Laser-induced molecular mixing of electron donor and acceptor in poly(ethyl methacrylate)

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Dicyanoanthracene molecules are ejected from a polymer film by pulsed UV laser irradiation and are transferred into another polymer film containing hexamethylbenzene, resulting in the formation of the charge-transfer complex in a polymer solid.

Intense irradiation with UV laser pulses has been considered to decompose organic molecules in polymer solids by multi-photonic chemical reactions.[1] However, we have recently shown that aromatic molecules dispersed in polymers hardly decompose by nanosecond laser irradiation and can be ejected from the polymer surfaces without decomposition.[2–4] The evidence that a large thermal jump dominates in laser ablation of doped polymers has been provided by transient thermal expansion of the polymer surfaces.[5] Based on these mechanistic studies of dopant-sensitized laser ablation, we have developed laser molecular implantation (LMI) as an innovative method to generate patterns of intact molecules on polymer surfaces.[6–8] The process involves the overlay of two polymer films: the source film, which contains dopant molecules absorbing the laser light, and the target film, which may be a neat polymer film. Molecules embedded in the source film are excited by a pulsed excimer laser and implanted into the target film in contact. From fluorescence measurements under total internal reflection conditions, the thickness of the implanted layer is estimated to be of a few tens of nanometers.[7] Our attention is now focused on space-selective chemical reactions in a controlled volume beneath a polymer surface by transferring reactants by LMI. This method can be applied for the fabrication of devices using a variety of organic functional molecules. The successful attempt described in this report is opening new prospects for nano-scale chemistry in solid macromolecular structures.

Poly(ethyl methacrylate) (PEMA, $\overline{M}_w = 3.4 \times 10^5$, Aldrich) films were prepared by spin coating on glass plates from chloroform (Nacalai Tesque Inc. HPLC grade) solutions. The typical thickness of the films was 3 μm when the concentration of PEMA in chloroform was 6 wt% and the spin speed was 1000 rpm. Source films were prepared from a saturated solution of 9,10-dicyanoanthracene (DCNA, Kodak) in PEMA–chloroform. Micro-crystals were removed by syringe filters (PTFE 0.2 μm, DISMIC-25 JP, Advantec Toyo). The concentration of hexamethylbenzene (HMB, Nacalai Tesque Inc.) in target films was 0.4 M. For each measurement a neat PEMA target film was irradiated under the same conditions and used as a reference. Only DCNA exhibited an absorption band in the spectral region above 320 nm and a XeF excimer laser pulse (351 nm, fwhm ≈ 30 ns) allowed the selective excitation of DCNA molecules. After irradiation, the fluorescence spectrum of the target film was recorded on a conventional spectrofluorometer (Hitachi F-4500) and the surface was observed by both a fluorescence microscope (Olympus BX 50) with a U-MWU filter unit (λ_{ex} < 400 nm; observation: 400–700 nm) and a scanning electron microscope (SEM) (JEOL JXA-8600X). In the case of repetitive irradiation, it was carried out at 1 Hz or less in order to avoid any cumulative heating effect.

DCNA and HMB are known to form exciplexes in solution and in the gas phase.[9–12] Fluorescence spectra of polymer films doped with DCNA and of films doped with both DCNA and HMB were recorded and used as standards. DCNA films emitted blue fluorescence with a maximum at 430 nm when excited at 380 nm. When HMB was introduced, the monomer fluorescence was quenched, and a broad and structureless band appeared at *ca.* 500 nm (green emission). The excitation spectrum of this compound corresponded to the superposition of the vibrational structure of DCNA monomer fluorescence and a broad charge-transfer band indicating complex formation in ground state between DCNA and HMB.

Laser-implanted area was first examined by fluorescence microscopy. With the first laser shot, the surface was implanted with a gold–yellow emissive compound. This compound was
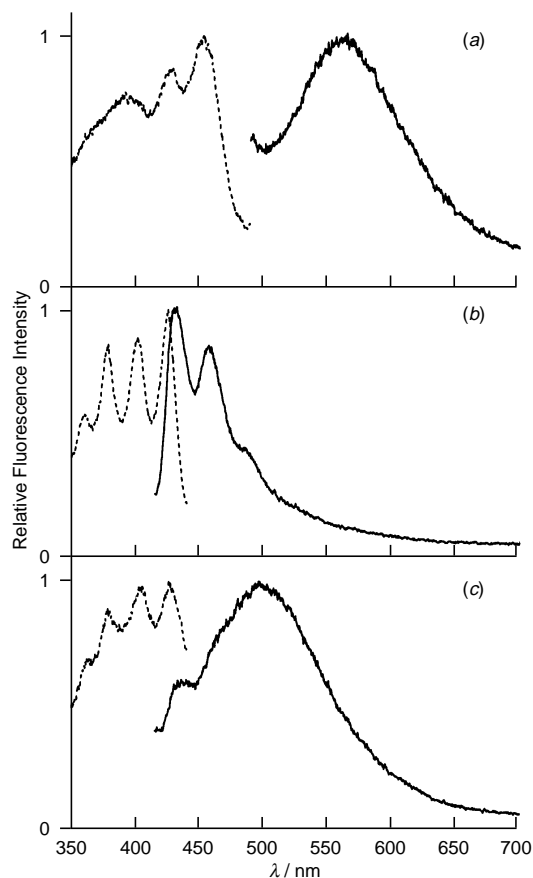

Fig. 1 Fluorescence (——, excited at 380 nm) and their excitation (- - -, observed at 550 nm) spectra of the target films after laser irradiation (laser fluence, 200 mJ cm^{-2}; source film ablation threshold, 400 mJ cm^{-2}). (*a*) The emission band of the yellow compound formed by the first laser shot appeared at *ca.* 560 nm. The excitation spectrum was shifted to longer wavelengths compared to monomeric DCNA. (*b*) After 10 shots irradiation, the emission spectrum of the implanted area almost corresponded to the monomer emission and the excitation spectrum was identical to the DCNA monomer absorption spectrum. (*c*) When HMB was involved in the target film a clear charge transfer band of the DCNA–HMB complex appeared at *ca.* 500 nm.
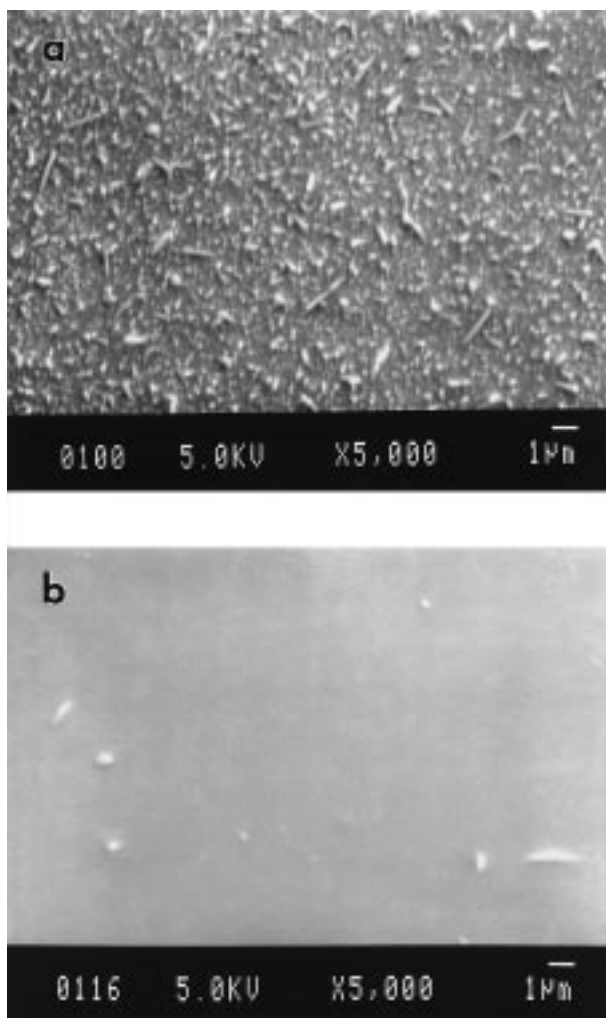
Fig. 2 SEM micrographs of the target film surfaces. (a) With the first laser pulse nano-crystals were formed on the surface of the target film. (b) By repetitive irradiation (10 shots), the nano-crystals almost disappeared and the surface recovered the original flatness.

melted a thin layer of the polymer surface and were dispersed into deeper layers of the surface, which resulted in the recovery of a smooth surface of the polymer. Changes in the fluorescence spectra of the target film also supports the aggregate dispersion by repetitive irradiation.

The yellow emissive aggregates formed by the first laser shot may be attributed to a specific crystal form of DCNA. Meso-substituted anthracene derivatives generally have two crystal forms, α and β, depending on the overlapping of aromatic rings[13,14] and some spectral changes have been reported in the case of thermal treatment of DCNA[15] The α-form is produced by recrystallization from solution while the β-form is obtained either by sublimation or by heating the α-form at temperatures above 453 K for 24 h. A similarity in the fluorescence spectra of the aggregates and the β-form crystal suggests that DCNA in the source film was sublimated by a high transient temperature rise and condensed on the surface of the target film to crystallize as the yellow emissive β-form.

Since the two films in contact were irradiated from the backside of the target film, the crystals formed on the surface of the target film absorb light efficiently, transform it into thermal energy by non-radiative processes and diffuse into a deeper layer of the film. The curve of the fluorescence intensity of the target films as a function of the shots number reached a constant value after a few laser shots indicating that most of the molecules are transferred by the first laser shots. The following shots provide the energy required to dissociate molecular aggregates and release the monomer into deeper layers of the target film where complex formation occur.

In this paper, light has been used for the first time to transfer molecules from one film to another and to mix two components in a polymer matrix without the transfer of the source film polymer matrix itself. LMI appears as a promising tool to induce a chemical reaction in a limited volume of macro-molecular solids leading to a wide range of applications, from the manufacturing of biochemical sensors to that of optical and electronic circuits by using organic functional molecules.

Notes and References

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always formed with the first laser shots irrespective of the existence of HMB in the target film. By increasing the number of laser shots, the yellow fluorescence disappeared and instead blue monomer fluorescence was observed for the target film not including HMB. When the target film contained HMB, the color of the implanted pattern turned to green fluorescence suggesting the formation of the charge transfer complex.

In order to confirm the complex formation in the polymer matrix, we also measured fluorescence spectra of those implanted polymer films (Fig. 1). After the first laser shot, the emission spectrum of the target film exhibited a broad band centered at *ca.* 560 nm and the excitation spectrum was shifted to a longer wavelength region compared to the DCNA monomer absorption band [Fig. 1(*a*)]. The emission changed to that of the DCNA monomer after 10 laser shots and then its excitation spectrum was almost coincident with the DCNA absorption spectrum [Fig. 1(*b*)]. When the target film was doped with HMB, an emission band centered around 500 nm clearly ascribed to the charge transfer emission emerged [Fig. 1(*c*)].

The origin of the yellow emissive compound should be solely ascribed to DCNA as it was found to be independent of HMB. Scanning electron microscope images of the surface revealed the presence of aggregates of a few hundreds of nanometers after the first laser shot [Fig. 2(a)]. The amount of those aggregates decreased with increasing the laser shot number [Fig. 2(b)]. This suggests that upon repetitive irradiation the nano-aggregates absorbed light, reached a high temperature,