proportional to the quantum yield of the photochemical decomposition and follows the 1/c dependence. In the plateau a thermal mechanism, i.e. the absorption of photons followed by the thermolization of the energy, provides the dominant contribution to the ablation. Therefore the photolysis quantum yield QY appears to be no longer of importance.

8. EXCIMER LASER ABLATION OF TRIAZENE POLYMERS

The alternate route to chromophore doped polymers as described above is the tailored synthesis of photopolymers containing a suitable chromophore group, e.g. triazene polymers of the following structure:

![Image of electron micrograph of laser ablated PMMA doped with T6; a) 2mol%, b) 5mol% (P = 5.8 Jcm⁻²).]
The polymers were synthesized according to the following general procedure: A bis(4-aminophenyl) ether, ketone, or sulfone ($R_1 = O$, CO, SO$_2$) was diazotized with the nitrite in hydrochloric acid. The resulting diazonium salt was reacted in situ directly with a substituted $\alpha,\omega$-diaminoalkane to yield the desired product in a polycondensation reaction. The polymers TP1 through TP9 were characterized by GPC, NMR spectroscopy, DSC, and TGA.

Molar masses of TP1 to TP9 are in the range of 50,000 to 120,000 g/mol ($M_w$), measured by GPC. From TGA-studies one can conclude that the N$_2$ and the R$_3$-N-R$_4$-N-R$_3$ unit are released in one step between 210 and 300°C. Some data are summarized in Table 7.

From these polymers films were prepared by casting from THF-solution. After drying films of 100 - 200 $\mu$m thickness were received. Technical details about the laser ablation procedure are described elsewhere [41,43].

Polymer TP8 was chosen as a representative example to illustrate the structures resulting from eximer laser irradiation. A scanning electron micrograph of an ablation crater

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Table 6. Structural formulas of investigated triazene polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$R_1$</th>
<th>$R_2$</th>
<th>$R_3$</th>
<th>$R_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>O</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>TP2</td>
<td>O</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$_2$H$_4$</td>
</tr>
<tr>
<td>TP3</td>
<td>—</td>
<td>OCH$_3$</td>
<td>CH$_3$</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>TP4</td>
<td>p-SO$_2$</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>TP5</td>
<td>m-SO$_2$</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>TP6</td>
<td>CO</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$<em>6$H$</em>{12}$</td>
</tr>
<tr>
<td>TP7</td>
<td>O</td>
<td>H</td>
<td>CH$_3$</td>
<td>C$_3$H$_6$</td>
</tr>
<tr>
<td>TP8</td>
<td>O</td>
<td>H</td>
<td>C$_2$H$_5$</td>
<td>(CH$_2$-CH=)$_2$</td>
</tr>
<tr>
<td>TP9</td>
<td>CO</td>
<td>H</td>
<td>C$_2$H$_5$</td>
<td>(CH$_2$-CH=)$_2$</td>
</tr>
</tbody>
</table>

---

Table 7. Physicochemical reference data of triazene polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ (g/mol)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\epsilon_1$/Lmol$^{-1}$cm$^{-1}$ at 308nm (in solution)</th>
<th>Photolysis quantum yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>71,000</td>
<td>330</td>
<td>27,700</td>
<td>0.26</td>
</tr>
<tr>
<td>TP2</td>
<td>46,000</td>
<td>353</td>
<td>24,900</td>
<td>0.39</td>
</tr>
<tr>
<td>TP3</td>
<td>53,000</td>
<td>367</td>
<td>11,300</td>
<td>0.17</td>
</tr>
<tr>
<td>TP4</td>
<td>107,000</td>
<td>336</td>
<td>23,200</td>
<td>0.12</td>
</tr>
<tr>
<td>TP5</td>
<td>207,000</td>
<td>293</td>
<td>22,500</td>
<td>0.16</td>
</tr>
<tr>
<td>TP6</td>
<td>62,000</td>
<td>352</td>
<td>17,200</td>
<td>0.13</td>
</tr>
<tr>
<td>TP7</td>
<td>19,000</td>
<td>331</td>
<td>23,900</td>
<td>0.74</td>
</tr>
<tr>
<td>TP8</td>
<td>9,000</td>
<td>334</td>
<td>22,400</td>
<td>0.64</td>
</tr>
<tr>
<td>TP9</td>
<td>69,000</td>
<td>357</td>
<td>18,400</td>
<td>0.16</td>
</tr>
</tbody>
</table>
produced is shown in Fig.13. The sample was irradiated with 100 pulses of 1.2 J/cm$^2$ fluence at 308 nm. Very sharp contours and steep edges were observed for the irradiated area.

Similar sharp contours have been found for all other polymers TP1 to TP9. This favorable behavior which has rarely been observed with any other materials, appears to be an unique property of triazene polymers. For triazene polymers the ablation is fully governed by the photolytic decomposition of the triazene groups.

A striking feature that distinguishes the triazene polymers from other photosensitive materials used in laser ablation is the absence of ejected material deposited around the crater. A possible reason for the absence of solid ablation products, the so-called “debris”, is the well-defined fragmentation of the polymers. Small gaseous products, in particular N$_2$, are acting as a driving gas which promotes at least the initial stages of the ablation.

For all triazene polymers the total ablated depth at given fluence (laser pulse energy per irradiated area) increases linearly with the number of pulses. In the low-pulse energy regime the fluence dependence is well described by the equation:

$$d(F) = \frac{1}{\alpha_{eff}} \ln \left( \frac{F}{F_0} \right)$$

(E4)

$d(F) =$ ablated depth per pulse
$F =$ laser fluence
$F_0 =$ threshold fluence
$\alpha_{eff} =$ effective absorption coefficients for ablation
(typical data: $\alpha_{eff} \approx 2 \times 10^4$cm$^{-1}$, $F_0 \approx 100$ mJ/cm, $F_0 \times \alpha_{eff} \approx 2$ kJ/cm)

A common feature of the triazene polymers is the absence of any simple relation between the effective absorption coefficients obtained from the ablation data and the molar absorption coefficients at 308 nm in solution. This lack of correlation is not unusual in
polymer ablation [44] and has been ascribed to nonlinear effects (saturation of absorption, multiphoton effects) and to absorption by laser induced plasma photoproducts [45].

9. RESOLUTION TESTS

The achievable structural resolution by laser ablation was tested for material TP1. A rectangular slit mask was imaged onto the sample (coated as described above) to illuminate a stripe of \( \approx 1 \mu m \) width. The sample was irradiated with 10 pulses of 0.2 J/cm\(^2\) fluence. The results are shown in Fig. 14.

Again, an unique feature is the absence of any solid polymer deposits around developed structures. Furthermore the high resolution tests with the triazene polymers material yield resolutions near to 0.4 \( \mu m \). These both facts render the triazene polymers very suitable for laser ablation structuring in microlithography.

CONCLUSION

Low molecular triazenes, added to common polymers, and triazene polymers are both suitable for laser ablation. The differences between PMMA doped with low molecular triazenes (A) and polymers containing triazene units in the main chain (B) are as follows:

(A)
- ablation depth \( \sim 70 \mu m/pulse \)
- ablation depth \( \sim 1/[\text{triazene}] \)
- low level of doping necessary for large effects
- photochemical produced \( N_2 \) is driving gas for the ablation
- change from photochemical into photothermal ablation as a function of laser fluence

(B)
- ablation depth \( \sim 2-3 \mu m/pulse \)
• ablation depth \( \sim 1/\alpha_{\text{eff}} \)
• unusual proportionality between photolysis and quantum yield
• sharp contours
• resolution 500\( \text{Å} \)
• no deposits around the ablation crater

REFERENCES