

Three-Dimensional Microfabrication With Conjugated Polymers

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Abstract:

In this paper we reported the microfabrication of three-dimensional structures using two-photon polymerization (2PP) in a mixture of MEH-PPV and an acrylic resin. Femtosecond laser operating at 800nm was employed for the two-photon polymerization processes. As a first step in this project we obtained the better composition in order to fabricate microstructures of MEH-PPV in the resin via two-photon polymerization.

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Introduction:

In the last few years, two-photon polymerization (2PP) has been used to fabricate complex three-dimensional micro- and submicron-structures¹⁻⁵, with potential applications in photonic crystals, optical devices, and 3D micromechanical actuators. The nonlinear nature of the two-photon absorption process confines polymerization to the focal volume of the ultrashort laser, allowing the fabrication of microstructures by moving the focal point three dimensionally through the resin. However, the application of this technology has been hindered because the properties of majority of the microstructures reported so far can not be changed externally. Thus new resin formulation containing active components that can still be polymerized by two-photon absorption. In order to explore possibilities in this direction, we prepared samples of the polymeric blend by different methods; films and solution. We measured the absorption and fluorescence spectra for all samples.

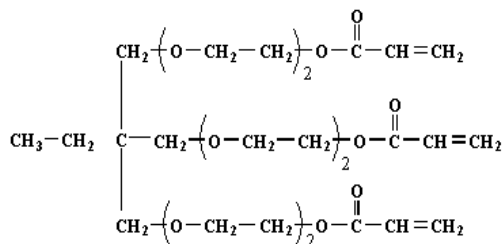
Experimental:

Variety of blends in a guest/host scheme are prepared. The host resin used consists of tris(2-hydroxyethyl) isocyanurate triacrylate, which gives

hardness to the polymeric structure, ethoxylated(6) trimethylolpropane triacrylate, which assists in decreasing the structures shrinkage upon polymerization [those monomers were both from Sartomer by the commercial names SR368 and SR499] and used ethyl-2,4,6-trimethylbenzoylphenylphosphine [Lucirin TPO-L], which acts as the polymerization photoinitiator, figure (1,a,b,c) gives the chemical structures of these components. As guest material we used the conjugated polymer poly[2-methyl-5-(2-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV)⁶, whose interesting optical and electrical properties have attracted considerable attention, figure (2) gives the chemical structures of these components. The resin included the following makeup: 70 wt% of SR368, 26 wt% of SR499, 2.9 wt% of Lucirin TPO-L and different concentrations (0.4, 0.2, 0.05, 0.1) wt% of (MEH-PPV). The components were weighted by a digital balance and it were mixed by a mini-rotator at speed 15rpm. For insure better mix, the samples were left on heater at 60°C, those samples were prepared as films, where put on the glass slides.

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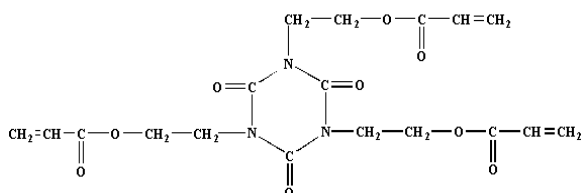
**Harvard University, Division of Engineering and Applied Science



SR499

(a) ethoxylated(6)trimethyl-
lolpropane triacrylate.

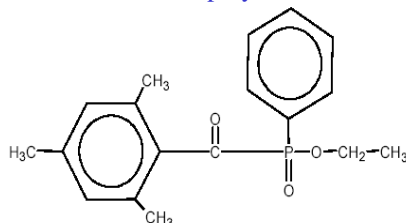
Reduces the shrinkage upon polymerization.



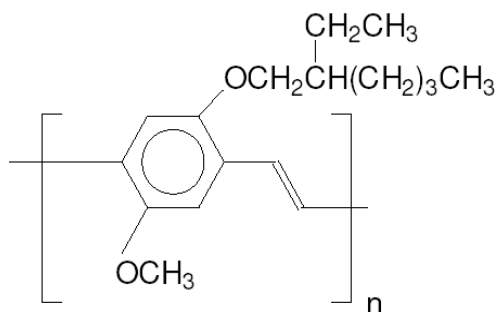
SR368

(b) tris(2-hydroxyethyl)isocyanurate triacrylate.

Gives hardness to the polymeric structure.



Lucirin TPO-L

(c) ethyl-2,4,6-
trimethylbenzoylphenylphosphinate.
Photoinitiator.Figure (1,a,b,c) gives the chemical
structures of host components.Figure (2) gives the chemical structure
of guest components (MEH-PPV).

The second sample were just (MEH-PPV) as solution where this polymer put in test tube.

The third samples were just (MEH-PPV) as film where prepared by put this polymer on glass slides and apply UV light to polymerize the polymer.

Discussion:

After finishing from preparation the samples, the absorption and fluorescence spectra measured for all samples, where the sample put in spectrophotometer device to measure absorption spectrum as shown in figure (3), which indicate that the absorption spectrum increase for blend with increasing the percentage weight of (MEH-PPV) in resin and also we can notice the absorption spectrum for (MEH-PPV) as film and as solution where in case of film the absorption spectrum more than solution, At last we can notice the absorption spectrum for resin without (MEH-PPV) is very close from zero.

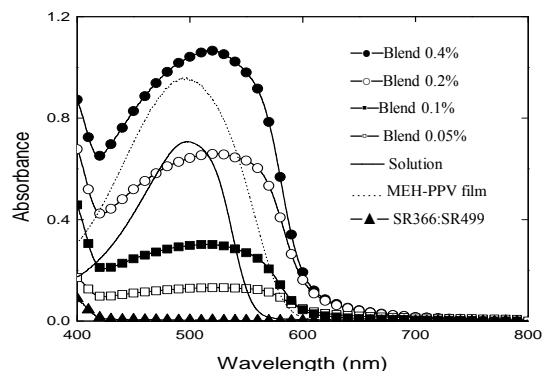


figure (3) Shows the absorption spectrum for all samples to comparison between them.

The other measurements were fluorescence spectrum. figure (4) shows fluorescence spectra of thin film prepared with pure MEH-PPV and the polymeric blend with acrylate resin. For excitation we used an Ar+ laser operating at 514nm on the samples. For all polymeric blends we observed a fluorescence peak around

600nm, which is characteristic of the MEH-PPV emission. For comparison, we also present the fluorescence spectrum of a pure MEH-PPV film. The fluorescence peak increase with the percentage weight of (MEH-PPV) in resin and also you can notice that the fluorescence peak for (MEH-PPV) increase in case solution. At last the resin without (MEH-PPV) did not have fluorescence spectrum.

We induced two-photon absorption polymerization using a Ti:sapphire laser oscillator that produce 130-fs pulses at

800nm. To fabricate structures we used an average laser power of 10mW, measured after the 0.65NA objective that focuses the laser beam into the first sample. This first sample was positioned in the z-direction using a motorized stage, and the laser beam was scanned in the x-y direction with a set of galvanic mirrors as shown in figure (5) where this (x,y,z) stage controlled by motion controller/driver and labview program. After the fabrication, the unpolymerized resin is washed away with ethanol and dried at room temperature.

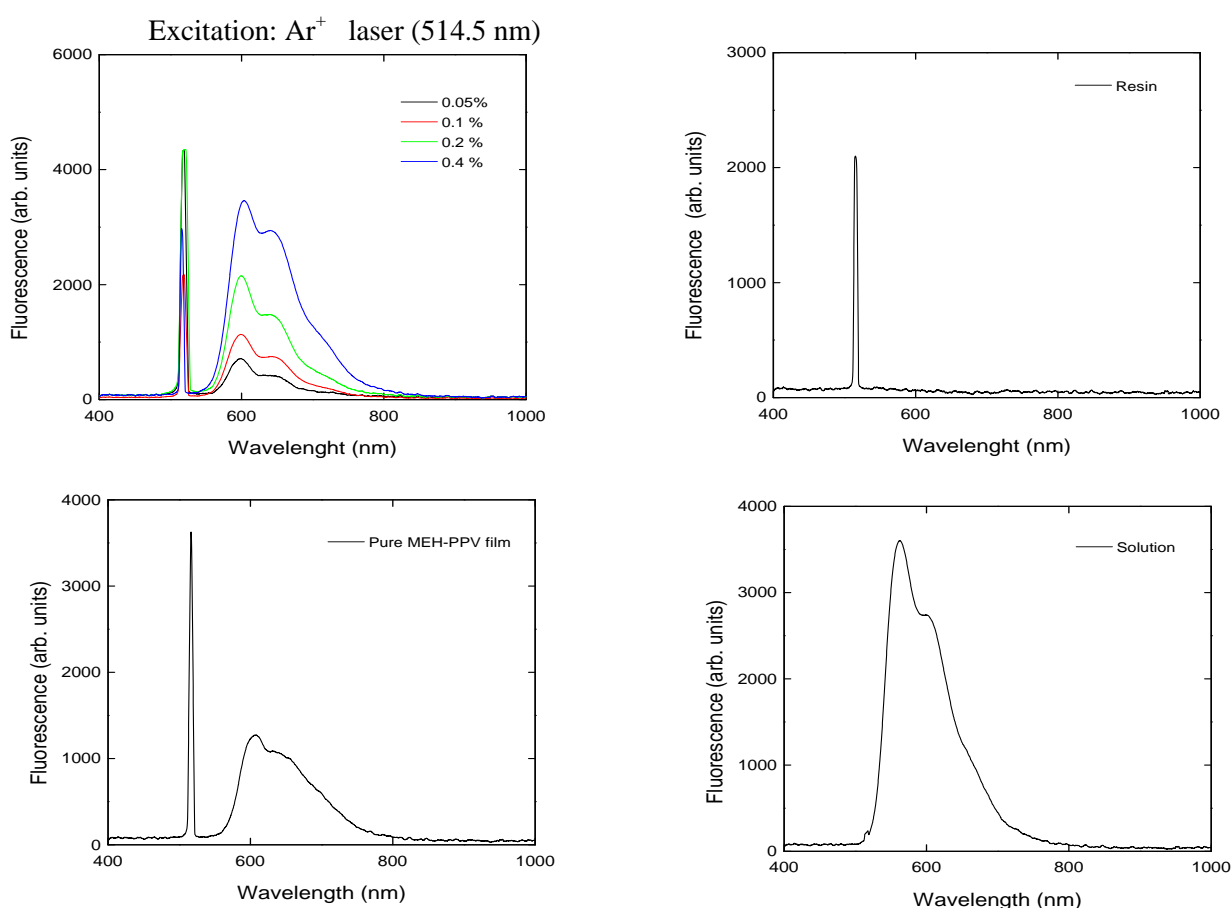


Figure (4) gives the fluorescence spectra for all samples.

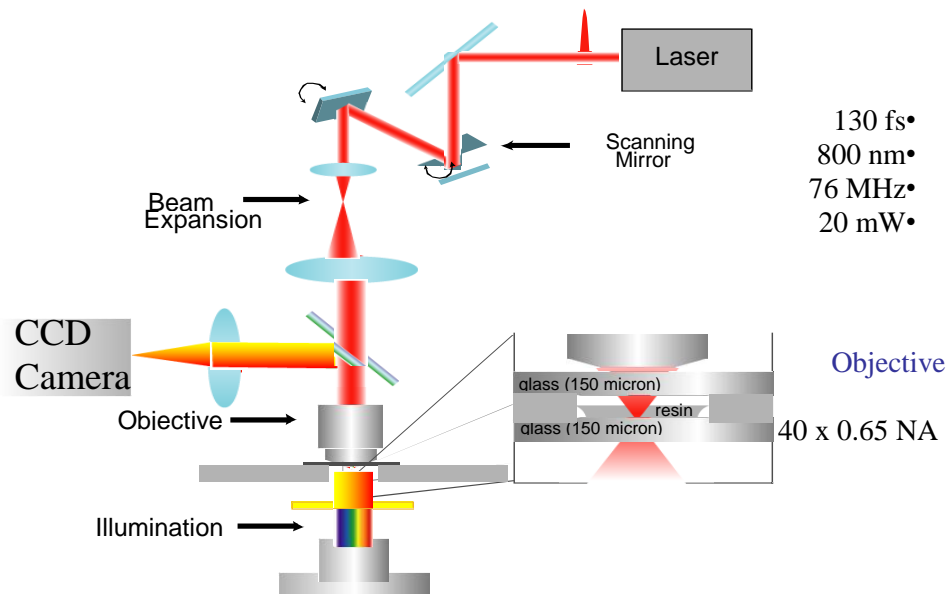
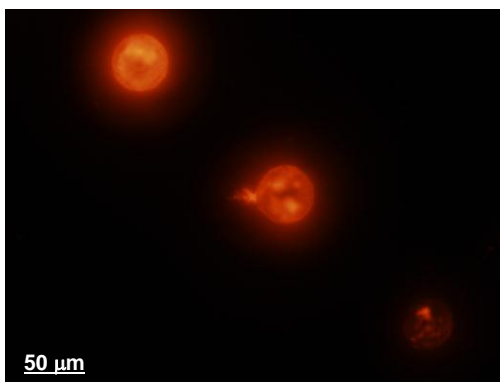


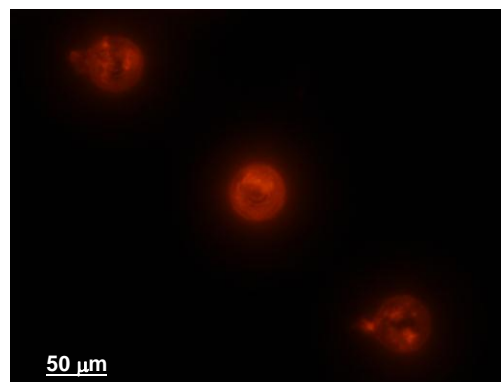
Figure (5) shows the system to fabricate 3D structures (Ti:sapphire laser) oscillator

The 3D structures put in fluorescence microscope device. The purposes from this process are comparison fluorescence between them. figures (6) shows the Sample 0.2 % in different exposure (1/15, 1/30). Figure (7) shows the samples 0.4% in (1/15) where the fluorescence microscopy is very clear and homogeneity. Figure (8) shows the scale for the fluorescence microscopy for 0.4%.

Figure (9) shows all samples present inhomogeneous distribution and the exposure was (1/15) for all these pictures, the samples 0.1 % and 0.05 %: fluorescence is very clear and very inhomogeneous, sample 0.4 %: fluorescence is very clear and homogeneity sample 0.2 %: fluorescence is also clear.



Exposure 1/15



Exposure 1/30

Figure (6) shows the Fluorescence Microscopy-Sample 0.2%

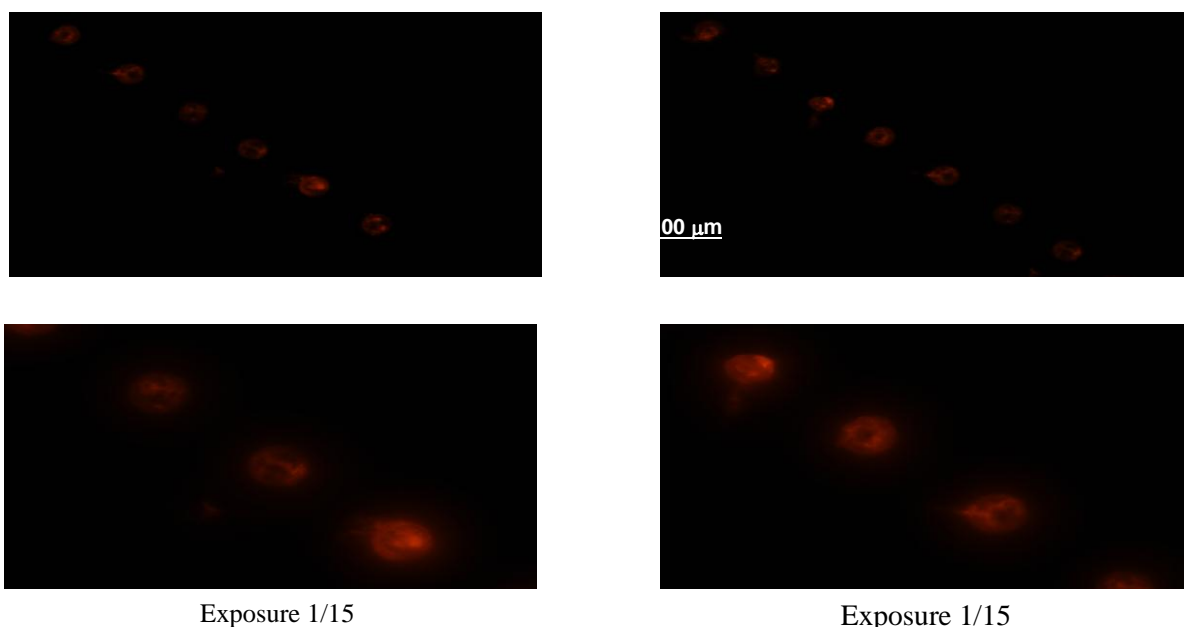


Figure (7) shows the Fluorescence Microscopy-sample 0.4%

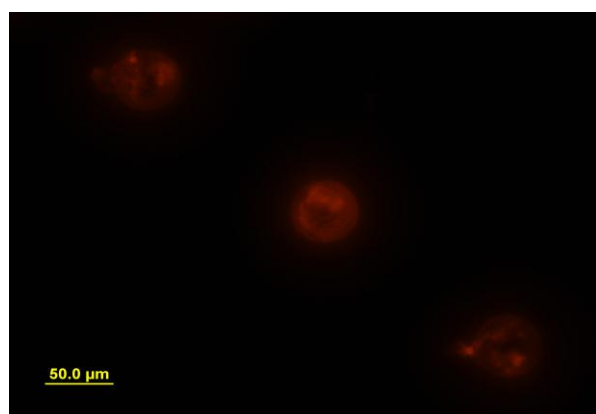


Figure (8) shows the scale for the fluorescence microscopy.

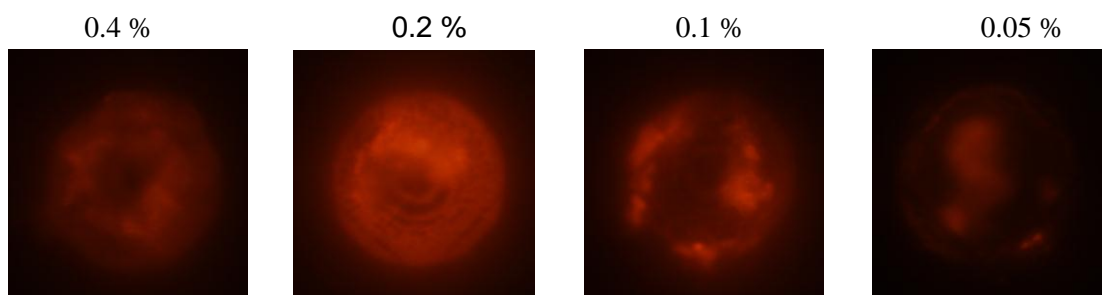


Figure (9) Exposure 1/15 for all these pictures, all samples present inhomogeneous distribution.

Samples 0.1 % and 0.05 %: fluorescence is clear and very inhomogeneous

Sample 0.4 %: fluorescence is clear homogeneity

Sample 0.2 %: fluorescence is clear and very homogeneity

Conclusion:

All results indicates the conjugated polymer preserves its optical properties in the polymeric blend. We found that the MEH-PPV distribution in the microstructure is not uniform, but still completely compatible with the ones usually observed in polymeric blends. in this way, the approach employed here is a promising alternative for the fabrication of microstructures containing conjugated polymers for application in polymeric-based displays, luminescent plastics and organic or plastic circuits. Although the structures shown here have dimensions of the order of tenth of microns, much smaller structure can be fabricated, allowing for instance the manufacture of pixel for display.

References:

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خلاصة:

في هذه البحث تم الحصول على تراكيب دقيقة ثلاثية الابعاد عن طريق استخدام طريقة البلمرة بفوتونين (2) و بمزج MEH PPV و أكريليك الراتنج، واستخدم ليزر جزء من ألف مليون مليون من الثانية ذات طول موجي 800 nm لعمليات البلمرة بفوتونين. وكخطوة اولى في هذا البحث حصلنا على التركيب الأفضل من MEH PPV في الراتنج لصناعة التراكيب الدقيقة الثلاثية الابعاد عن طريق البلمرة بفوتونين.