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Micropatterning of polyurethanes with lasers†

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Abstract: The micropatterning of a series new poly(carbonate-urethanes) with IR and excimer lasers is discussed. A series of segmented polyurethanes consisting of a soft segment and a hard segment was prepared. The soft segment, a thermodegradable polycarbonate diol, degrades by a *syn*-elimination at higher temperature. The hard segment was selected as to increase the sensitivity of the polymers for UV excimer laser ablation. The thermal and mechanical properties of the segmented polyurethanes (SPU) were investigated. By varying the building blocks in the polymer (soft and hard segments), the ablation properties were studied in terms of absorption coefficient and threshold value. Polymers with an aromatic chain-extender and an diisocyanate showed the highest absorption coefficient at wavelengths of 248 and 193 nm. Irradiation of these polymers led to cavities with high dimensional quality, sharp edges and no accumulation of degradation products near the cavities (no debris formation). Ablation with an IR laser led to a decrease in film thickness of the polymer deposited on a substrate. This was investigated with FTIR/ATR analysis and atomic force microscopy. Debris formation was found near the cavities. The differentiation of polarity between the exposed and unexposed areas was not efficient enough to use them as a coating for printing plates.

Keywords: micropatterning; laser; polyurethanes; ablation

INTRODUCTION

There is a great interest in the development of polymers for lithographic applications.[1–8] Patterning and/or inducing a chemical change of a surface impacts a number of technologies, including semiconductor circuitry,[9] sensors,[10,11] printing plates,[12] tissue engineering,[13,14] and micromechanical devices.[15] A number of technologies can be applied for the fabrication of microstructures.

Laser ablation is a powerful flexible technique for rapid patterning of very small features, which can be applied on a number of different materials. Typical applications are drilling in printed circuit boards, removal of short cuts in electronic circuitry, wire stripping, printing plates,[12] fabrication of waveguides, micro-lenses and alignment structures in polymers. In the medical area laser ablation is applied for local tissue removal.[16–20]

By selecting the appropriate wavelength of the laser light, both 'cold' (eg ArF-excimer laser[21] at 193 nm) or thermal processes (eg Nd:YAG laser[12] at 1.06 μm, CO_2 laser[22] at 10.6 μm) can be initiated at material interfaces.

The interaction of the pulsed ultraviolet excimer laser radiation with organic polymer surfaces leads to photoablation or ablative photodecomposition (APD).[23] It results in etching of the polymer surface and explosive ejection of decomposition products at supersonic velocities. Ablation with excimer lasers leads to higher resolution in comparison with IR lasers. These lasers are therefore more suitable for the development of microdevices, eg sensors, MEMS, etc.

When IR lasers are used, the impact of the photons on an organic surface induces thermal degradation of the polymer structure. Until recently, pulsed solid-state lasers, that use a solid rod of neodynium (Nd)-doped material such as yttrium aluminum garnet (YAG) as their lasing medium, did not offer the

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required pulse energies within the IR range ($\lambda = 1064\,\text{nm}$). However, current technological advances have led to development of a new generation of diode-pumped (DPSS) solid-state lasers. They emit sufficient energy outputs (10^7–$10^{11}\,\text{mW cm}^{-2}$) to create opportunities for machining, marking or patterning processes.[24,25] The entire output beam from a DPSS laser can be focused to achieve spot sizes of 15–30 µm over large working distances. This technology eliminates the need for photo-masks and allows material modification in a 'direct-write' fashion. Therefore, this process offers excellent opportunities in the design of dry imaging systems (ex printing plates) which are applicable under daylight conditions.

In this paper, the development of a series of new segmented polyurethanes (SPU) is discussed. These polymers are not only thermodegradable, but also sensitive for UV excimer ablation. The SPUs are based on a thermosensitive prepolymer, namely a polycarbonate diol. This prepolymer degrades by *syn*- or β-H elimination[26–30] into low molecular weight products, such as carbon dioxide. The other building blocks are chosen in such a way that they increase the sensitivity towards UV excimer ablation. The polymers are ablated with an IR and two excimer lasers, namely a KrF[31,32] ($\lambda = 248\,\text{nm}$) and an ArF excimer ($\lambda = 193\,\text{nm}$) laser.

EXPERIMENTAL

The materials used were: 1,6-hexamethylene diisocyanate (HDI, Aldrich), 1,4-phenylene diisocyanate (PDI, Aldrich), 4,4′-methylenedi(cyclohexyl) isocyanate (DesmW, Aldrich), 4,4′-diphenylmethane diisocyanate (MDI, Acros), bisphenol S (BS, Acros), 1,4-butanediol (BD, Aldrich), poly(1,6-hexamethylene carbonate) diol (PC, $M_n = 860\,\text{g/mol}$) (Aldrich). Bis[4-(β-hydroxyethoxy)phenyl] sulfone (BPSOE) was synthesized according to Reference 33.

The mechanical properties were determined on a THE Hounsfield strain stress apparatus with a rate of $1\,\text{mm min}^{-1}$. The measurements were performed on a series films (4.2 mm wide, 20 mm long, mm thick). The samples were prepared by heat compression. Differential scanning calorimetric (DSC) data were obtained using a TA. Instrument Modulated DSC-2920 apparatus at a heating rate of $10\,°\text{C min}^{-1}$ under a of flow nitrogen.

Excimer laser ablation

The experiments were carried out with a Lumonics Pulse Master 848 (suitable for both KrF and ArF gas mixtures) and by means of an optical set-up. A Molectron J3 pyroelectric joulemeter, put at far distance from the image plane, is used for energy density measurements. The polymers as coatings on PET were exposed to the laser with various energy densities and numbers of pulses. The ablated structures have a rectangular or circular shape with a diameter of about 30 × 30 µm or 50 × 50 µm.

IR laser ablation

All polymers were cast on an anodised aluminium plate together with an infrared absorber in a 9/1 polymer/IR-abs-ratio (with a total of $1\,\text{g m}^{-2}$). The plates were laser beam recorded in a Creo Trendsetter TSFH with five different laser powers (ranging from 293 to $685\,\text{mJ m}^{-2}$). The infrared absorber was obtained from FEW Chemical. The chemical structure of the dye S 0094 (trade name, $\lambda_{max} = 813\,\text{nm}$) is shown in Fig 8.

FTIR analysis

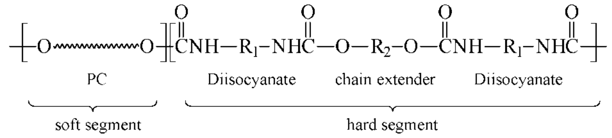
This was performed with a BioRad FTS65 spectrometer equipped with a microATR-accessory from Harrick (SplitPea, 250 µm silicon crystal). For improving the S/N ratio, a total of 16 scans/spectrum were taken. No ATR or baseline correction was applied. FTIR/ATR spectra of the laserbeam recorded polymer/IR-absorber layers taken from 100% density areas. All spectra were taken with a resolution of $4\,\text{cm}^{-1}$. The depth of the cavities and the roughness of the surfaces were measured with an atomic force microscope (AFM, Digital Nanoscope IIIa). The measurements were preformed in tapping mode under air conditions with a scan rate of 0.1 Hz (type of tip: OTESPA-70, L = 160 µm).

RESULTS AND DISCUSSION

Selected polymers

The segmented polyurethanes consist of a soft segment (polycarbonate diol, PC) and a hard segment (diisocyanate and chain-extender) as depicted in Fig 1. The thermosensitive prepolymer, poly(1,6-hexamethylene carbonate) diol, degrades by a *syn*-elimination as shown in Fig 2.

In previous papers[34,35] we reported the influence of the substituents at α and β positions of the carbonate group on the degradation temperature of the polymers. Theoretical calculations on small carbonate structures gave us microscopic information about the degradation pattern. The mechanism has a partial ionic character, with C_α and C_β having partial positive and negative charges respectively in the transition state as depicted in Fig 2.



$$\underbrace{-\!\!\left[O\sim\sim\sim O\right]}_{\text{soft segment}}\underbrace{\left[\overset{\overset{O}{\|}}{C}NH-R_1-NH\overset{\overset{O}{\|}}{C}-O-R_2-O-\overset{\overset{O}{\|}}{C}NH-R_1-NH\overset{\overset{O}{\|}}{C}\right]\!\!-}_{\text{hard segment}}$$

Figure 1. Segmented polyurethane.

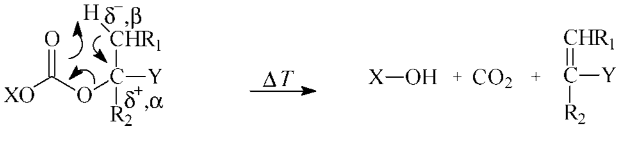
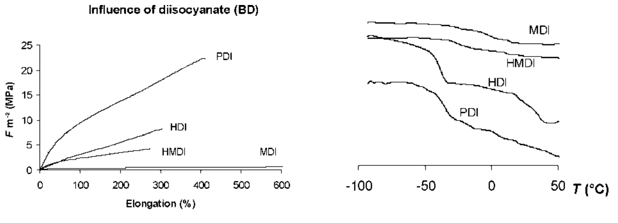


Figure 2. *Syn*-elimination.



Tensile strength experiment

DSC experiment

Figure 3. Influence of the various diisocyanates on the thermal and mechanical properties (1,4-butanediol as chain extender).

The hard segment is based on aromatic and/or aliphatic compounds. In a previous paper,[36] the influence of the building blocks on the mechanical and thermal properties of the segmented polyurethanes are discussed.

All polyurethanes[37–42] were synthesized in a two-step procedure. In a first step, an isocyanate end-capped prepolymer was formed, which was chain extended with a diol to yield a $(AB)_n$ multiple block copolymer structure.

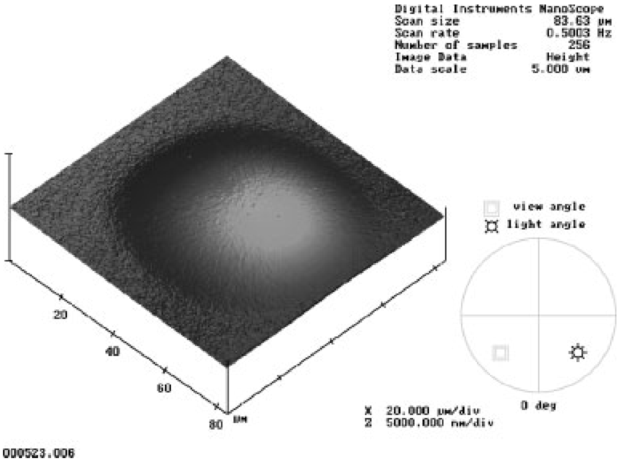
Mechanical and thermal properties of the segmented polyurethanes

As described before,[36] the thermal and mechanical properties can be varied by changing the different building blocks of the SPU. The flexibility of the monomers had a great impact on these properties as shown in Fig 3.

The low flexibility of MDI and DesmW led to poor phase separation of the polymers as found in the DSC experiment. The modest ability for hydrogen-bond formation between the hard segments of these polyurethanes resulted in a lower tensile strength and elasticity modulus than for the polymers based on HDI and PDI (flexible monomers).

Micropatterning of segmented polyurethanes with U.V. excimer lasers

The segmented poly(carbonate-urethanes) were ablated with two types of lasers, a KrF ($\lambda = 248$ nm) and an ArF ($\lambda = 193$ nm) excimer laser. As described before,[43] the building blocks in the segmented polyurethanes were varied with the aim of finding polymer structure with good ablation properties, in terms of no debris formation, a high absorption coefficient, a low threshold value and high dimensional quality of the cavities. The objective was to use such polymers as photoresistant coatingings on different substrates for numerous applications, eg printing plates, sensors.



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Digital Instruments NanoScope
Scan size              83.63 µm
Scan rate             0.5003 Hz
Number of samples        256
Image Data            Height
Data scale            5.000 um
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X  20.000 µm/div
Z  5000.000 nm/div
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Figure 4. Deformation of the polymer coating (SPU: PC 860 g mol^{-1}, HDI and BD).

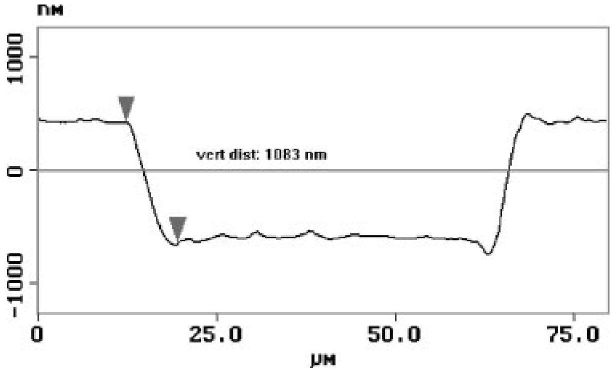


Figure 5. SPU (PC 860 g mol^{-1}, PDI and BS).

Ablation with a KrF excimer laser

The polymers based on aliphatic compounds can be classified as low absorbing polymers at a wavelength of 248 nm. The irradiation of aliphatic segmented polyurethanes led to the deformation, instead of ablation, of the polymer coating at low energy densities (50–70 mJ cm^{-2}) as seen in Fig 4. Destruction of the polymer film is observed at higher energy densities. Due to the low absorption coefficient of the polymer, the photons can penetrate through the polymer coating, resulting in the photodecomposition of the underlying PET substrate. The degradation products erupted and deformed the polymer coating. The polymers based on aromatic compounds (diisocyanate and chain-extender) are more sensitive to laser ablation. Irradiating segmented polyurethanes containing an aromatic diisocyanate and chain-extender

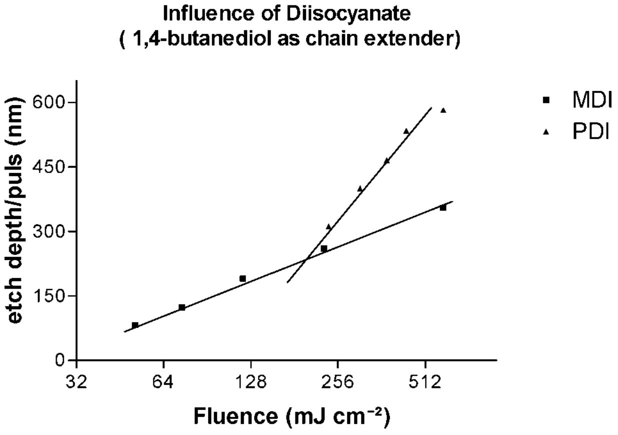


Figure 6. Etch depth in function of the energy density.

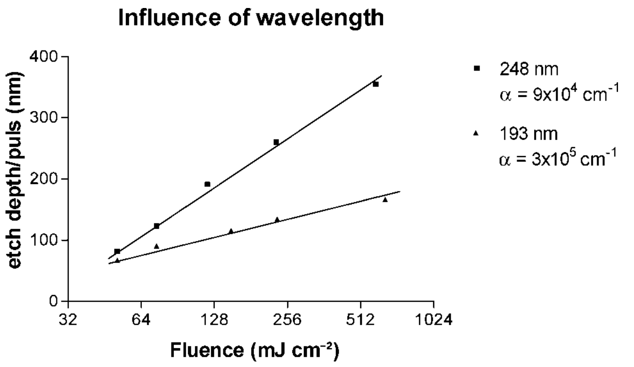


Figure 7. Influence of the wavelength on the ablation properties.

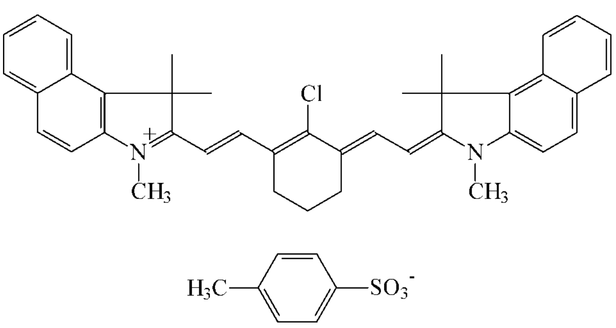


Figure 8. Chemical structure of the infrared absorber.

led to cavities with sharp edges and excellent dimensional profiles as illustrated in Fig 5.

The Literature[22] describes the etch depth upon a single pulse, l_f, at a given fluence, F, as inversely propertional to the absorption coefficient, α:

$$l_f = (1/\alpha)\ln F/F_0$$

where F_0 is the threshold fluence for ablation. In the plot of this function, the slope is an estimate for the absorption coefficient and the X intercept for the threshold value for ablation.

The polymers with MDI as a building block had the highest absorption coefficient and the lowest threshold value (Fig 6). These segmented polyurethanes are therefore the most suitable for use as coating for UV excimer ablation at 248 nm.

Ablation with an ArF excimer laser

Irradiation of aliphatic segmented polyurethanes with a 193 nm ArF excimer laser resulted in cavities with sharp edges of well dimensional quality.

The SPUs based on aromatic chain-extender and diisocyanate showed by far the best ablation properties in terms of highest absorption coefficient and lowest threshold value, with MDI as most sensitive component.

The segmented polyurethanes were more sensitive for laser ablation at 193 nm than at 248 nm. A SPU (PC 860 g mol^{-1}, MDI, BD) was ablated with both lasers, and the absorption coefficient was determined as shown in Fig 7.

Micropatterning of segmented polyurethanes with IR lasers ($\lambda = 1.06\,\mu$m)

A segmented polyurethane, based on PC (860 g mol^{-1}), PDI and BPSOE as chain-extender was exposed to an IR laser with five different laser energy densities (ranging from 293 to 685 mJ m^{-2}). The polymer–infrared-absorber blend was cast on an anodised aluminium plate. The IR absorber (see Fig 8 for chemical structure) transfers the laser light into thermal energy. The exposed areas were analysed with a FTIR/ATR to determine the chemical decomposition.

As shown in Fig 9, there was a decrease in peak intensity at 1715 cm^{-1} assigned to the carbonyl stretching of the coating. The dotted curve in the Fig 10 represents the absorption spectrum of the unexposed polymer minus the absorption spectrum of the ablated polymer at 685 mJ m^{-2}. From these data we concluded that the polymer degrades, since the intensity of the recorded peak at 1715 cm^{-1} is correlated with the amount of ablated polymer. At the exposed areas, there was a decrease in polymer

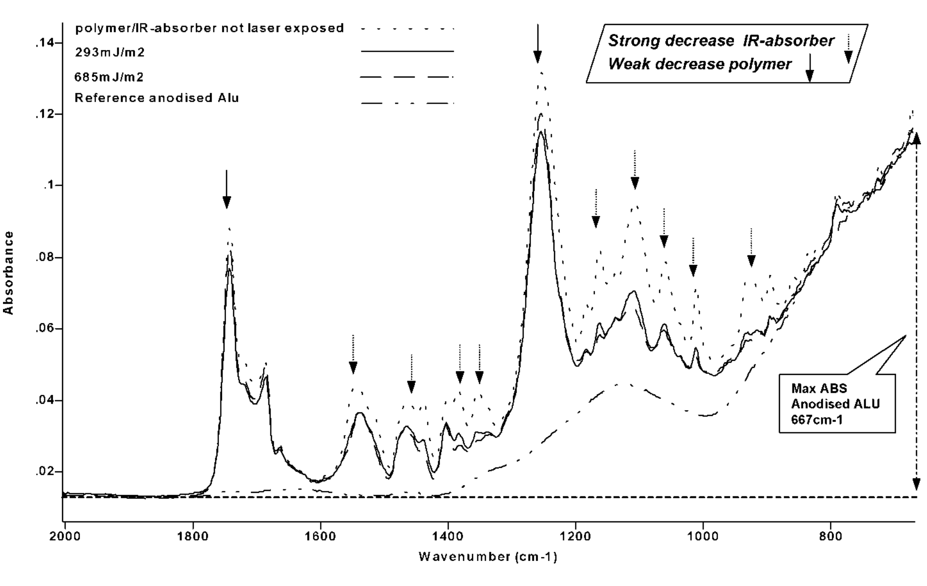


Figure 9. Overlay of the IR spectrum of the polymer/IR-absorber on the Al-plate with respect to laser power (autoscale A1-background, 667 cm^{-1}).

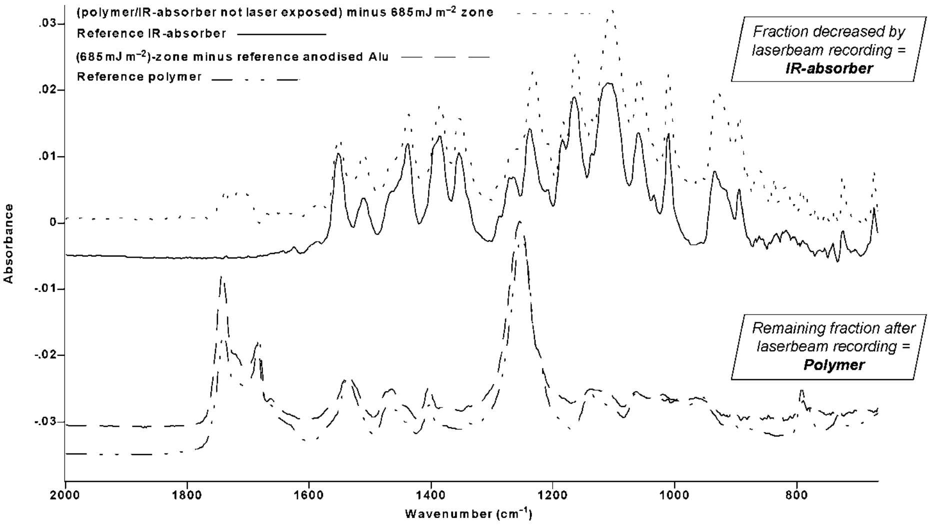


Figure 10. Overlay of the IR spectrum of the reference polymer, the IR-absorber and the exposed polymer.

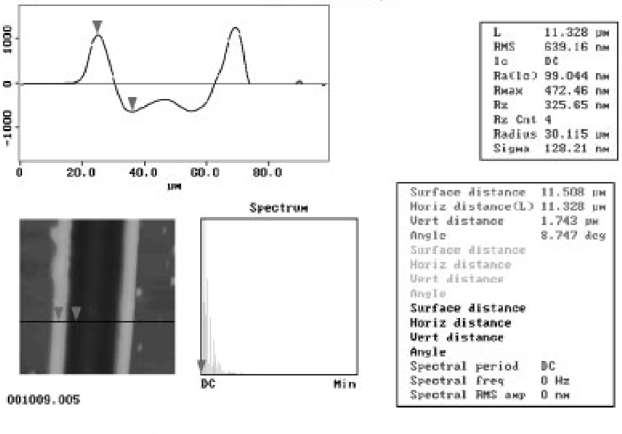
thickness with increasing laser power. The accumulation of the degradation products (debris formation) is shown near the cavities by atomic force microscopy in Fig 11. The depth of the cavities increased at higher energy densities, resulting in a decreasing polymer thickness. After the ablation, the aluminium plate was exposed to an alkaline solution to remove the degradation products. The unexposed areas became more hydrophilic and the exposed areas remained hydrophobic.

This was probably due to part of the degradation products migrating into the pores of the Al plates leading to better attachment of the polymer film and the Al plate at the exposed areas. At the unexposed areas the polymer coating is partially removed from the plate.

CONCLUSION

The micropatterning of a series new poly(carbonate-urethanes) with IR and excimer lasers was studied. The mechanical and thermal properties of the segmented polyurethanes, based on a thermodegradable polycarbonate diol, were investigated. The mobility or flexibility of the different building blocks of the SPU apparently has a great influence on these properties. The polymers were coated on a substrate (PET or Al) and ablated with an IR or UV excimer laser (KrF: $\lambda = 248$ nm; ArF: $\lambda = 193$ nm). The ablation properties, in terms of absorption coefficient and threshold value, were studied with an excimer laser. Polymers with an aromatic chain-extender and aromatic diisocyanate show the highest absorption coefficient and lowest threshold value at wavelength of 248 and 193 nm. Irradiation of these polymers led to cavities with high dimensional quality, sharp edges and no accumulation of degradation products near the cavities (no debris formation).

Irradiation of a segmented polyurethane with an IR laser led to the thermal degradation of the polymer, resulting in a decreasing film thickness. In comparison with excimer laser ablation, debris formation was found near the cavities. This was investigated with FTIR/ATR analysis and AFM.



```
L          11.328 µm
RMS        639.16 nm
Ic         DC
Ra(Ic)     99.044 nm
Rmax       472.46 nm
Rz         325.65 nm
Rz Cnt     4
Radius     30.115 µm
Sigma      128.21 nm
```

```
Surface distance      11.508 µm
Horiz distance(L)     11.328 µm
Vert distance         1.743 µm
Angle                 8.747 deg
Surface distance
Horiz distance
Vert distance
Angle
Surface distance
Horiz distance
Vert distance
Angle
Spectral period       DC
Spectral freq         0 Hz
Spectral RMS amp      0 nm
```

Figure 11. AFM of ablated polymer.

ACKNOWLEDGEMENTS

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