



## Luminescent microstructures in bulk and thin films of PMMA, PDMS, PVA, and PS fabricated using femtosecond direct writing technique

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### ABSTRACT

We present here the luminescent properties of microstructures obtained through femtosecond (fs) laser direct writing (LDW) in bulk, and thin films of polymers such as poly methyl methacrylate (PMMA), poly dimethyl siloxane (PDMS), polystyrene (PS), and poly vinyl alcohol (PVA). We report the transmission, emission, excitation, laser confocal and ESR data from the modified regions acquired with the intention of understanding the fs irradiation effects in these polymers. Formation of different optical centers in the laser irradiated regions has been identified as the reason for emission characteristics which are dependent on the excitation source. Such emitting microstructures demonstrate their utility in memory based devices. ESR studies reveal the existence of peroxide type free radicals in PMMA, PDMS and PS after fs laser irradiation.

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Fabrication of three-dimensional photonic devices in transparent materials by fs laser direct writing technique is a versatile technique derived from nonlinear absorption process transpiring at the focus and has gained considerable attention and importance due to many applications in the fields of photonics and optofluidics [1,2]. fs LDW facilitates penetration depths greater than few hundreds of microns and permits genuine three-dimensional micro- and nano-structuring. Multi-photon processes involved in the interaction between the fs pulses and material occurs only in the vicinity of the focal spot and therefore the surface of the material remains intact. Researchers have already reported the fabrication of a variety of photonic devices in wide range of glasses and polymers [2–6]. Due to low thermal diffusion fs laser writing results in superior structure formation compared to other micromachining techniques [7]. The ability to control refractive index inside the bulk finds relevance in photonics whereas the capacity to create channels within the bulk find applications in optofluidics. Some of the distinct applications of fs LDW achieved in polymers include fabrication of waveguides and couplers [8], three-dimensional photonic crystals [9], modification of the polymer surface wettability [10,11], memory based devices [12,13]. A complete understanding of the fs pulse interaction with such materials with changes in pulse duration, energies, shapes, focusing conditions, etc. is imperative for arriving at optimum writing conditions to achieve device quality structures [14]. Herein we report our results on the fabrication and optical characterization in general, and emission observed

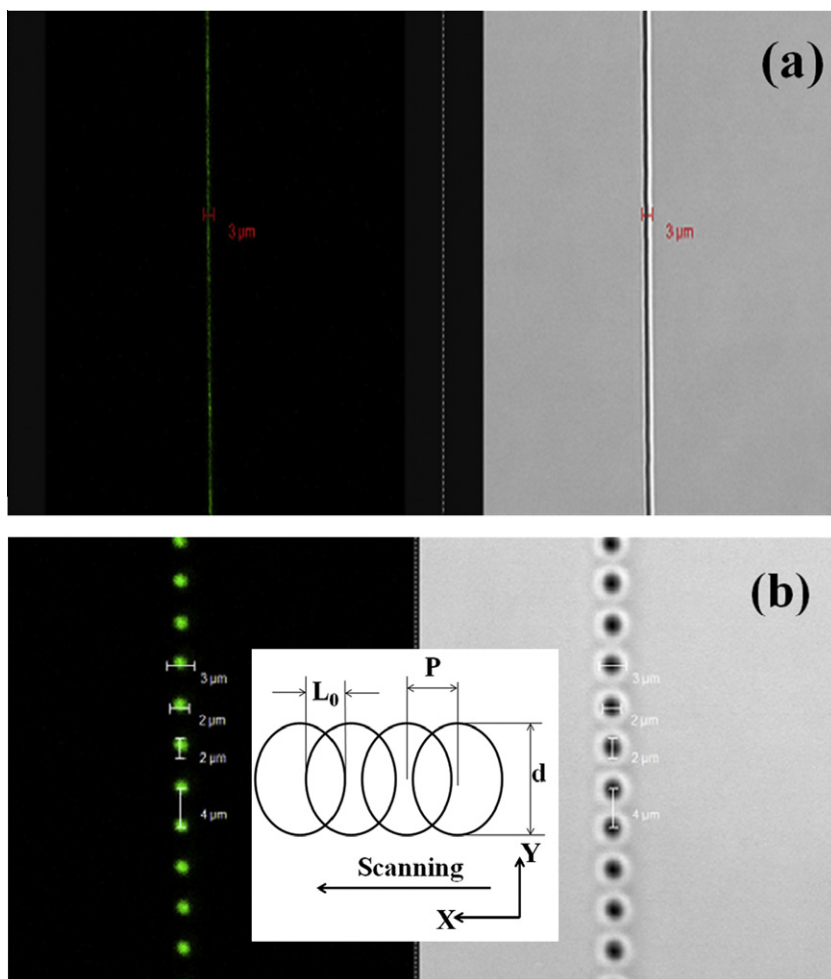
from irradiated regions in particular, of several microstructures in PMMA, PDMS, PS, and PVA obtained using fs pulses.

All the microstructures reported here were written with a 1 kHz, 800 nm Ti:sapphire oscillator–amplifier laser system, producing ~1 mJ, ~100 fs pulse width. Complete details of the setup are reported in our earlier works [15–17]. Energies were measured near the sample to account for all transmission and reflection losses. Bulk PMMA and PS were purchased from Goodfellow, US and UK, respectively. PDMS was homemade and PVA solution was prepared and coated on a glass plate as a thick film. All the bulk polymers were cut into 1 cm × 1 cm dimensions and edges were polished followed by sonication before the LDW experiments were carried out.

Figure 1a shows typical microstructure in bulk PMMA achieved at 100 nJ and 1 mm/s speed with 40× objective. We found that smooth and narrow structures were formed when the input pulse energy was reduced from μJ to nJ. By controlling the scanning speeds, and at low energies (~nJ), we obtained micro-voids instead of straight line structures due to diminished cumulative effects. Figure 1b shows the formation of the micro-voids at 33 nJ and 4.5 mm/s scanning speed using the same 40× system. Inset of Figure 1b demonstrates the technique for achieving micro-voids.  $L_0$  is the overlap region of two consecutive focused spots while pitch  $P$  is defined as the distance between the centers of two consecutive pulses imprinting on the sample. The pitch was varied by setting scanning speeds according to the relation  $P = s/f_p$  where  $f_p$  is laser pulse repetition frequency (1 kHz in our case). Now,  $L_0$  can be written as  $L_0 = d - p = d - (s/f_p)$ . Thus, by controlling scanning speed and energy (thereby reducing thermal effects) we could create either straight line structures or micro-voids.

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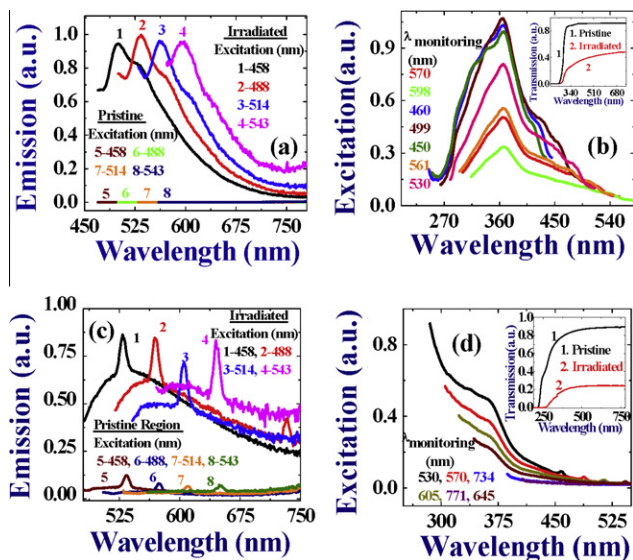


**Figure 1.** (a) Confocal microscope image of microstructure fabricated in PMMA bulk at 100 nJ energy, 1 mm/s speed, 40 $\times$  objective. Structure width obtained was  $\sim$ 3  $\mu$ m. Pseudo green color represents emission from the modified region. (b) Micro-voids formation in PS bulk at 33 nJ energy and 4.5 mm/s scanning speed with 40 $\times$  microscope objective (Crater size 2  $\mu$ m). Excitation wavelength was 488 nm. Inset of (b) indicates overlap of pulses which demonstrates straight line or micro-void structures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

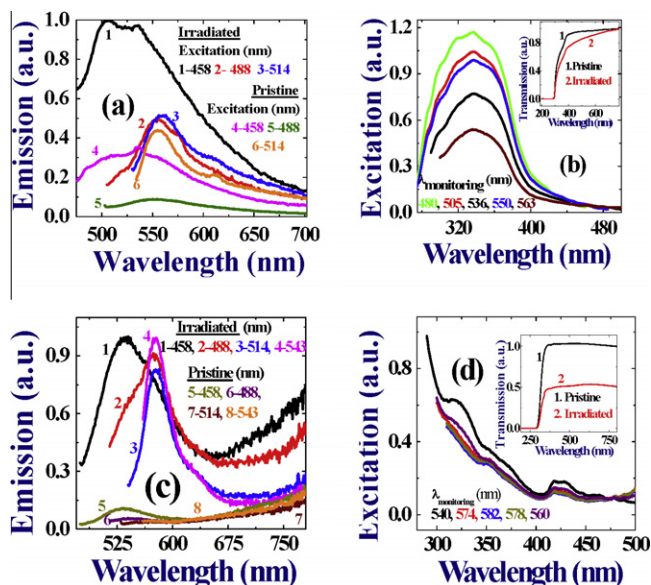
We have also fabricated the microstructures over a large area to record the emission and excitation spectra from these laser irradiated regions. To accomplish this an array of closely spaced lines were drawn in PMMA (energy 10  $\mu$ J, speed 1 mm/s, period 30  $\mu$ m), PDMS (50  $\mu$ J, 1 mm/s, 10  $\mu$ m), PS (1  $\mu$ J, 0.5 mm/s, 30  $\mu$ m), and PVA (10  $\mu$ J, 1 mm/s, 20  $\mu$ m). All the four polymers are transparent to visible light before fs laser irradiation and hence do not show any emission when excited with visible light. However, due to multiphoton absorption, these polymers get modified chemically and optical centers are produced that exhibit emission when excited at different excitation wavelengths. Figures 2a and c & 3a and c depict the observed emission due to different excitation wavelengths in PMMA, PDMS, PS, and PVA. We noticed strong emission from the modified regions of all polymers when excited with any of 458, 488, and 514, 543 nm (except for PS) light. We strongly feel that the formation of optical centers resulting from fs laser irradiation is responsible for the emission observed. The change in emission peak with the excitation wavelengths is interpreted as due to the formation of diverse optical centers. The sharp peaks observed in the emission spectra of pristine PDMS (depicted in Figure 2c) could be attributed to the defects and/or impurities in the sample. We observed this emission was amplified when irradiated with fs laser. The origin of these sharp peaks is under investigation. Interestingly, excitation spectra collected by monitoring different emission wavelengths show similar spectrum

for these polymers. Some of the curves were scaled up for better clarity.

We found it quite interesting that the emission peaks differed considerably with the excitation wavelength recorded at room temperature. Low temperature studies of spectral narrowing were reported earlier in some of the organic molecules [18]. By monitoring different wavelengths of the emission peaks, we observed the same excitation spectra for all polymers which are illustrated in Figures 2b and d & 3b and d for PMMA (maximum at 366 nm), PDMS (maximum near 300 nm), PS (maximum at 337 nm), and PVA (maximum below 300 nm), respectively. This is comprehensible since all optical centers are from the same monomer units, leading to similar excitation spectrum. In case of PDMS and PVA excitation spectra (Figures 2d and 3d) the maximum peaks were not well resolved since the second order of excitation coincided with the monitoring wavelengths. Insets of these figures show the modifications of transmission spectrum due to fs irradiation. It is evident that the small decrease in transmission, and thus increase in absorption, towards UV region for fs laser irradiated polymers. This change is attributed to the formation of different optical centers due to nonlinear absorption process resulting in polymer chain scission. The change observed beyond 400 nm is due to scattering/diffraction losses from the irradiated regions in polymers. Strong emission from such microstructures has imminent applications in the fields of photonics and microfluidics. For example, Nie



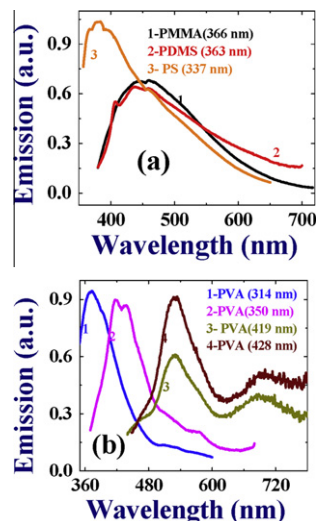
**Figure 2.** (a) Emission spectra of pristine and irradiated PMMA (energy 10  $\mu\text{J}$ , speed 1 mm/s, period 30  $\mu\text{m}$ ). (b) Excitation spectra of irradiated PMMA (inset shows the transmission spectra of the same irradiated and pristine PMMA). (c) Emission spectrum of pristine and irradiated PDMS (energy 50  $\mu\text{J}$ , speed 1 mm/s, period 10  $\mu\text{m}$ ). (d) Excitation spectra of irradiated PDMS (inset shows the transmission spectrum of irradiate PDMS with 30  $\mu\text{J}$  energy, 1 mm/s speed and 60  $\mu\text{m}$  period and pristine PDMS).



**Figure 3.** (a) Emission spectra of pristine and irradiated PS (energy 1  $\mu\text{J}$ , speed 0.5 mm/s, period 30  $\mu\text{m}$ ). (b) Excitation spectra of irradiated PS (inset shows the transmission spectra of the same irradiated PS and pristine PS). (c) Emission spectrum of pristine and irradiated PVA (energy 10  $\mu\text{J}$ , speed 1 mm/s, period 20  $\mu\text{m}$ ). (d) Excitation spectra of irradiated PVA (inset shows the transmission spectra of same irradiated PVA and pristine PVA).

et al. [13] have demonstrated multilayer optical bit memory in PMMA using fluorescent fs laser modified regions.

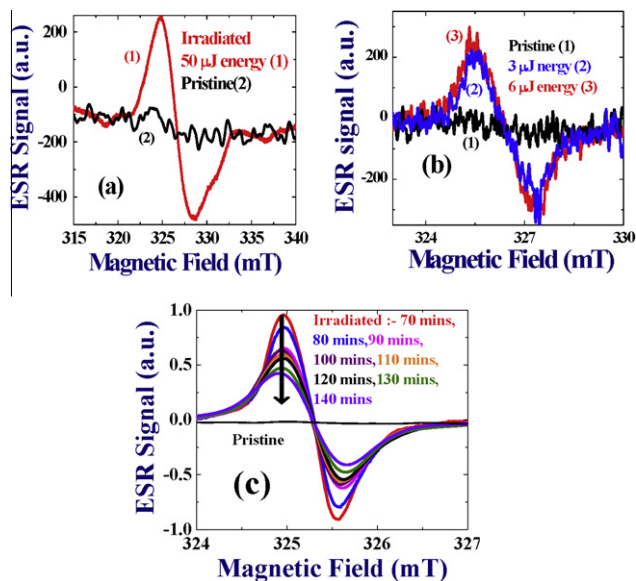
Figure 4a and b shows emission from fs irradiated polymers when excited near excitation peaks. The maximum excitation or absorption in PMMA occurs at 366 nm which can be ascribed to the absorption of aldehyde or ketone groups undergoing  $n \rightarrow \pi^*$  transition [19,20]. PDMS shows similar emission spectrum (Figure 4a) to PMMA when excited at 363 nm as we perceive PMMA and PDMS both contain similar groups except for the presence of sili-



**Figure 4.** (a) Final emission spectra of irradiated PMMA, PDMS, and PS. (b) Emission spectra collected from irradiated regions of PVA excited with different peak wavelengths observed from the excitation spectra. Excitation wavelengths are enclosed in parentheses for different polymers.

con in PDMS. In the case of PS emission can be ascribed to different optical centers such as *trans*-stilbene, diphenylbutadiene (DPBD), and diphenylhexatriene (DPHT) [21]. PDMS excitation spectra demonstrated peak below 300 nm (Figure 2d). PS excitation maximum occurred near 340 nm while PVA excitation maximum transpired near 300 nm along with several other peaks. Origin of the emission from fs modified PVA is still under investigation. Watanabe et al. [22] earlier have shown the luminescence through defect formation in vitreous silica and Kudrius et al. [23] have shown the similar effect in sapphire. In both the cases, it is due to the formation of luminescent defects, or optical centers that are responsible for the observation of photoluminescence behavior. However, such reports on the luminescence of fs laser irradiated polymers are sparse and yet to be explored. Further studies at low temperatures are in progress to understand the emission and excitation spectra of optical centers created by fs irradiation.

We examined the ESR spectra from the modified regions of these polymers in order to verify the contribution of free radical presence to the observed emission. Figure 5a and b shows fs laser modified PMMA (50  $\mu\text{J}$  energy, 1 mm/s speed) and PDMS (3, 6  $\mu\text{J}$  energy with 1 mm/s speed). We could not observe free radicals in fs modified PMMA during our earlier studies since the ESR spectra were recorded after few days [15]. However, fs laser irradiated PMMA exhibited free radicals when the ESR spectrum was collected within 2 days of exposure. In the case of PDMS we observed free radicals even after 6 months. This demonstrates the dependence of life time and stability of free radicals in different host environments. Figure 5c shows the ESR spectrum recorded in PS irradiated grating fabricated with 30  $\mu\text{J}$  energy, 1 mm/s speed with period 15  $\mu\text{m}$ . We observed no ESR signal in case of pristine PS. We collected several spectra after 1 h of fabrication in different time intervals. Irradiated PS demonstrated decrease in ESR signal with time. Irradiated regions of PMMA and PDMS polymers also showed ESR signal at the same magnetic field. Interestingly, fs irradiated regions of PVA did not show any ESR signal. All these polymers exhibited ESR signal at the same magnetic field of 326 mT with 'g' value of 2 indicating the existence of peroxide type free radicals [15]. PMMA and PS illustrated decrease in ESR signal in few days of time while the PDMS showed ESR signal even after 6 months indicating that the free radicals are stable in this polymer. However, the emission from the irradiated regions of polymers did not decay



**Figure 5.** (a) ESR spectrum of irradiated PMMA at 50  $\mu\text{J}$  energy, 1 mm/s speed. (b) ESR spectrum of irradiated PDMA at 3 and 6  $\mu\text{J}$  energy with 1 mm/s speed. (c) ESR spectrum of irradiated PS varying with time. Decrease in ESR signal intensity is indicated by the arrow.

even one year after the exposure. This clearly suggests that the free radicals which contributed to ESR signal do not lead to the emission.

Earlier studies [13,15,24,25] suggest that when these polymers are irradiated with ionizing radiation free radicals are generated. If a polymer is irradiated in vacuum the radical concentration produced in the polymer depends on the irradiation dose. When these vacuum-irradiated polymers are exposed to air, the free radicals trapped in the material are transformed into peroxide radicals through the reaction with molecular oxygen. Kaptan and Guven [24] have irradiated PMMA with  $\gamma$  radiation in a vacuum and reported a nine-line ESR spectrum. They have shown the transformation of nine line ESR spectrum into a single peak anti-symmetric peroxide type free radical formation with exposure to air. Velter-Stefanescu et al. [25] have collected ESR spectra for electron-irradiated PMMA and observed only a peak ESR signal at 326.5 milliTesla (mT). Nie et al. [13] have reported typical characteristic nine line spectrum of PMMA immediately after fs laser irradiation. However, our data depicted a single peak in the ESR spectra for PMMA, PDMS and PS since the experiment/irradiation was carried out in the atmospheric environment and room temperature. Low temperature ESR studies on the vacuum irradiated polymers are under investigation. Our future studies will include fabrication of nano-structures and their complete characterization.

In conclusion, we have utilized fs LDW for fabricating micro-structures in various polymers and were able to characterize the emission from fs laser modified regions. Fabrication of such luminescent micro-structures using modification at higher scan speeds

and low energies has direct relevance in memory based devices owing to economic viability and the ease of preparation. We have demonstrated the formation of different optical centers by fs laser irradiation through the emission studies in polymer materials. We have also confirmed the formation of peroxide type free radicals in PMMA, PDMS and PS polymers after fs irradiation. From the earlier studies [22,23] and the current studies it can be concluded that most of the materials exhibit the formation of luminescent centers by fs laser irradiation. Formation of paramagnetic centers in glasses and crystals need to be explored.

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