

# Ablation of Poly(2-Hydroxyethyl Methacrylate) by 193-nm Excimer Laser Radiation

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## SYNOPSIS

Data on the ablation of poly(2-hydroxyethyl methacrylate) (PHEMA) by 193-nm radiation pulses, produced by an ArF excimer laser, are presented for the first time and are compared with the data for poly(methyl methacrylate) (PMMA). The ablation rate of PHEMA is lower than that of PMMA and some possible explanations are advanced. The other features of the etch curves are similar and confirm a predicted ablative behavior of the addition polymers susceptible to depolymerization. Geometric aspects of the ablated polymer's surface, and the influence of inhomogeneities in the material, are also presented and discussed.

## INTRODUCTION

The excimer lasers are capable of generating short-pulsed, ultraviolet radiation at megawatt peak power. They are based on a dimer formed by an excited halogen atom, such as fluorine or chlorine, combined with the ground state of a rare gas, such as argon, krypton, or xenon. Wavelengths that can be produced by the excimer lasers currently available include 193 nm (ArF), 248 nm (KrF), 308 nm (XeCl), and 351 nm (XeF).

The removal of material from the surfaces of solid organic polymers by pulsed (10–20 ns per pulse) ultraviolet radiation emitted by excimer lasers was discovered in 1982. A Japanese group was the first to report the clean etching of a polymer, poly(methyl methacrylate) (PMMA), with the radiation produced by a KrF excimer laser.<sup>1</sup> Almost concomitantly, Srinivasan et al. reported on the photoetching of poly(ethylene terephthalate),<sup>2,3</sup> and PMMA<sup>4</sup> by the ArF laser. Srinivasan and his colleagues at the IBM Thomas J. Watson Research Center have subsequently done extensive work in order to elucidate the photochemistry and mechanism of the interaction of the ultraviolet laser radiation with polymers and to extend the applications of the excimer lasers. They have coined the term “ablative photodecom-

position” for the phenomenon of spontaneous cleavage and ejection of organic solid materials caused by the excimer laser radiation.

A significant body of experimental data has accumulated on the interaction of far- and near-ultraviolet radiation from excimer lasers with various polymers, such as PMMA,<sup>1,4–18</sup> poly( $\alpha$ -methylstyrene),<sup>10</sup> poly(ethylene terephthalate),<sup>2,3,6–8,19–21</sup> polyimides,<sup>5–8,15,16,19,21–25</sup> poly(vinylidene fluoride),<sup>26</sup> poly(methyl isopropenyl ketone),<sup>5</sup> polycarbonates,<sup>5,7</sup> cellulose derivatives,<sup>5,27,28</sup> and other polymeric materials.<sup>5,29</sup> The feasibility of using the excimer laser radiation for the processing of micro-electronic components by direct etching became an important issue.<sup>5,29–31</sup> Although the conventional, photolithographic, wet systems are well developed and extensively used in microelectronics, the superior quality of the etching by laser ablation, the possibility of processing polymers resistant to chemicals and heat (e.g., polyimides), and the elimination of the development (wet) stage will eventually lead to more widespread use of excimer lasers for this technology.

The use of excimer lasers in surgery is another fast developing area. A number of investigators have reported on the ablation of the ocular tissues (cornea,<sup>32–35</sup> lens<sup>35,36</sup>), skin,<sup>37</sup> and cardiovascular tissue.<sup>38,39</sup> Against this background of limited data, the excimer laser corneal surgery for visual correction,<sup>40–43</sup> and the laser angioplasty for treating cardiovascular diseases<sup>44,45</sup> are rapidly moving ahead to become well established techniques.

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The ablation mechanism has remained unclear to some extent and more investigation is probably required. However, a mechanism proposed by Srinivasan's group<sup>2,3,13,14,30,46-48</sup> is generally accepted. According to this hypothesis, in any polymeric system excited with photons of energy greater than about 3.6 eV ( $\lambda < 340$  nm), the decomposition and ablation is predominantly photochemical, being caused by the excitation of chemical bonds to energy levels that are above the dissociation energy. The result is the scission of bonds and the production of a large number of small, volatile fragments during the absorption of the radiation pulse. Since the numerous fragments need a large free volume, an enormous pressure builds up in the small volume within the polymer at the site of irradiation, and they are ejected explosively. Presumably, the process is too quick for the fragments to transfer heat to the polymer and the excess energy is carried away. The mechanism is indeed consistent with many experimental observations. For instance, the simple fact that etching is "clean," without charring or melting, supports substantially a photochemical mechanism.

Nevertheless, other results reported both by various investigators<sup>11,12,19,21-24</sup> and by Srinivasan's group<sup>4,7,15,16</sup> suggested that thermal processes could be also involved and become increasingly significant at higher wavelengths and/or fluences. (The fluence is the energy incident per unit area, commonly expressed in J/cm<sup>2</sup> or mJ/cm<sup>2</sup>.) Two types of thermal processes can occur, the photothermal process (or photopyrolysis) and the thermally-activated photoprocess. The processes' possible contribution to the ablation mechanism cannot be ignored. The mechanism should be rather regarded as a combination of photochemical and thermal dissociations that do not preclude each other. The former is clearly predominant at shorter wavelengths, but the latter may become important at longer wavelengths of the laser radiation.

This study was motivated by the need to explore the behavior of an acrylic polymer, poly(2-hydroxyethyl methacrylate) (PHEMA), as compared to PMMA, on exposure to short-pulsed 193-nm wavelength radiation emitted by an ArF excimer laser. It appears that, apart from PMMA, no other acrylic polymer prone to thermal depolymerization has been investigated in this respect. It is of interest to check the prediction<sup>7</sup> that the addition polymers, which are susceptible to depolymerization through an unzipping mechanism, also display discontinuities in their etch curve, that is, the plot of etch depth per laser pulse (known also as "ablation rate") vs. radiation fluence.

PHEMA is the main representative of a generic class of hydrophilic acrylic polymers, which absorb water to become flexible gels known as hydrogels. The applications of hydrogels as biomedical polymers span an impressively broad range.<sup>49-51</sup> Our choice of PHEMA stems from our ongoing studies on the alteration of hydrogels for enhanced biocompatibility of the ocular implants or for enticement of new characteristics pertaining to cells' behavior at the hydrogel-biological matrix interface.

## EXPERIMENTAL

Commercial buttons of PHEMA, supplied by Richdome Ltd., UK, were processed with a diamond-tool lathe into disks (14 mm diameter, 2 mm thickness), kept in an oven at 60°C for at least 12 h, and then exposed to pulsed laser radiation.

Radiation pulses were produced by a Questek Model 2820 (Questek, Inc., Billerica, Massachusetts) excimer laser filled with an argon-fluorine gas mixture and helium as a buffer gas. The laser produced 193-nm pulses with a width of approximately 20 ns. An anamorphic telescope was used to expand the narrow, quasigaussian, dimension of the beam. To select a section of uniform intensity from the center of the expanded beam, an iris was used, which was imaged onto the surface of the PHEMA disk with a 75-mm focal length, fused silica lens. The fluence at the polymer surface was varied by changing the distance between the imaging lens and the surface. One cut was made at each fluence. The distance between iris and lens was adjusted in order to keep the image of the mask in focus on the polymer surface, and the size of the iris was adjusted so that the diameter of the ablated area was about 2.5 mm. The iris diameter ranged from 8 to 13.5 mm.

The laser was fired at 10 Hz and each pulse was counted until the polymer had been etched away to a depth of approximately 0.5 mm. The aspect ratio of the cut was kept low to avoid any effect a high ratio may have had on the ablation rate. A fan was used to blow the fumes resulting from the ablation away from the path of the next pulse.

The depth of each cut was measured using a microscope (250 $\times$ ), by focusing on the top surface and then measuring the distance shift required to focus down onto the base of the cut. By taking an average of four measurements from different parts of the cut, an accurate measure of the average cut depth was obtained. The measurement was repeatable with  $\pm 5$   $\mu$ m. The ablated diameters, ranging from 2.2 to 3.9 mm, were measured to within  $\pm 0.02$

mm with the microscope and a micrometer. They were then used to calculate the incident fluence. The incident energy was measured using a Gentec ED-200 joulemeter, both before and after each cut was made. The average of 120 pulses (60 before and 60 after ablation) were taken and the result scaled up, because at 193 nm the detector is only 85% efficient.<sup>52</sup> The standard deviation of energy measurements showed a pulse-to-pulse energy variation of  $\pm 4.0\%$ . The averaged energy from a large number of pulses is therefore required.

Care was taken to allow the laser to warm up for 20 s at the desired repetition rate (10 Hz) before any energy measurements were made, and before the start of each cut. Although the pulse energies were measured at a rate of 1 Hz, a shutter allowed the laser to operate nearly continuously at 10 Hz. This removed the effect of the laser pulse energy being slightly dependent on the repetition rate of the laser.

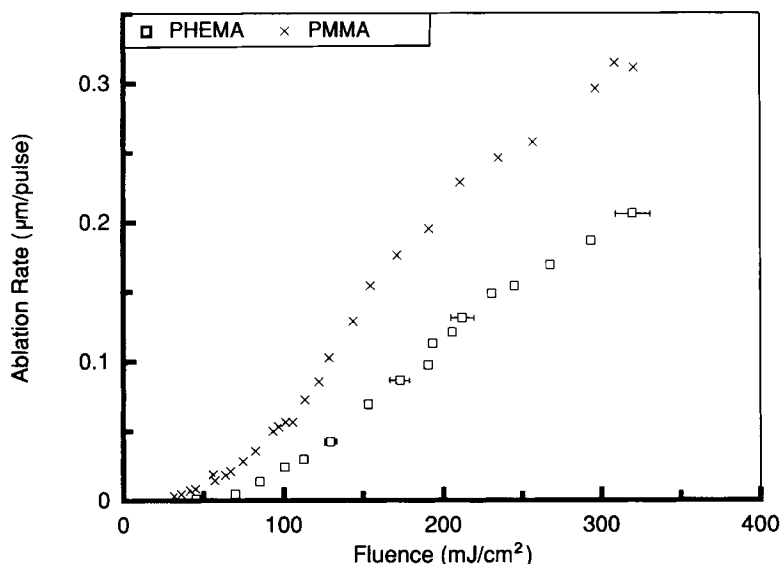
Figure 1 shows plots of the ablation rate as a function of fluence for PHEMA and for PMMA. The etch curve for PMMA<sup>18</sup> was included for comparison.

For examination of finer details in the geometry of etching, we have used scanning electron microscopy. The irradiated polymer specimens were coated with a 20-nm layer of gold in a diffusion coater and

then were examined in a Philips 505 scanning electron microscope.

## RESULTS AND DISCUSSION

A Beer-Lambert type empirical equation<sup>19,28</sup> was commonly employed to describe the ablation of polymers by the ultraviolet laser radiation. Consequently, it has become customary to represent the etch curve as a semilog plot, that is, ablation rate vs. logarithm of fluence, in the hope that the slope will be equal to the reciprocal of absorptivity of various polymers at that wavelength. It was found, however, that no polymer for which the absorptivity was known obeyed this equation.<sup>30</sup> Some explanations, new models for mechanism, or modified equations have been advanced<sup>15,16,19</sup> in order to account for this situation. The disagreement between slopes and reciprocal of absorptivity was significant, even within limited fluence ranges, more or less deliberately chosen by various authors for their apparently greater linearity and higher rate of etch depth increase. For this reason, and because semilog plots are inherently less accurate, their use may not be really justified, and we have represented our etch curves as normal plots (Fig. 1).



**Figure 1** Etch curve for PHEMA (□) and PMMA (×) at 193 nm. Error bars for the ablation rate measurements are smaller than the symbol height (PHEMA). For fluences below 125 mJ/cm<sup>2</sup>, the error bars for fluence measurements are smaller than the symbol width, and they increase with increasing fluences. In PHEMA curve, four error bars are shown for the fluence measurements. The errors for PMMA are lower than those for PHEMA and they are not presented.

PHEMA etch curve will be discussed in connection with various interpretations given to curves obtained for PMMA as the only acrylic polymer so far studied. In earlier works,<sup>4,7</sup> using semilog plots, Srinivasan found that PMMA differed from condensation polymers when ablated by 193-nm radiation. The slope at low fluence was almost the same as that of condensation polymers, but at about 110 mJ/cm<sup>2</sup> a break in the plot occurred and the rate of ablation was accelerated. It was suggested that at a certain fluence, the thermal depolymerization of PMMA through an unzipping mechanism overtook its photolysis. It was also suggested<sup>7</sup> that only the addition polymers with great susceptibility to thermal depolymerization display this behavior.

However, when the etch curve of PMMA was measured over a much larger range of fluences (up to 18,000 mJ/cm<sup>2</sup>),<sup>15</sup> no break could be detected in a semilog plot until 8000 mJ/cm<sup>2</sup>, which was regarded as an indication for a genuine change in mechanism in the favor of thermal processes.

In more recent papers<sup>13,14</sup> the PMMA etch curve was studied in detail up to 1000 mJ/cm<sup>2</sup>, and the conclusion was somewhat different. Three regions were identified in the semilog plot. At lower fluence, the slope is small and the production of monomer (MMA) is low until at about 65 mJ/cm<sup>2</sup>. From this point to 230 mJ/cm<sup>2</sup> there is a region with higher slope and linearity, which was considered to represent the true ablative photodecomposition. At 230 mJ/cm<sup>2</sup>, where the MMA yield is maximum, there is a drop-off in the slope and this was interpreted as a limiting effect of the etching caused by the absorption of radiation by the monomer ejected in the process. The mechanism in all regions was considered purely photochemical, including the depolymerization process itself.<sup>6</sup> Thermal components of the ablation mechanism were acknowledged only to occur substantially at fluences in excess of 2000 mJ/cm<sup>2</sup>.<sup>15</sup> There is some contradiction between Srinivasan's previous results,<sup>4,7</sup> suggesting an acceleration of ablation rate at 110 mJ/cm<sup>2</sup> due to a thermal depolymerization, and his latest results,<sup>13,14</sup> advocating two changes in acceleration, at 65 and 230 mJ/cm<sup>2</sup>, both determined by a photochemical depolymerization. However, it is obvious that, regardless of the mechanism and of the graphic representation, PMMA etch curve displays at least one break in the plot very likely due to the depolymerization. The assumption that the slope discontinuities are specific to addition polymers susceptible to depolymerization by unzipping is supported by the experimental etch curves for condensation polymers<sup>7</sup>

which cannot undergo depolymerization in the same manner. So far, it could not be correlated with data for other depolymerizable addition polymers, since the only polymer of this type investigated, poly( $\alpha$ -methyl styrene),<sup>10</sup> displayed a straight line from 100 to 450 mJ/cm<sup>2</sup> (five experimental points).

A close examination of the etch curve obtained for PHEMA (Fig. 1) reveals the existence of three regions with different slopes. The first break in the plot occurs somewhere between 90 and 110 mJ/cm<sup>2</sup> and marks an acceleration in the ablation rate. At about 230 mJ/cm<sup>2</sup> there is another change in the slope to a lower value. The fluence corresponding to the first break in PHEMA plot is higher than that previously reported for PMMA (65 mJ/cm<sup>2</sup>).<sup>13</sup> This is probably normal since the two polymers are not identical; besides, our own measurements on PMMA etching<sup>18</sup> indicate a first break in the plot in the range 80–90 mJ/cm<sup>2</sup>. In fact, this fluence is not sharply defined,<sup>13</sup> and different values obtained by different investigators do not invalidate the existence of an onset for significant depolymerization. The second break in the etching curve of PHEMA is the same as that found for PMMA (230 mJ/cm<sup>2</sup>).<sup>13,14</sup> Here, it appears that the fluence is high enough to break significantly bonds other than those connecting the monomers. This leads to a reduced ablation efficiency and possibly the beginning of plasma formation.

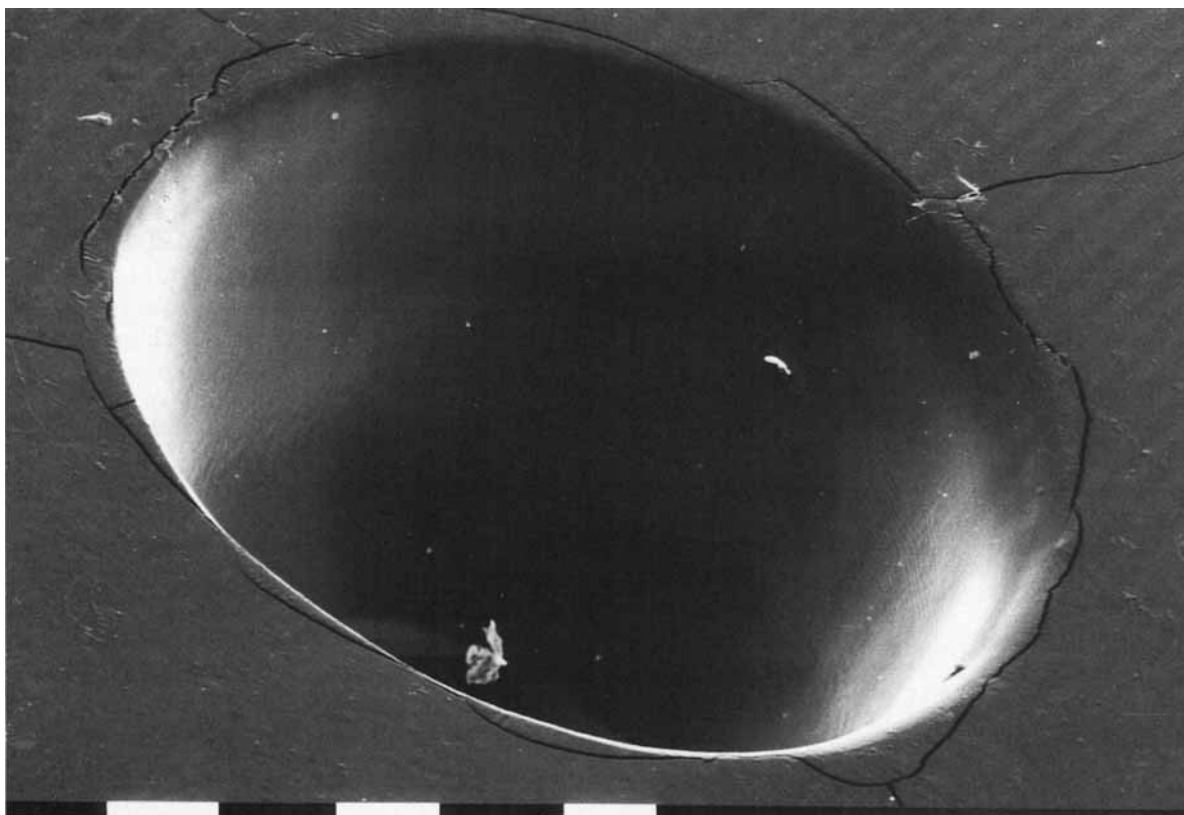
As seen in Figure 1, the ablation rate of PHEMA is significantly lower than that of PMMA, a difference that is surprising by its magnitude and difficult to explain. Investigating the ablation of polymers by 193-nm laser radiation, Cole et al.<sup>10</sup> have found that polymers with higher absorption coefficients display a reduced ablation rate, as compared to those with lower absorption coefficients, because the radiation is mostly absorbed at or near the surface of the polymer. This phenomenon has been noticed, however, at higher fluences; on the contrary, at lower fluences the ablation rate of the high-absorbing polymers was enhanced presumably due to more photons absorbed per unit volume. For instance, poly( $\alpha$ -methyl styrene), a strong absorber in far ultraviolet, was ablated at a higher rate than PMMA, but only up to about 100 mJ/cm<sup>2</sup>, when its ablation rate was clearly surpassed by that of PMMA. In poly( $\alpha$ -methyl styrene)/PMMA blends of various compositions, the less the concentration of aromatic polymer, the higher the fluence at which the ablation rate becomes inferior to that of pure PMMA. The above findings cannot account for our results (Fig. 1); the etch rate of PHEMA is consistently lower

than that of PMMA over the whole range of fluence, with no change in the aspect of the curve. Besides, it is not known whether PHEMA has a higher absorption coefficient at 193 nm. In fact, the absorptive properties in the vacuum ultraviolet of very few polymers have been so far evaluated.<sup>53</sup>

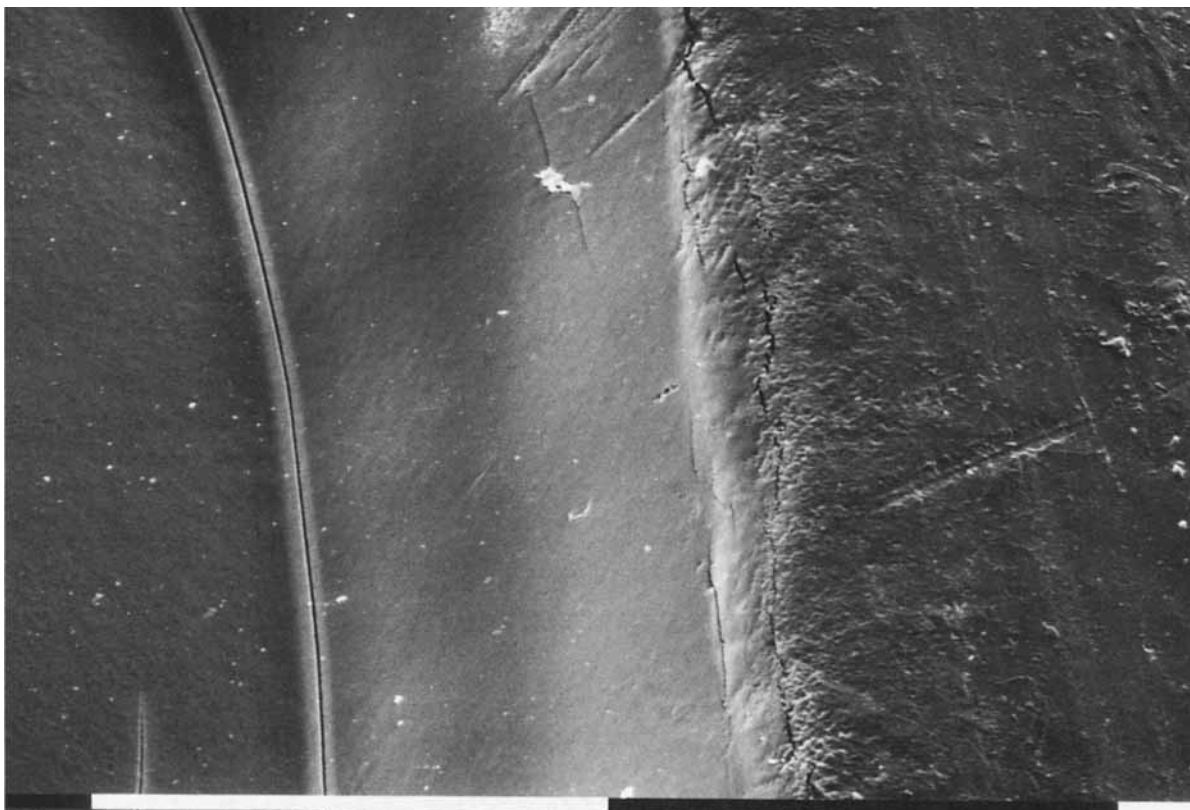
It is then unlikely that the lower ablation rate of PHEMA is due to a probably higher absorption coefficient.

A possible explanation is that the quantum yield of monomer during ablation of PHEMA is consistently lower than that of PMMA, probably due to a higher monomer bond strength or a greater degree of crosslinking. This is more acceptable than the presumption that more monomer is produced from PHEMA as compared to PMMA, hence more radiation is absorbed by the ejected material. In fact, a higher production of monomer or other molecular species should result in a higher ablation rate, which is not the case. Thermal behavior of acrylic polymers has been extensively studied, but there are very few reports on the thermal degradation of PHEMA itself. Razga and Petranek<sup>54</sup> have used pyrolysis gas

chromatography to investigate the products from PHEMA and related polymers in which the hydroxylic hydrogen was substituted by methoxy or acetoxy groups. They have noticed the formation of monomers, and a large amount of ethylene dimethacrylate resulting from PHEMA only, which was explained by a reaction of "crosslinking." This crosslinking, in fact a transesterification, can occur only when unsubstituted hydroxyl groups are involved. The significant production of ethylene dimethacrylate from PHEMA has been later confirmed<sup>55</sup> when PHEMA, copolymers of HEMA, and a number of poly(alkyl methacrylates) were investigated comparatively by pyrolysis at 400–440°C followed by mass spectrometry and gas chromatography. Other investigators<sup>56</sup> have found that the thermal degradation of PHEMA led to even more complex mixtures; methacrylic acid and acetaldehyde have also been detected. Thermomechanical behavior of PHEMA has also been studied<sup>57</sup> and it was found that the temperature of thermal degradation under load varied between 290 and 330°C. Varma and Patnaik<sup>58</sup> have used dynamic thermo-



**Figure 2** SEM micrograph of a hole produced in PHEMA by exposure to 193-nm laser radiation (2000 pulses at 300 mJ/cm<sup>2</sup>). The white bar marker is 100  $\mu$ m.



**Figure 3** SEM micrograph of an edge of a hole produced in PHEMA by exposure to 193-nm laser radiation (1500 pulses at  $100 \text{ mJ/cm}^2$ ). The white bar marker is  $100 \mu\text{m}$ .

gravimetry in order to investigate the thermal behavior of copolymers of HEMA with MMA and with some alkyl acrylates. They found that all copolymers had lower activation energies for decomposition as compared to PMMA or poly(methyl acrylate).

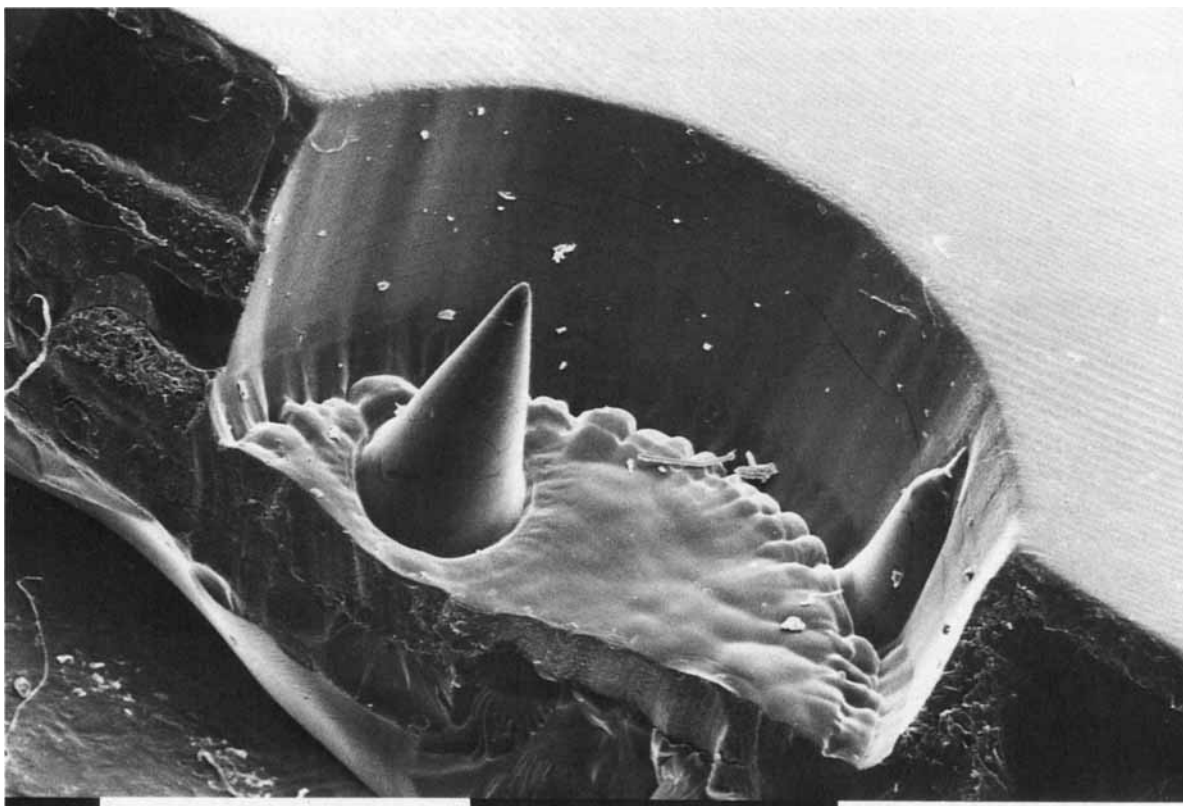
From this minimal information it is rather difficult to decide whether the amount of degradation products from PHEMA is larger than from PMMA. It seems, nevertheless, that the PHEMA degradation products mixture contains, apart from monomer, many compounds of which some may absorb strongly far-ultraviolet radiation. We do not know, however, if photochemical degradation of PHEMA, induced by the 193-nm laser radiation, would result in similar products.

Another reason for the lower etch rate of PHEMA may be the presence of water in the polymer. Water may interfere with the bond breaking process through the absorption of excess energy. PHEMA and related swellable polymers are indeed hygroscopic materials, which start taking up water even on simple exposure to the ambient atmosphere. We have exposed to 193-nm laser radiation two samples

of PHEMA, fully hydrated in doubly distilled, deionized water; the equilibrium water content was 38% w/w. The rate values measured for these samples ( $0.083 \mu\text{m/pulse}$  at  $169 \text{ mJ/cm}^2$ , and  $0.108 \mu\text{m/pulse}$  at  $206 \text{ mJ/cm}^2$ ) fit very well within the etch curve for PHEMA. This result can have two meanings; either that the "dried" samples of PHEMA used for the etching experiments took enough water from the surroundings to have the same radiation-absorbing effect as a fully hydrated sample, or that the presence of water has no influence on the etching process.

Obviously, the above tentative explanations are not satisfactory. Probably a combination of all explanations is operative, which would thus explain the large difference between the ablation rates of PHEMA and PMMA. More investigations, however, are needed.

A number of radiation-etched polymer specimens were studied by scanning electron microscopy (SEM). Figure 2 shows a 1-mm diameter hole produced by 2000 pulses of 193-nm radiation. The smoothness of the internal wall is remarkable, and



**Figure 4** SEM micrograph of a fractured hole produced in PHEMA by exposure to 193-nm laser radiation (8000 pulses at  $180 \text{ mJ}/\text{cm}^2$ ), showing two cones induced by inhomogeneities in the polymer. The white bar marker is 1 mm.

the difference between the laser-processed surface and the lathe-cut top surface, as well as the lack of damage along the edges, should be noted. Cracks, as illustrated in Figure 2, occurred in most of our experiments. These cracks are probably caused by shrinkage during the vacuum desiccation drying process used in the preparation of the samples for electron microscopy. It does appear, however, that the slight heating during the ablation has had some effect on the polymer.

In Figure 3, the smoothness of another hole edge can be seen at a higher magnification. Figure 4 shows a larger hole (2.5-mm diameter), which, prior to the microscopic examination, was fractured. The two large cones are the results of inhomogeneities in the polymer, very likely a microparticle of a certain contaminant. Although the formation of spikes, cones, or pyramids, due to inhomogeneities in materials, is well known in the surface etching technology, there has been little published on this issue. Marshall et al.<sup>59</sup> have recently given a reasonable explanation for the phenomenon. Briefly, the inhomogeneity is highly resistant to ablation and therefore shields the underlying material. As the ablation advances and the successive layers are progressively removed, a larger and larger area around the inhomogeneity is thrown into shadow and consequently the base of the cones (or pyramids) expands.

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## CONCLUSIONS

The ablative photodecomposition of PHEMA by exposure to 193-nm excimer laser radiation displays features very similar to that of PMMA. Two breaks occurred in the etch curve at about  $100 \text{ mJ}/\text{cm}^2$  and  $230 \text{ mJ}/\text{cm}^2$ , confirming thus a predicted typical behavior of the addition polymers susceptible to depolymerization.

The main difference between PHEMA and PMMA ablation was the significantly lower ablation rate of the former, for which satisfactory explanations could not be advanced.

Technically, the etching of PHEMA using exci-

mer laser radiation is a convenient procedure to create submicroscopic geometric features or highly smooth and clean surfaces. The intimate geometry of the etching was entirely defined by the laser beam. However, the presence of inhomogeneities in the polymer can cause unexpected protuberances on the etched surface.

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