Three-dimensional microfabrication with conjugated polymers

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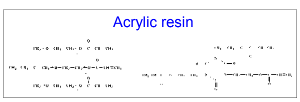
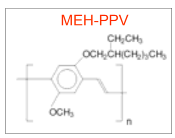
Introduction

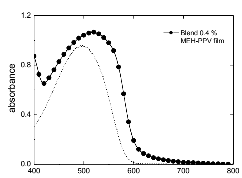
In the last few years, two-photon polymerization (2PP) has been used to fabricate complex three-dimensional micro- and submicro-structures, with potential applications in photonic crystals, optical devices, and 3D micromechanical actuators. However, the application of this technology has been hindered because the properties of majority of the microstructures reported so far cannot be changed externally. We therefore looked for new resin formulations containing active components, that can still be polymerized by two-photon absorption. To this end, we prepared a variety of blends in a guest/host scheme using a acrylate resin and the conjugated polymer poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV), whose interesting optical and electrical properties have attracted considerable attention.





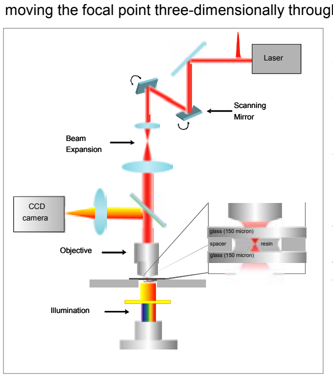
Absorption of MEH-PPV blend

This figure shows the UV-Vis absorption spectrum of polymeric blend containing MEH-PPV (0.4 %). For comparison, we also present the absorption spectrum of a pure MEH-PPV film.

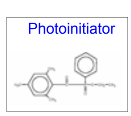


Two-photon polymerization

The nonlinear nature of the two-photon absorption process confines polymerization to the focal volume of the ultrashort laser, allowing fabrication of microstructures by moving the focal point three-dimensionally through the resin.



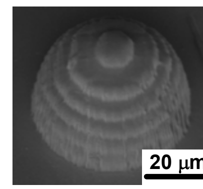
We induced two-photon absorption polymerization using a Ti:sapphire laser oscillator that produces 130-fs pulses at 800 nm. To fabricate structures we used an average laser power of 10 mW, measured after the 0.65-NA objective that focuses the laser beam into the resin. The resin sample was positioned 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. After fabrication, the unpolymerized resin was washed away with ethanol and dried at room temperature.



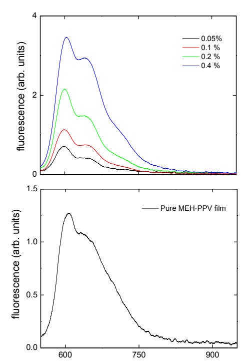
Lucirin TPO-L (ethyl-2,4,6-trimethylbenzoylphenylphosphinate) was used as the polymerization photoinitiator.

Microstrcucture

This figure shows the scanning electron micrographs of a three-dimensional microstructure fabricated using acrylate resin containing conjugated polymer MEH-PPV. The microstructure shows excellent integrity and good definition.



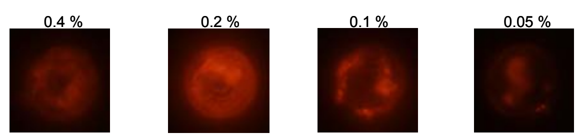
Fluorescence



This figure shows the fluorescence spectra of thin films prepared with pure MEH-PPV and the polymeric blend with the acrylate resin. For excitation we used an Ar ion laser operating at 514 nm.

For all polymeric blends we observed a fluorescence peak around 600 nm, which is characteristic of the MEH-PPV emission. For comparison, we also present the fluorescence spectrum of a pure MEH-PPV film.

Fluorescence microscopy image of the resin doped with MEH-PPV, excited at 543 nm. The structure exhibits fluorescence at approximately 600 nm, characteristic of MEH-PPV, indicating that the conjugated polymer preserves its properties in the polymeric blend. It can also be seen that the MEH-PPV distribution in the polymeric blend is not uniform, which is typical of polymeric blends.



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 tenths of microns, much smaller structures can be fabricated, allowing for instance the manufacture of pixel for displays.

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