Polymers containing azobenzene derivatives have been the subject of intensive research for two decades owing to their unique “smartness”, i.e., the ability to tailor and/or control materials properties by photoisomerization. In particular, it was shown that photoisomerization creates optical anisotropy by nonpolar orientation, and poling by polar optical excitation (all optical poling), and it triggers molecular movement far below the glass transition temperature ($T_g$) of the polymer (photo-assisted poling), and polymer mass movement proceeds in spatial gradients of the excitation light (surface relief gratings). In solid polymers, photoisomerization of azobenzene derivatives creates free volume and drives efficient chromophore and polymer segmental and chain motion far below the polymer’s $T_g$; an effect which is at the origin of photo-assisted and all optical poling and surface relief gratings. Most of the studies reported to date on azo-polymers used single photon isomerization, and it is of critical importance to investigate two- or multiphoton isomerization of azobenzene derivatives in polymers since it would trigger additional studies and applications of azobenzenes containing polymers at the interface of nonlinear optics and photochemistry, in that all of the effects that have been demonstrated in azo-polymers by one-photon isomerization may be reproduced by two- or multi-photon isomerization with potential applications in nanophotonics. In two-photon absorption, the photoreaction can be induced by tightly focused lasers into confined volumes - a resolution of 120 nm has been achieved for three dimensional nanofabrication in photopolymerizable resins. In this presentation, I will discuss our recent work on light induced molecular movement and induced plasticity in azo-polymers by one- and two-photon isomerization. Nanoscale polymer movement is induced by a tightly focused laser beam in an azo-polymer film just at the diffraction limit of light both by one- and two-photon isomerization. The deformation pattern which is produced by photoisomerization of the azo dye is strongly dependent on the incident laser polarization and the longitudinal focus position of the laser beam along the optical axis. The anisotropic nanofluidity of the polymer film and the optical gradient force played important roles in the light induced polymer movement. The limits of the size of the photo-induced deformation were explored, and it was found that the deformation depends on the laser intensity and the exposure time. The smallest deformation size achieved was 200 nm in full width of half maximum; a value which is nearly equal to the size of the diffraction limited laser spot. Beyond the limit of light diffraction, a nano protrusion was optically induced on the surface of the films by metal tip enhanced near-filed illumination. A silver coated tip was located inside the diffraction limited spot of a focused laser beam (460 nm), and an enhanced near-field, with 30 nm light spot, was generated in the vicinity of the tip due to localized surface plasmons. A nano protrusion with 47 nm full width of half maximum and 7 nm height was induced with a resolution beyond the diffraction limit of the light.

References: