

# Laser-Induced Dissociation of an Energetic Polymer: A Spectroscopic Study of the Gaseous Products

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Received: March 23, 2000; In Final Form: August 17, 2000

Previous studies of GAP (glycidyl azido polymer) laser-induced decomposition (*Propellants, Explosives, Pyrotechnics* **1996**, 21, 258), revealed that the shock wave produced from a diluted polymer is more energetic than from the neat polymer. In this paper, direct measurement of the energy disposal into molecular products is reported using spectroscopic methods. Chemiluminescence probes electronically excited species, and laser-induced fluorescence, ground-state radicals. It is found that the initial velocity and internal energy content of small diatomic molecules is larger in some diluted polymers than in the neat one. This finding is in line with a simple model based on the assumption of a self-sustained reaction following initial laser excitation.

## 1. Introduction

Pulsed UV laser ablation (rapid removal of material by evaporation) of polymers has been studied since the early 1980s. This method is commonly used to etch selectively predetermined parts of a polymer's surface,<sup>1</sup> to drill holes, and otherwise to modify the material. The ablation mechanism has been extensively studied, but a universally accepted model is still not available. The removal of solid material has been related to a complex process, starting with the absorption of laser pulse radiation. Early on, it was assumed that only strongly light absorbing substances could be etched.<sup>2</sup> It is clear now that even materials that are transparent at low light intensities can be etched by focusing the initiating laser beam.<sup>3</sup> The energy of a single UV photon is sufficient to break the typical chemical bonds of the polymer, but bond-cleavage alone cannot lead to ablation of matter from the surface. For successful ablation, bond recombination must be avoided,<sup>4</sup> and the fragments must be quickly removed from the surface. These two conditions are fulfilled if a large amount of energy is delivered to the products in a sufficiently short time; high-power pulsed lasers turn out to be ideal energy sources for this application and are commonly employed for this purpose. The removal of material is often rather violent, as flash photographs shows.<sup>3,5,6</sup> Gaseous and particulate matter are ejected on a short time scale, frequently during the laser pulse which is in the  $10^{-8}$ – $10^{-12}$  s range. The details of the ablation mechanism are still a matter of debate; both photochemical and thermal processes and several photo-thermal mechanisms were suggested in the literature.<sup>7–10</sup>

A visible luminescent plume often accompanies the ablation of solid materials, as has been shown by several groups. Dyer et al.<sup>5</sup> reported that in the case of polyimides, the main emission bands are due to CN and C<sub>2</sub>. The emission was related to the formation of a shock wave, created by the rapid compression of ambient gas by the expanding gases released from the surface. As the pressure is reduced (typically to below 0.5 mbar), the shock is formed away from the surface, and the luminescence

becomes weaker. At pressures exceeding 15 mbar, the ideal blast model (strong shock wave) is approached. Geohagen<sup>11</sup> studied the emission accompanying the ablation of the high TC superconducting material YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>, recording visible emission whose spectrum was not reported. He also proposed a shock wave mechanism for the formation of the electronically excited species when the ambient pressure was high, and a drag force mechanism for the low-pressure regime. Some emission was recorded under high vacuum ( $10^{-6}$  mbar) conditions.

“Energetic” polymers containing reactive groups such as the azido (–N<sub>3</sub>) group are being increasingly used in the propellant industry.<sup>12,13</sup> The decomposition of these polymers is highly exothermic, and under appropriate conditions the reaction can be self-sustaining. When irradiated with a pulsed laser, the polymers undergo fast decomposition, in a process that is similar to ablation. However, in distinction with the case of inert polymers, the decomposition reaction is exothermic and may evolve into self-propagation; therefore, the amount of material ejected per laser pulse can be much larger than in the case of inert polymers.

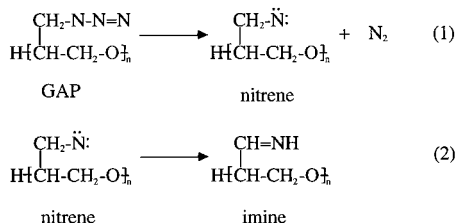
We have reported the laser-induced decomposition of the energetic polymer GAP (glycidyl azido polymer) that contains an azido group.<sup>14–16</sup> The present work follows these earlier studies, in which some unexpected results were recorded. A brief summary of the previous results is given in order to introduce not only the results but also the concepts and notation. A fuller account may be found in ref 15 and 16.

The decomposition of GAP begins by the dissociation of an N–N bond to form molecular nitrogen, and a nitrene radical (Scheme 1). The final products are N<sub>2</sub>, CO, H<sub>2</sub>, H<sub>2</sub>O, HCN and some small hydrocarbons. The irradiation of a solid GAP sample by either a pulsed IR<sup>14</sup> or UV<sup>15,16</sup> lasers leads to dissociation accompanied by a copious release of gaseous and particulate matter. In the presence of an inert gas (such as N<sub>2</sub>), the rapid expansion of the ejected material led to the formation of a shock wave propagating away from the sample. As described in ref 15 the shock propagation was monitored by using the deflection of a continuous He:Ne probe laser beam placed parallel to the sample at a fixed vertical distance *h*. When the shock front arrives at the probe laser's beam, part of the beam is deflected

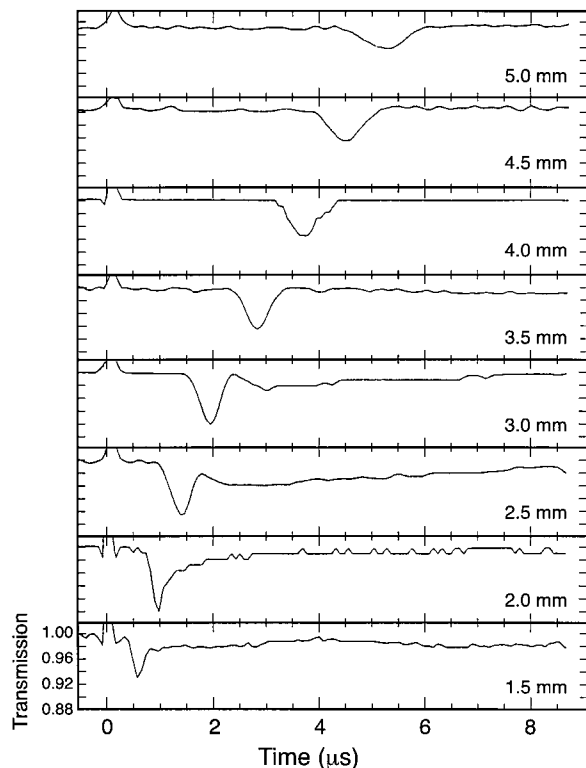
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**SCHEME 1: Schematic Representation of GAP Thermal Decomposition**

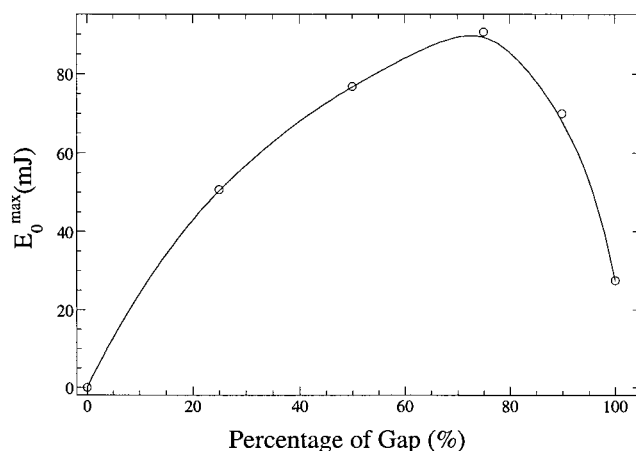
<sup>a</sup> The first step is the extrusion of molecular nitrogen from the azido residue, to form a nitrene. The nitrene either dissociates further (e.g., by forming CN, CH and NH radicals, or isomerizes to an imine, that dissociates to the final products.



**Figure 1.** Transmission of the monitoring (He-Ne) laser intensity as a function of time after the initiating laser pulse. Maximum attenuation is attained at longer times as  $h$ , the distance between the He-Ne laser beam and the sample, is increased. The value of  $h$  is shown at the upper right corner of each frame. The sample was neat GAP, nitrogen gas pressure was 400 Torr and the UV laser energy reaching the sample  $\sim 23$  mJ. (Taken from ref 15.)

and an attenuated signal is observed. Figure 1 (taken from ref 16) shows the intensity of the monitoring laser beam as a function of the time after initiating laser pulse, for several values of  $h$ , the vertical distance of the probe laser beam from the GAP polymer's surface. The figure shows that the time to reach maximum attenuation,  $T_m$ , increases monotonically and that the attenuation depth decreases gradually as  $h$  increases.

Assuming that this attenuation signal is due to the deflection of the monitoring laser beam by the shock wave,<sup>15</sup> a plot of  $h$  vs  $T_m$  represents the development of the radial shock away from the initiating location. According to this interpretation, the shock's front, which advances as a hemisphere with a radius  $R$ , arrives at the distance  $h$  after a time interval  $T_m$ ; the velocity of the radial shock front,  $U(t)$ , is obtained from the slope of the  $h$  vs  $T_m$  plot. It was found that the conditions required for a strong shock are not fulfilled in this case. A weak shock limit



**Figure 2.** Shock wave intensity (expressed as  $E_0^{\max}$ ) vs GAP percentage in diluted polymers. (Data taken from ref 15.) A clear decrease in the shock wave intensity is observed as the GAP percentage increases beyond 75%.

expression<sup>17</sup> was used in our previous analysis.<sup>15,16</sup> In that approximation, tabulated numerical solutions of the shock wave equations were used to find the shock creation energy  $E_0$  (see Appendix 1). It was found that in the laser ablation of GAP,  $E_0$  was larger than the laser pulse energy,  $E_L$ , while for the inert polymer, which served as a reference,  $E_0$  was much smaller than  $E_L$ .

The approximate theory that takes into account counter pressure does not describe properly the development of the micro blast wave, generated after UV laser irradiation of energetic polymers. One deviation from the assumptions underlying Sedov's theory's<sup>17a</sup> is the fact that the shock formation time is not negligible in compare to measured shock travel time. Under these conditions, the calculated  $E_0$  is not constant but increases initially and then decreases. The maximum value of  $E_0$ ,  $E_0^{\max}$  is reached only after the shock traveled a distance of 1–5 mm; the time required for this travel is a few microseconds. The calculated  $E_0^{\max}$  values may thus be considered as empirical parameters characterizing the shock, rather than firm theoretically based values.

Laser irradiation of a mixed polymer, in which GAP was diluted by an inert polymer (in which a chlorine atom substituted the azido group), also resulted in shock wave formation. In some cases the shock's intensity, as measured by its velocity and the calculated energy  $E_0^{\max}$ , was larger than that obtained upon irradiation of neat GAP! This unexpected result prompted us to measure  $E_0^{\max}$  as a function of the polymer's composition. As Figure 2 (also taken from ref 16) shows,  $E_0^{\max}$  increases with the GAP percentage up to about 75%, and then shows a pronounced decrease. In contrast, weight loss (Figure 7 of ref 16) was found to increase monotonically with the GAP percentage.

A simple model was offered in an attempt to account for the apparently surprising dependence of the shock's intensity on the polymer's composition. The model assumes that the laser initiates a self-sustaining thermal reaction in the system. According to this model, a certain critical temperature,  $T_c$ , must be attained in order for the reaction to become self-sustaining. At this temperature, the rate of heat generation by the reaction's exothermicity equals the rate of heat loss due to dissipation processes. The maximum temperature attained in the region illuminated by the laser is determined by the laser pulse's energy density and the by the polymer's composition. It is well established that ignition of solid explosives proceeds from microstructural discontinuities called "hot spots".<sup>18</sup> The laser initiation

of GAP decomposition is assumed to involve hot spots whose density determines the temperature of the bulk. The laser's pulse creates a number of hot spots (their number depends on the laser's fluence), and heating continues until  $T_c$  is attained; after that the reaction is sustained by its own exothermicity, and the hot spots increase in size. In the diluted polymers, the hot spots are further apart than in concentrated ones, leading to a higher critical temperature  $T_c$  and consequently to a higher velocity of the ejected molecules. Therefore, as the polymer becomes diluted, a smaller amount of material may be ejected, but with a greater velocity. The balance between these two parameters leads to a maximum  $E_0^{\max}$  at an intermediate composition.

According to this model, heat transfer from the radiation field to the propellant raises the temperature gradually of the solid, until the critical temperature,  $T_c$  is attained. Under certain simplifying assumptions, the following equation for  $T_c$  can be derived (see eq 8.40 of ref 19 and the discussion leading to it)

$$T_c = (E_a/R)[\ln(q^0 \rho \lambda T_0 A / q^2)]^{-1} \quad (1)$$

where  $E_a$  and  $A$  are the activation energy and the preexponential factor of the decomposition rate constant of the chemical process, respectively.  $R$  is the gas constant,  $q^0$  the heat released in the chemical reaction per unit mass consumed,  $\rho$  the density of the solid,  $\lambda$  the thermal conductivity of the solid,  $T_0$  the ambient temperature, and  $q$  the heat flux, which initiates the reaction (the laser energy flux in the laser ablation case). Equation 1 is derived under the assumption that the heat transfer to the unreacted solid zone is the main dissipation process.

In the laser-induced decomposition of GAP, we may assume that the quantities appearing in eq 1, except  $q^0$  are constant for all polymer compositions. As the polymer is diluted,  $q^0$  becomes smaller, and according to eq 1  $T_c$  increases. The physical interpretation is, that the temperature needed in order to sustain a self-propagating reaction in a diluted polymer is higher than in a concentrated one. In other words, a diluted polymer must be heated to a higher temperature during the UV laser irradiation period than neat GAP, before the threshold for a self-sustained reaction is attained. This in turn will lead to a higher velocity of the released gases and thus to a stronger shock.

In an attempt to check the validity of the assumptions underlying the model, we carried out some real-time experiments on the system. In this paper we report chemiluminescence (CL) and laser-induced fluorescence (LIF) experiments on neat and diluted GAP polymers. Upon UV ablation of GAP, in the presence of ambient gas, visible light emission was observed from gaseous particles emanating from the heated solid. The characteristics of this emission and of the emitting electronically excited species were studied. These real time measurements made it possible to estimate the translational velocity of the molecules leaving the surface, and hence, check the assumptions of the proposed model. In addition, ground-state CN radicals formed in the ablation process were monitored by LIF, allowing the measurement of their velocity and internal energy as a function of the polymer's composition. The results are in good qualitative agreement with the model.

## 2. Experimental Section

The solid polymer was prepared as previously described.<sup>14</sup> For the GAP/inert mixtures, the procedure described in ref 16 was used. The laser irradiation setup, and the instrumentation used to measure the chemiluminescence of gaseous products was based on the apparatus previously used to detect shock wave

propagation, described in detail in ref 15. Therefore, only a brief summary is given here, emphasizing the changes.

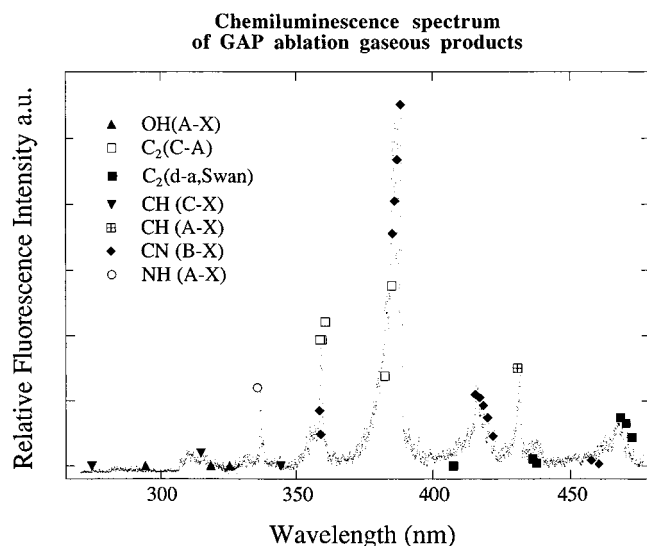
The sample, a 1 mm thick, 17 mm diameter disk of the solid polymer, was mounted on a rotating brass plate inside an evacuable cubic aluminum cell. The pressure was adjusted to the desirable value, and the sample irradiated by a mildly focused pulsed (10 Hz) UV laser beam. A frequency tripled Nd:YAG laser operating at 355 nm (Continuum model 681) with a pulse width of 10 ns was used. Luminescence was collected at right angles to the laser beam at a height  $h$  above the sample. Raising or lowering the sample holder with respect to the optical observation point was used to vary  $h$ . A lens system was used to restrict observation mostly to a small volume ( $\sim 1 \text{ mm}^3$ ). The emitted light was focused on the entrance slit of a 0.34 m monochromator (SPEX 340E), and detected by a photomultiplier or an ICCD detector (Princeton Instruments ICCD576G/RB). The laser pulse was used to initiate the timing sequence. The overall time resolution of the system was about 10 ns with the photomultiplier, and 50 ns with the ICCD. In all experiments the initiating laser beam was focused to the same spot size of about 0.02 cm diameter.

In the laser-induced fluorescence (LIF) experiments, the same cell and light collecting systems were used. A tunable dye laser (Lambda-Physik DL3002 pumped by an excimer laser) was used to excite the fluorescence of gaseous products, at a predetermined height  $h$  above the sample. The dye laser beam was perpendicular to both the UV laser beam and to the direction of the fluorescence detection. A digital delay generator (SRS model DG535) controlled the time delay between the two laser pulses with an accuracy of about 10 ns.

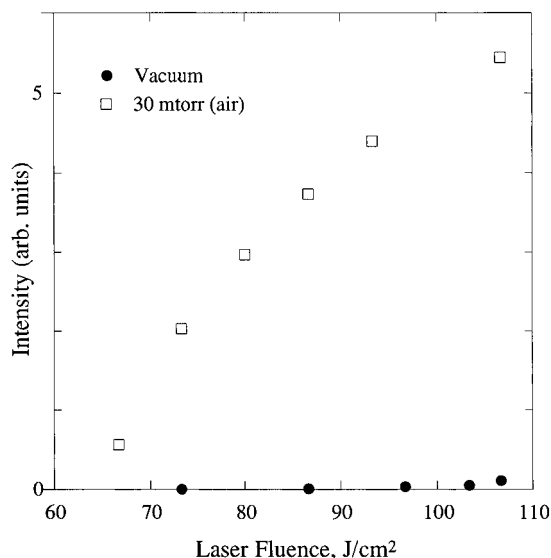
## 3. Results

The yellow hue of GAP is due to a broad absorption band whose maximum is at about 280 nm, extending to about 400 nm. At 355 nm the absorption cross section as measured by low intensity light sources is rather small, so that total absorption occurs only with samples that are more than 1 mm thick. In the laser ablation experiments, total absorption appears to take place over a much smaller thickness. Irradiation of a fresh sample was often found to lead to an intense luminescence signal that disappeared after a brief exposure to the laser beam. We assume that it was due to impurities adsorbed on the surface. This initial irradiation period led to changes in the sample's color and texture: a white opaque circle appeared on the yellowish transparent solid marking the area irradiated by the UV laser. Subsequent irradiation of the same area led to the observation of a fairly reproducible chemiluminescence signal. It appears that the initial irradiation, in addition to removing adsorbed contaminants, modifies the polymer's surface, forming a species that absorbs more strongly than GAP at 355 nm. All the data reported below were obtained after the polymer was briefly exposed to the 355 nm laser beam.

Under these conditions, light emission is observed from the polymer's surface as well as from a plume extending into the gas phase. The plume, clearly visible to the eye in a darkened room, extends several centimeters into the cell. Its emission intensity depends on the pressure of ambient gas in the cell, attaining a maximum between 0.1 and 1 Torr, depending on the laser pulse's fluence (energy density per unit area), the polymer's composition and the gas used. Under high vacuum conditions (at pressures lower than  $10^{-5}$  Torr), chemiluminescence is observed only above a certain threshold energy density (typically  $100 \text{ J/cm}^2$ ). The threshold energy was found to decrease with increasing pressure in the cell. The ablation



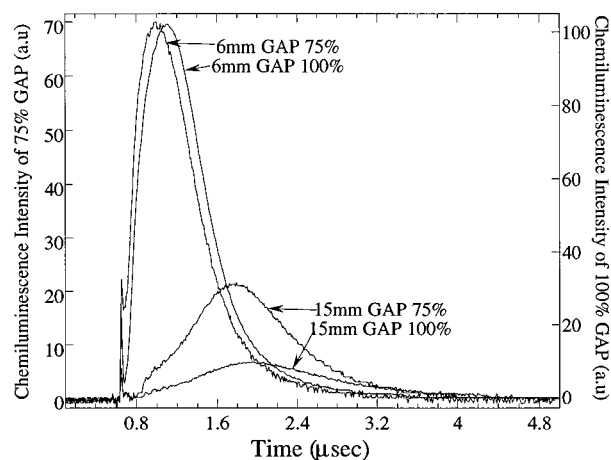
**Figure 3.** Luminescence spectrum observed in the gas phase upon irradiation of GAP by 355 nm laser radiation, in the presence of 70 mTorr air. The dotted curve is the observed spectrum; the symbols represent the calculated positions and relative intensities of the main vibronic bands. The assignment of this spectrum, referred to in the text as the chemiluminescence spectrum of GAP, is discussed in section 4. The positions and relative intensities of the calculated spectra were taken from the following sources: CN,<sup>20,26</sup> CH,<sup>22</sup> C<sub>2</sub>,<sup>21</sup> NH,<sup>23</sup> OH.<sup>24</sup>



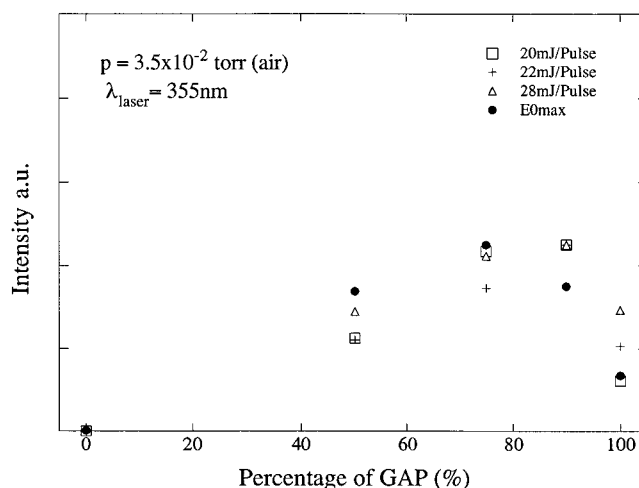
**Figure 4.** Chemiluminescence intensity of CN\* (measured at 387 nm) as a function of pressure and laser fluence. Under vacuum, no chemiluminescence is observed at low laser fluence.

process, as monitored by the etch-depth was found to be independent of the ambient gas pressure.

**3a. Chemiluminescence Data.** Figure 3 shows a typical chemiluminescence spectrum obtained in the presence of about 70 mTorr air, with pure GAP. The same spectrum was obtained when argon replaced air as the surrounding gas. All major bands could be assigned to diatomic species, as shown in the figure and detailed in Table 1S. Most of the quantitative measurements were taken on the CN  $B(^2\Sigma(v=0)) \rightarrow X(^2\Sigma(v=0))$  transition around 387 nm. Figure 4 demonstrates that at high vacuum, no chemiluminescence is observed. The time dependence of some typical chemiluminescence signals is shown in Figure 5. It is seen that for a given observation height  $h$ , the signal reaches its maximum at shorter time intervals when the 75% polymer is irradiated, than when neat GAP is used. For instance, under



**Figure 5.** CN radical chemiluminescence intensity as a function of time after the initiating laser pulse, at different heights above the sample. It is seen that the maximum intensity is reached earlier in the case of the more dilute sample.

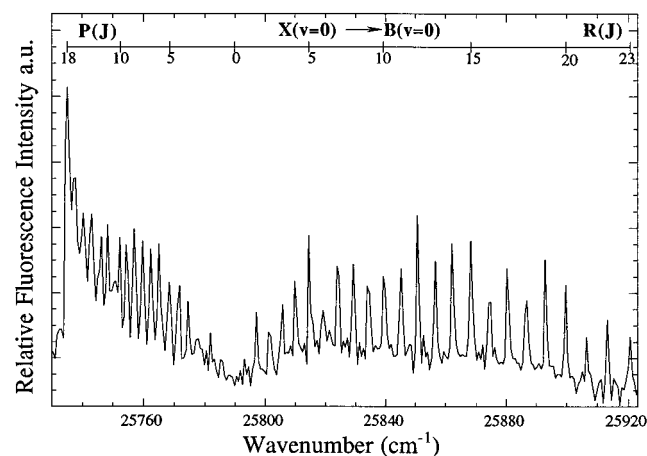


**Figure 6.** Chemiluminescence intensity as a function of the polymer's composition. The shock wave intensity (expressed as  $E_0^{\max}$ ) is also shown (data of Figure 2).  $E_0^{\max}$  was normalized to 1 at 75% GAP.

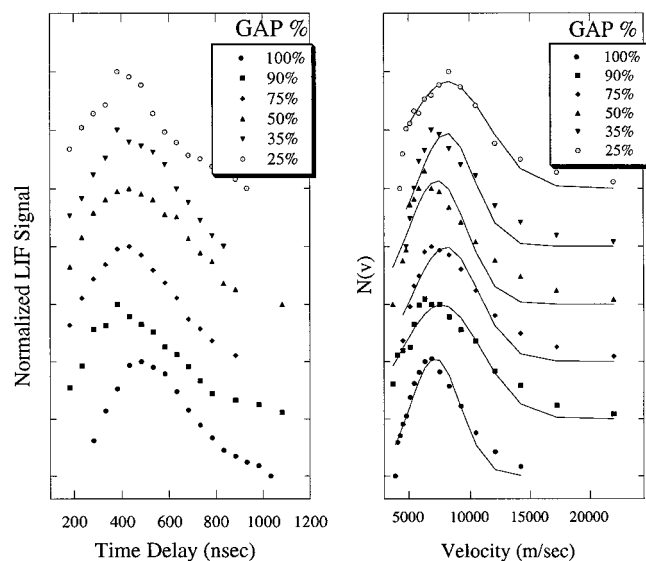
the conditions of the experiment, at  $h = 6$  mm, the maximum is reached after  $0.98 \mu\text{s}$  with the 75% sample, and after  $1.12 \mu\text{s}$  with neat GAP. Thus, a typical velocity of the particles leading to chemiluminescence is  $6100 \pm 500$  m/s for the 75% composition, and  $5300 \pm 500$  m/s for neat GAP. Although these differences are not large, they were found to be consistent in many sets of experiments. Figure 6 shows the time-integrated intensity of the chemiluminescence as a function of the polymer's composition; for comparison; the dependence of the shock wave intensity ( $E_0^{\max}$ ) on the polymer's composition is also shown (data of Figure 2). Both follow the same pattern — a maximum is reached at a concentration between 75% and 90% GAP. Similar data were obtained also for chemiluminescence of NH monitored at the A ( $^3\Pi$ )  $\rightarrow$  X ( $^3\Sigma^-$ ) transition.

**3b. LIF Data.** Figure 7 shows a typical fluorescence excitation spectrum, obtained with a 90% polymer. In this experiment, the dye laser was scanned across the CN  $B(^2\Sigma(v=0)) \leftarrow X(^2\Sigma(v=0))$  absorption band, and emission was monitored around 389 nm. The assignment was confirmed by the good agreement with the calculated line positions, also shown in the Figure. Further confirmation was provided by the measured lifetime of the emitting species  $-56 \pm 5$  ns, close to the literature value<sup>27</sup> of 62 ns.





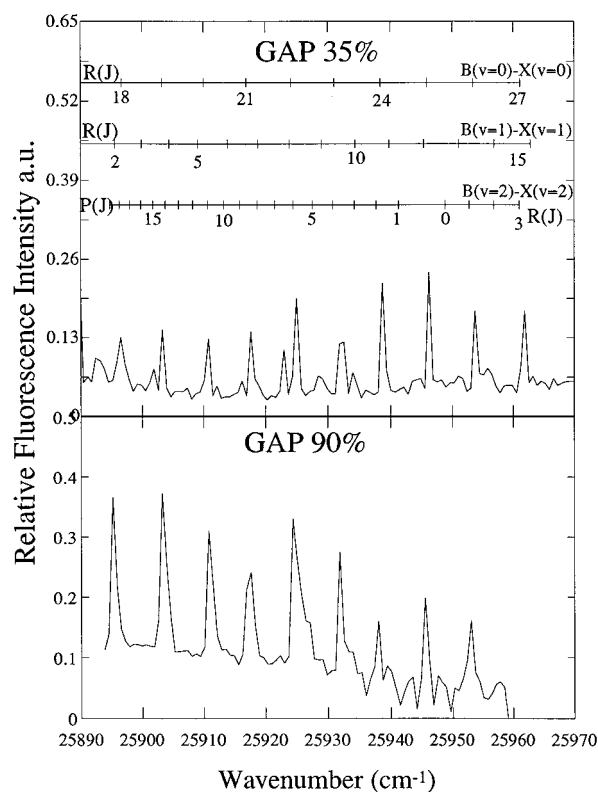
**Figure 7.** Laser-induced fluorescence excitation spectrum of CN radicals produced by 355 nm laser ablation of neat GAP. Emission was monitored at  $389 \pm 5$  nm through the monochromator. Experimental conditions: laser fluence  $28 \text{ J/cm}^2$ , ambient pressure  $10^{-4}$  Torr,  $h = 7.5$  mm.



**Figure 8.** (a) Intensity of the CN LIF signal as a function of the time delay,  $t_D$ , between the initiating laser and the monitoring laser, for different polymer compositions. Experimental conditions as in Figure 7, the line monitored was R(12). (b) Velocity distribution of the CN radicals, for different polymer compositions, obtained from the time delay data

The velocity distribution of the CN radicals was measured by tuning the dye laser to one of the rotational bands of transition, and measuring the emission intensity as a function of the time delay,  $t_D$ , between the 355 nm initiation laser and the dye probe laser. Figure 8a shows typical results: it is seen that the delay time at which a maximum signal is attained, increases with the GAP concentration in the sample. The data were converted to velocity distribution using the Jacobian  $N(v) = N(t)t^2/h$ ,<sup>25</sup> as shown in Figure 8b. The solid lines in Figure 8b represent a two parameter fit to help visualization.

It is seen that the most probable velocity increases from about  $7000 \pm 700$  m/s for neat GAP, to about  $8500 \pm 900$  m/s for the 25% composition. These values are in line with the general trend of the chemiluminescence measurements—the velocity of the ejected particles is in general higher in diluted polymers than in concentrated ones. (The 50% sample appears to deviate from this general trend—we used only one preparation for this concentration and did not repeat the experiment.)



**Figure 9.** Part of the laser-induced fluorescence excitation spectrum of CN ( $X \rightarrow B$  transition): (upper panel) 35% GAP; (lower panel) 95% GAP. The calculated  $\Delta V = 0$  rotational lines are shown for  $v'' = 0$ ,  $v'' = 1$  and  $v'' = 2$ .

All rotational transitions observed in the spectrum shown in Figure 7 could be assigned as due to the  $v'' = 0$  vibrational level of the CN radical. According to the assumptions of the model, the solid polymer is heated to a higher temperature as GAP is diluted with an inert polymer. This should be reflected in the energy disposal into the products: if the surface is hotter, enhanced vibrational and rotational excitation of the CN radicals leaving it should be observed. Figure 9 shows a portion of the excitation spectrum obtained with 90% GAP and with a 35% polymer compositions under identical experimental conditions. Many additional rotational transitions are seen in the latter. They could be assigned to  $\Delta v = 0$  transitions from the vibrationally excited-state  $v'' = 1$  or  $v'' = 2$  of CN in the ground electronic state. The spectra of other dilute polymers (e.g., 25%) also showed an increase in the population of excited vibrational states. Although a quantitative estimate of the population ratio of the different vibrational state cannot be made from these data, it is safe to estimate the population of the  $v'' = 1$  level as less than 2% for both neat GAP and the 90% composition. This estimate is based on the Franck–Condon factors for this molecule, strongly favoring  $\Delta v = 0$  transitions (see Table 2S), and the absence of lines originating from the  $v'' = 1$  level. For the 35% composition, the ratio is estimated to be about 10%.

#### 4. Assignment of the Transitions Observed in Chemiluminescence

The assignments were based mostly on the observed frequencies. Relative intensities were less reliable, since the emission spectrum is a combination of several exposures taken using the ICCD. Within a given frame (approximate width 56 nm) intensities are comparable, but between frames, the error may be as high as 30%. The most intense feature is the band

extending from 378 to 388 nm. It is assigned to the  $\text{CN } \text{B}(^2\Sigma) \rightarrow \text{X}(^2\Sigma) \Delta v = 0$  transitions (blue side) and the  $\text{C}_2 \text{C}(^1\Sigma) \rightarrow \text{A}(^1\Sigma) \Delta v = 0$  transitions (red side). As indicated in Figure 3, the CN "band" is probably actually due to transitions from several vibrational levels, the  $v'' = 0$  to 3 levels. This is supported by the bands appearing between 415 and 420 nm, that are assigned to the  $\Delta v = +1$ . Table 2S lists the Franck Condon (FC) factors for this system. For the  $\Delta v = 0$  series they decrease monotonically as  $v$  increases, from 0.92 at  $v = 0$  to 0.59 at  $v = 3$ , while for  $\Delta v = +1$ , they increase over the same range from 0.08 to 0.17.<sup>26</sup> At the resolution used, the different vibronic bands are not resolved. Nonetheless, the  $\Delta v = 0$  is blue shaded, and the  $\Delta v = +1$  is red shaded, as expected from the FC factors. The relative intensities of transitions originating from the same  $v'$  level are also in line with this assignment. A  $\Delta v = -1$  transition is expected at about 358 nm. The relatively strong band appearing there is probably due mostly to  $\text{C}_2 \text{C}(^1\Sigma) \rightarrow \text{A}(^1\Sigma) \Delta v = -1$  transitions, but the CN B-X (FC factors 3–10 times smaller than the corresponding  $\Delta v = 0$  bands) contribution is important too. The relatively narrow bands at 430 and 336 nm can be assigned to the CH (A-X) and NH (A-X) transitions, respectively. In both cases the  $\Delta v = 0$  is much more intense than any other is, so that the absence of  $\Delta v \neq 0$  sequences is explained. The bands around 308–318 nm may be due to several molecules. We propose OH and CH as the major contributors. Finally, the 465–470 nm band is most likely due to the  $\Delta v = -1$   $\text{C}_2$  Swan bands. A stronger band of this series was observed at around 510 nm (not shown in Figure 3) and assigned to the  $\Delta v = 0$  bands of this transition. These assignments were supported by laser-induced fluorescence spectra, in which ground state OH and CN radicals were definitely identified, using rotational resolution. Emission spectra were obtained with the same resolution as the chemiluminescence ones, and were indistinguishable from them.

## 5. Discussion

**5a. Preliminary Remarks on Chemiluminescence.** The chemiluminescence clearly arises from fragments created upon the decomposition of the reactive polymer – there is no signal from an inert polymer (Figure 6). At low laser fluence it is due solely to a collisional process – in the absence of ambient gas it disappears (Figure 4); at high laser fluence it is observed even under high vacuum conditions. A reaction between ejected particles and ambient gas molecules may be ruled out, since argon is as efficient as air in producing the chemiluminescence. The decrease of the CL intensity upon increasing  $h$  is simply due to the smaller fraction of emitting molecules in the light-collecting zone.

Figure 3 indicates that essentially all of the emission bands could be assigned to diatomic species. The precursors responsible for the emission cannot be definitely identified at this point. Nonetheless, the most likely candidates are large molecules escaping from the polymer's surface and travelling at high velocity. The energy released upon dissociative collisions with ambient gas molecules is sufficient to form the diatomic species and also to excite them electronically, as discussed in the next subsection.

**5b. Collisional Origin of the Chemiluminescence.** The lifetime of the excited radicals (such as CN in the B state) is short,  $\sim 60$  ns, see section 3). Thus, the distance covered by the excited molecules from their point of formation is only of the order of 1 mm, even when travelling at  $10^4$  m/s, prior to their radiative decay. Experimentally, chemiluminescence is observed

at heights of the order of 10 mm (or even larger) away from the polymer's surface, meaning that they must be formed in the electronic excited state, *at the location in which they are monitored*. The chemiluminescence is thus due to a collisional process and the time delay observed between the laser pulse and the appearance of the chemiluminescence maximum intensity might be related to the time it takes for the precursors to reach the observation zone.

Several highly exoergic reactions that can lead to the formation of electronically excited diatomic molecules suggest themselves:

- a collision between an atom and a larger fragment both formed at the polymer's surface
- a collision between two large fragments
- a collision between two atoms, necessitating a third body for stabilization of the product
- the decomposition of a large fragment colliding with an ambient gas molecule
- a collision between a ground-state CN radical, traveling at very high velocity, with ambient gas molecules

The first two options can be discarded, as they predict the observation of chemiluminescence in the absence of an ambient gas. (They may be operative at high laser fluences, since under these conditions the concentration of emitted molecules is high enough to induce collisions among themselves). The third is also rather unlikely, considering the very low probability of a three-body collision at an ambient pressure as low as 30 mTorr.

The fourth and fifth options are therefore considered to be the more likely ones.

A simple calculation shows that when a big enough molecular fragment traveling at these velocities collides with an ambient gas molecule, the collision energy is sufficient (thermodynamically) to produce electronically excited CN, if the fragment is heavy enough. For instance, a fragment of mass 70 amu ( $\text{C}_4\text{H}_5\text{N}$ ) traveling at 5800 m/s will produce  $\text{CN}^*$  or even  $\text{NH}^*$  upon collision with an argon atom, if the center of mass kinetic energy is entirely converted to the internal energy of the diatomic. We therefore consider the fourth option as the most likely one.

The laser-induced fluorescence experiments show that radicals such as CN, NH and OH are formed in their *ground* state even under high vacuum conditions and low laser fluence. This raises the possibility that the chemiluminescence could result from the collision of these radicals, traveling at 5–8 km/s, with an argon atom. The kinetic energy of this collision is sufficient to produce the B State of CN, in line with the fifth option. However, when the two particles are of similar masses, the collision tends to be elastic. Thus, the chance of converting the entire collisional energy, which essentially resides in translation of the nuclei, to electronic excitation would appear to be small. The fact that the electronically excited diatomic molecules appear to be formed mostly at  $v = 0$  (for neat GAP) is also an indication of the involvement of a large precursor in the forming process of the excited radicals. Statistically, excess vibrational energy is likely to reside in the larger fragment that is formed in the collision, leaving the diatomic product in a low vibrational state.

The data of Figure 8 can now be qualitatively rationalized: The heat of the reaction produces a large amount of small molecular fragments, mostly  $\text{N}_2$  and some CO and  $\text{H}_2$ . They are ejected in a direction perpendicular to the surface, and form a directional jet, as indeed observed visually. Larger fragments are entrained in this jet, and are carried along with the smaller ones, much in the manner of seeded molecular beams.<sup>28</sup> The

distribution of velocities of gaseous particles leaving the polymer's surface is further discussed in section 5d.

**5c. Weight Loss, Shock Formation and Chemiluminescence.** The ejection of material from the polymer leads to weight loss. The ejected material may be gaseous or particulate, as shown for inert polymers by rapid photography.<sup>5</sup> It is expected that very heavy particles will move at a slower rate than small gaseous particles, and will have a small contribution to the shock formation. Thus, one might expect to observe, in principle, a difference between the two phenomena. On the other hand, the chemiluminescence and the shock's intensity, both arising from gas-phase collisional origin, are expected to display distinct similarities. These assumptions are supported by the following observations:

(1) When a 355 nm laser is used to initiate decomposition, weight loss increases monotonically (though not linearly) with GAP content, but  $E_0^{\max}$  shows a pronounced maximum at about 75% GAP (Figure 2 and ref 15). The chemiluminescence light intensity dependence on GAP content is similar to  $E_0^{\max}$  dependence (Figure 6).

(2) The chemiluminescence intensity rose linearly with the initiating UV laser pulse energy at low energies, and reached a constant value at higher laser energies. A similar dependence was observed for the shock wave's intensity (ref 15). In contrast, weight loss continued to rise with the laser's pulse energy throughout the whole range used in the experiments.

These observations are qualitatively rationalized as follows: Weight loss results from any process that fragments the polymer. Shock formation and chemiluminescence are due only to high velocity gaseous molecules ejected from a limited depth near the surface. Polymer decomposition that takes place beyond a certain depth contributes to the weight loss, but the increment to the shock's formation is negligible.

The dependence of the time required for the chemiluminescence to reach maximum intensity at a given  $h$  upon the polymer's composition is also consistent with the postulated mechanism. The optical collection system is optimized for observing emission from the excited molecules formed by collisions at the nominal height  $h$ . Therefore, the maximum emission intensity is found for molecules formed at that height and the different time delays are inversely proportional to the velocity of their precursors. The shorter time observed as the polymer is diluted from 100% GAP is thus due to a higher average velocity of the ejected particles, which in turn is due to higher  $T_c$  (cf. eq 1).

**5d. Analysis of the LIF Data.** The LIF measurements on CN radicals were performed under high vacuum precluding collisions in the gas phase; the radicals were thus formed at the solid's surface. These measurements therefore provide direct information on the velocity of species formed by the ablation process. As seen from Figure 8, the velocity of CN radicals increases, on the average, as the GAP content in the polymer decreases. Furthermore, it is found that the velocity distribution of CN under high vacuum conditions ( $p < 10^{-4}$  mbar) is similar to that of the precursors of the CN chemiluminescence (measured at a pressure of about 30 mbar). The most probable velocity deduced for neat GAP is  $7000 \pm 700$  m/s in LIF and  $5300 \pm 600$  in chemiluminescence. The similarity between these values supports the model of jet formation, in which all entrained particles travel with approximately the same velocity, regardless of their mass. In the chemiluminescence experiments, the finite ambient pressure may result in slowing down the jet.

The LIF measurements indicate that the energy disposal into the CN radicals emanating from the surface cannot be ascribed

to an equilibrated thermal source. A translational velocity of 6 km/s corresponds to a Maxwell–Boltzmann distribution of about 6700 K, assuming that the major gaseous material has a molecular weight of 28 ( $N_2$ , CO). At this temperature, a considerable portion of the CN radicals should be vibrationally excited. At this temperature, the population ratio  $n(v'' = 1)/n(v'' = 0)$  should be about 0.65, whereas experimentally it is less than 2% for neat GAP (indicating a vibrational temperature of about 750 K). The rotational temperature of the spectrum shown in Figure 7 may be estimated from the relative line intensities to be  $800 \pm 150$  K. This value is smaller than the translational temperature and approximately equal to the vibrational one. The data are consistent with the state of affairs emerging from the chemiluminescence data: gases are ejected from the surface with a high translational energy, due to a rapid expansion of gases from a small area. The gases, containing a large amount of  $N_2$  and CO, form a jet traveling at high translational velocity in a direction normal to the polymer's surface. The CN radicals entrained in this jet are partially rotationally and vibrationally excited; assuming that their internal degrees of freedom were equilibrated with the surface's temperature, the latter is estimated to be 750 K for neat GAP under the conditions of the experiments shown in Figure 7.

If the jet model is correct, the velocity of CN radicals ejected from the surface upon laser ablation is due to a combination of a statistical distribution characterized by a translational temperature  $T$ , and a stream velocity  $v_s$  of the gas emanating from the surface. We tried to fit the data of Figure 8 by simple one- or three-dimensional Maxwell–Boltzmann velocity distributions of the forms

$$N(v) = (m/2\pi kT)^{1/2} \exp\{-m(v_z - v_s)^2/2kT\} \quad (2a)$$

$$N(v) = (m/2\pi kT)^{3/2} 4\pi v^2 \exp\{-m(v - v_s)^2/2kT\} \quad (2b)$$

Preliminary results indicate that the general trend found for both  $T$  and  $v_s$ , is an increase as the polymer is diluted, but both fits did not yield satisfactory quantitative agreement with the experimental results. Further refinements of the model are being explored.

Whereas CN is found to be formed essentially only in  $v = 0$  in the concentrated samples; diluted polymers (such as the 25% and 35% samples), clearly show more pronounced vibrational excitation (Figure 9). Lines due to  $v'' = 1$  and  $v'' = 2$  are clearly observed. These findings are an unequivocal proof that the diluted samples are heated to higher temperatures than the concentrated ones, as predicted by the model.

## 6. Summary

In this paper, real time methods—chemiluminescence and laser-induced fluorescence (LIF) were used to probe the formation of gaseous products in the UV laser ablation of GAP. These methods allowed the measurement of the appearance time of some diatomic molecules, such as CN, OH,  $C_2$ , CH and NH. Most quantitative data were obtained for CN. It was found that electronically excited molecules are formed in a collisional process, near the point of observation. Ground-state molecules are also formed at the surface.

The chemiluminescence intensity dependence on GAP content was found to be similar to that of the shock wave intensity: it increases monotonically up to maximum at about 70–80% GAP, and decreases at higher GAP content, suggesting a common mechanism for the two phenomena. The data are thus consistent with a model, previously suggested to account for the intensity

of a shock wave formed by the ablation. According to this model, a polymer that is diluted by an inert one, is heated by the laser to a higher temperatures than a neat GAP polymer in order to reach a self-sustaining reaction. The model predicts that the velocity of molecules formed by the ablation of a diluted polymer should be greater than the velocity of molecules formed from a concentrated polymer. This prediction was confirmed.

The measured time dependence of both chemiluminescence and LIF indicates that in the ablation of GAP, gases are ejected from the surface with a high translational energy, due to a rapid expansion of gases from a small area. The gases, containing a large amount of N<sub>2</sub> and CO, form a jet traveling at high translational velocity in a direction normal to the polymer's surface. Large and small fragments are entrained in this jet, much in the manner of seeded molecular beam. The observed velocity distribution of the fragments is due to the combination of the jet velocity and a distribution of relative velocities. In diluted polymers, the resulting velocity is higher than in concentrated ones.

**Acknowledgment.** We thank Dr. L. Kalontarov for an enlightening discussion. This work was supported by the Research and Development Directorate of the Ministry of Defence of Israel. The Farkas Center for Light Induced Processes is supported by Minerva mbH, Munich.

**Supporting Information Available:** Appendix 1S details the calculation of  $E_0$ . Table 1S lists the assignments of the chemiluminescence bands and Table 2S compares experimental chemiluminescence with Franck–Condon factors of diatomic molecules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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