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Laser Implantation of Pyrene Molecules into Poly(methyl methacrylate) Films

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This paper describes a novel method to dope solid polymers with aromatic molecules without using solvents. The method is spatially selective, and the resolution is essentially in the micrometer range. The basic idea comes from our recent studies on laser ablation of polymer films doped with aromatic molecules.[1] When polystyrene films doped with anthracene were irradiated with a 351 nm laser pulse, intact anthracene molecules were detected by time-of-flight mass spectrometry even below the ablation threshold.[2] Calculation of the temperature rise at the irradiated surface suggested that one dopant molecule should absorb 20–30 photons without leading to the decomposition of the molecule itself during the laser pulse. To explain such unusual phenomenon, we have proposed "cyclic multiphotonic absorption mechanism", namely, the repetition of internal conversion and photoexcitation in the excited states.[3] This is supported by the fact that the absorbance of the polymer films at the laser wavelength varies depending on dopant molecules, while no complete bleaching takes place for biphenyl and pyrene.[4] Based on these studies, we propose that one dopant molecule can absorb many photons in a polymer matrix, heat up the surrounding polymer network, and be ejected with a high translational energy from the expanded network. If this is true, then we should be able to transfer dopant molecules by laser irradiation between two polymer films in contact. Here it is important to emphasize that this process does not involve ablation of the polymer[5] or polymer transfer;[6] only the guest molecule is transferred from one polymer host to another.

Poly(methyl methacrylate) (PMMA) films including 2.5–3.5 wt % pyrene were prepared by spin-coating on quartz plates and used as dopant source films. Neat films were also prepared by the same method and used as target films for implantation. The typical thicknesses of both films were 2.5 μm. A source film was overlaid with a target film and irradiated with excimer laser pulses (248 nm, fwhm of 30 ns) passing through the target film as shown in Figure 1. While molecules were laser-implanted even when the distance between source and target films was *ca.* 10 μm in air, we present here results of the case when two films were in direct contact. Before and after laser irradiation, the fluorescence spectra of the target and the source films were measured with conventional instruments. The surfaces of the implanted films were also inspected using a fluorescence microscope.

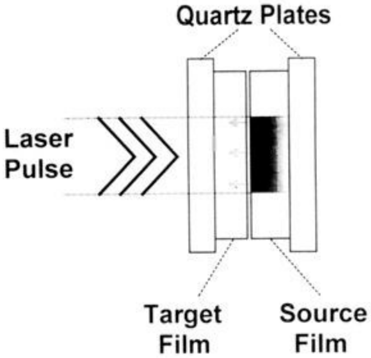

Figure 1. Schematic diagram of the experimental setup.

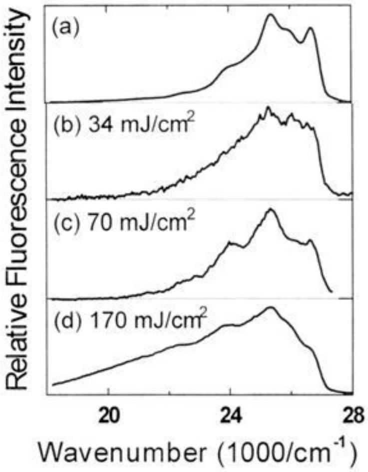

Figure 2. Fluorescence spectra of polymer films: (a) a source film (2.5% pyrene in PMMA) before irradiation, (b)–(d) target polymer films irradiated by one laser shot. The laser intensity is indicated in the figure. The ablation threshold was *ca.* 100 $\mathrm{mJ/cm^2}$.

The irradiated area of target films became fluorescent, and the fluorescence intensity increased with both the number of laser shots and the laser intensity. The fluorescence spectra were very similar to that of the original source film, as shown in Figure 2, which indicates that pyrene molecules were transferred to the target films. The ablation threshold of a PMMA film doped with 2.5% pyrene is around 100 $\mathrm{mJ/cm^2}$. The laser intensities used are indicated in the Figure 2. Clearly, pyrene molecules are transferred well below the ablation threshold and without decomposition. When target films were implanted with an intensity above the ablation threshold, the longer wavelength part of the fluorescence spectra increased. This is ascribed to the formation of excimers because the excitation spectra are almost identical to the monomer absorption spectrum. The possibility of reaction resulting in pyrene derivatives can be excluded by the following experiment. We strongly scraped the implanted surface with a piece of cotton soaked with ethanol and prepared an ethanol solution from the scraper. This solution showed complete monomer fluorescence of pyrene, which suggests that no reaction took place. By the scraping, we were not able to remove all of the fluorescent molecules from the target films. However, the fluorescence spectra of the target films after the scraping also changed to that of the monomer. We consider that ethanol used in the scraping permeated the PMMA matrix and helped disperse the pyrene molecules homogeneously. Therefore, it appears that above the ablation threshold, pyrene aggregate is formed at the surface.

Under a fluorescence microscope, the implanted area produced at laser intensity less than the ablation threshold emitted fluorescence homogeneously, implying that the pyrene molecules are well dispersed in the polymer. On the contrary, fluorescent particles of a few micrometers were found on target films above the ablation threshold. By the scraping described above, the fluorescent particles disappeared, and the surface became homogeneously emissive. It is clear that even above the ablation

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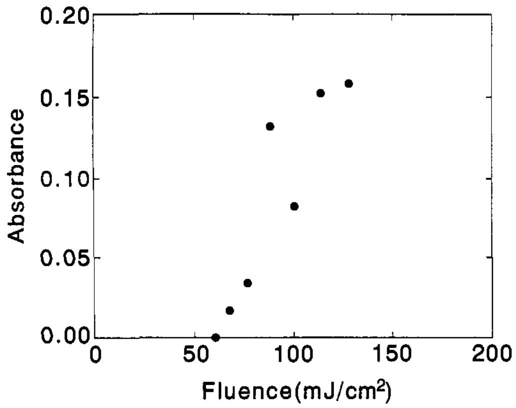

Figure 3. Absorbance of target films at 338 nm after implantation with five laser pulses. The concentration of pyrene in the source film was 3.5%, and the ablation threshold was *ca.* 75 mJ/cm^2.

threshold, the dopant molecules can be transferred to a target film without decomposition.

An important question remains: how deeply are the pyrene molecules implanted? Neither wiping with water-immersed cotton nor using adhesive tapes with strength of 58 g/cm^2 could remove the fluorescent patterns on the target films. To estimate the thickness of the implanted layer, we measured absorbance at peak wavelength (338 nm) of pyrene for the target films after the implantation as shown in Figure 3. With laser intensity less than the ablation threshold, absorbance of the implanted area was around 0.02. Assuming that the average concentration of implanted pyrene is the same as that of the original source film, we obtained the value of 25 nm from the smallest absorbance of the implanted surfaces (0.02). The absorbance increased with laser fluence and reached 0.15, indicating a nearly 200 nm implantation depth using the above assumptions. However, from a preliminary result using total internal reflection fluorescence, we estimate that the concentration of pyrene at the surface of a highly implanted target film would be a few times higher than that of the source film, and, therefore, the thickness of the implanted layer should be around 100 nm at most.[7]

We have recently developed nanosecond time-resolved interferometry and revealed that the polymer surface transiently expands with laser irradiation followed by complete recovery of the flat surface below the ablation threshold.[8] Furthermore, we have reported that polymer matrices are transiently heated up to high temperatures around 500 K[2,9] by laser irradiation, even below the ablation threshold. This is considered to lead a marked increase of the free volume in the polymer, which allows embedded dopants to move vigorously in the source film and eject from the polymer matrix. The ejected molecules have high translational energies and may cause a local heating of the target surface. Moreover, direct heat transfer from the source film to the target film may occur when these two films are in contact. Thus, we can expect that the efficiency of molecular implantation will be high in the contact mode.

Organic molecules have a great variety of functions such as photoelectron transfer, electro- and photochromism, ion sensitivity, biomolecular recognition, nonlinear optical response, and so on. These functions are potentially applicable toward building various kinds of devices if the molecules can be doped into polymer and be fixed to a given area of a device. It is, however, difficult to find a common solvent for the molecules and polymer. Moreover, it is difficult in practice to realize spatially selective doping in a polymer matrix. Here we have demonstrated for the first time that spatially selective implantation of intact aromatic molecules into polymer films is possible by using laser irradiation. We believe that this method will open up new research in both pure and applied chemistry, since the laser irradiation can move the molecules from one place to the other and mix them with the other molecules, which may allow reactions to be initiated in solid polymers.

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(7) To estimate the depth of the pyrene penetration into the target film, we also measured the fluorescence intensity as a function of incident angle by using a hemicylindrical ATR prism. Assuming that the distribution of pyrene molecules in the vicinity of the polymer surface is represented with a step function, we could obtain values of 25–100 nm for the depth of the penetration.

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