

# Photoluminescence of fullerene-doped copolymers of methyl methacrylate during laser irradiation

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Photoluminescence (PL) intensities of C<sub>60</sub>-doped poly(methyl methacrylate-co-ethyl acrylate) (P(MMA-co-EA)) and poly(methyl methacrylate-co-methacrylic acid) (P(MMA-co-MAA)), increase gradually during laser irradiation in air. Concomitantly, their PL peaks are broadened and blue-shifted. C<sub>70</sub>-doped copolymers exhibit a rapid increase in PL intensity soon after the start of laser irradiation, but the PL intensities then decrease to a minimum upon further irradiation. After that, their PL intensities increase again, similar to that of C<sub>60</sub>-doped copolymers. By analyzing UV-visible spectra, these increases in PL are attributed to the formation of some fullerene oxide-copolymer complex by laser induced photochemical oxidation reactions. © 2003 Kluwer Academic Publishers

## 1. Introduction

Because of rich  $\pi$ -electron conjugation encompassing their quasi-spherical molecular surfaces, fullerenes may be applied to develop a completely new class of optoelectrics materials. Thus, many groups [1–4] have studied their photoluminescence (PL). Due to their high molecular symmetry, the HOMO-LUMO (highest occupied molecular orbital to lowest unoccupied molecular orbital) transition of fullerenes is dipole forbidden, exhibiting only very weak luminescence at room temperature. However, the photoluminescence of fullerene-doped polymers is different from that of pure solid fullerene films. Therefore, the physical and chemical properties of fullerene-doped polymers have attracted much recent attention [5–11]. Fullerene C<sub>60</sub>- or C<sub>70</sub>-doped poly(methyl methacrylate) (PMMA) films display intense visible PL [5, 6]. Qian [7] and Li [8] studied photoluminescence of C<sub>60</sub>-doped poly(vinyl carbazole) (PVK) and proposed that effective charge and energy transfer processes occurred in this film. Zhang [9] reported that the PL intensity of C<sub>60</sub>-doped polystyrene (PS), when irradiated by a laser at 488 nm, increased about ten-fold relative to the initial PL intensity. He proposed this PL increase might be caused by photo-oxidation of the film area subjected to laser irradiation [9]. Xie tried to use this property for optical data storage in a C<sub>60</sub>-doped PS film based on the great increase of its PL after laser irradiation in air [10]. Therefore, fullerene-doped polymers are potential candidates for optically encoded information storage materials for ROMs (read only memories).

The PL increases from fullerene-doped PMMA, poly(methyl phenyl silane) (PMPS) and poly(phenyl

silsesquioxane) (PPSQ), all of which have different main chain structures, were compared with fullerene-doped PS [11]. Fullerene-doped PMMA exhibited the greatest PL increase among these four kinds of polymers after extended laser irradiation in air [11]. In our search for fullerene-doped polymers with drastic PL increases after laser irradiation, two copolymers of methyl methacrylate were selected as doping matrices, namely, poly(methyl methacrylate-co-ethyl acrylate) (P(MMA-co-EA)) and poly(methyl methacrylate-co-methacrylic acid) (P(MMA-co-MAA)). The photoluminescence spectra during laser irradiation in air of the two fullerenes, C<sub>60</sub> or C<sub>70</sub>, doped into both P(MMA-co-EA) and P(MMA-co-MAA) are reported in this paper. These PL results are compared to those of fullerene-doped PMMA. We also explore the possible cause for these PL increases as laser irradiation proceeds.

## 2. Experimental

C<sub>60</sub> and C<sub>70</sub> fullerene powders with purities of 99.95% and 99.0% were bought from SES Research Inc. P(MMA-co-EA) ( $\bar{M}_w$ : ~101,000 (GPC); <5 wt% EA) and P(MMA-co-MAA) ( $\bar{M}_w$ : ~34,000 (GPC) and  $\bar{M}_n$ : ~15,000 (GPC); the molar ratio of MMA/MAA = 1/0.016) were purchased from Aldrich Chemical Company, Inc. (U.S.A.). PMMA was bought from Kanto Chemical Co. Inc (Japan). These polymers were used directly without any purification. C<sub>60</sub>- or C<sub>70</sub>-doped P(MMA-co-EA), P(MMA-co-MAA) and PMMA compositions, each having a 1/65 (wt/wt ratio), were individually dissolved into toluene. Films of all the fullerene-doped copolymers were prepared from

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toluene solutions by evaporating the solvent under ambient atmosphere at room temperature. The films were then heated at 67°C in a vacuum oven in order to vaporize all residual toluene.

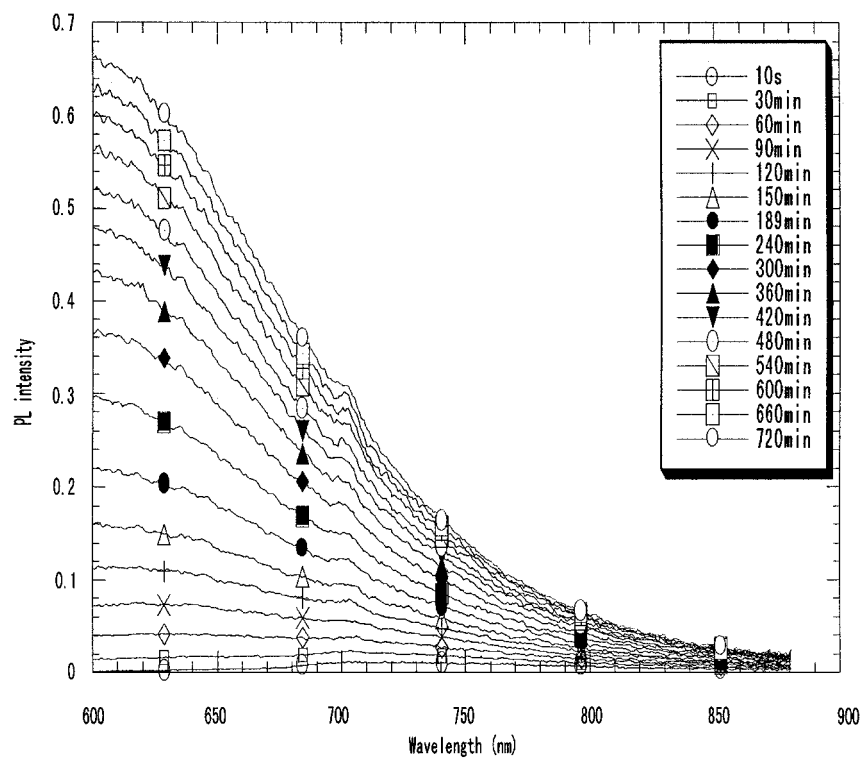
An argon ion laser with power of 13.7 mW and wavelength of 488 nm was used as the excitation source for PL measurements. The diameter of laser beam was about 0.7 mm and the power density was 35.6 mW/mm<sup>2</sup>. If the power density was low, i.e., 0.36 mW/mm<sup>2</sup>, then the PL would be weak, and photochemical oxidations between fullerene, oxygen and copolymers would be slow. Therefore, any PL increases after laser irradiation would be small. PL spectra of fullerene-doped copolymer films during laser irradiation in air were measured *in situ* by an IMUC-7000 (Photal Otsuka Electronics) instrument. In all

cases, a neutral density filter ND-10 with 10% transmittance was inserted in front of the detector. A Carl Zeiss D-7082 Oberkochen Microscopic Spectrophotometer with a measurement spot size of 20 μm was used to measure the UV-visible absorption spectra of fullerene-doped copolymer films before and after laser irradiation.

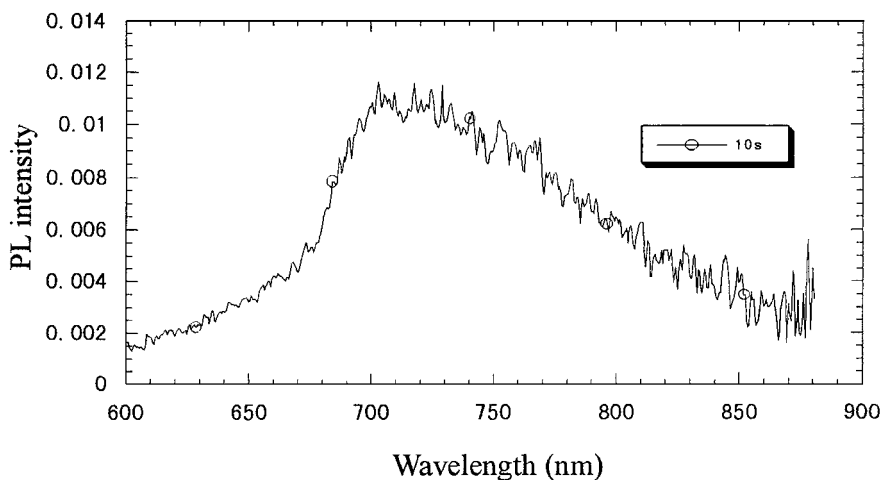
### 3. Results and discussion

#### 3.1. Increase of photoluminescence (PL) from C<sub>60</sub>-doped copolymers

Photoluminescence (PL) spectra of a C<sub>60</sub>-doped P(MMA-co-EA) film during laser irradiation in air are shown in Fig. 1. After only 10 s of laser irradiation, the PL of C<sub>60</sub>-doped P(MMA-co-EA) (shown in Fig. 1a) is



(a)



(b)

Figure 1 Photoluminescence (PL) spectra of a C<sub>60</sub>-doped P(MMA-co-EA) film during laser irradiation at 488 nm (C<sub>60</sub>/P(MMA-co-EA) composition = 1/65 wt/wt; thickness: 140 μm) (a) and the enlarged PL spectrum under 10 s of laser irradiation (b).

so weak that it was very difficult to distinguish the spectral shape. Thus, an enlarged Y-axis for the PL after 10 s of laser irradiation is shown in Fig. 1b. This shows that C<sub>60</sub>-doped P(MMA-co-EA) has a broad PL band with a broad peak which maximizes at about 702 nm. However, its PL intensity increases with increasing laser irradiation time and the PL peak both broadens and exhibits a blue-shift. In fact, a clear PL light was observed visually during irradiation after a longer period of laser irradiation. However, no PL light could be observed by eye shortly after laser irradiation started. Unfortunately, because PL could only be detected at wavelength greater than 600 nm when using laser excitation at 488 nm, the exact position of the PL peak could not be measured after several hours of laser irradiation.

PL spectrum of C<sub>60</sub>-doped P(MMA-co-MAA) displays a much broader PL band than that for C<sub>60</sub>-doped P(MMA-co-EA) after only 10 s of laser irradiation (Fig. 2a). This spectrum exhibits a broad band with

a sharp peak at about 705 nm. The PL intensities of C<sub>60</sub>-doped P(MMA-co-MAA) also increase with an increase of laser irradiation time (Fig. 2b) in a manner similar to that of C<sub>60</sub>-doped P(MMA-co-EA). Its PL peak is broadened and shifts to short wavelengths. The PL of undoped films of P(MMA-co-EA) and P(MMA-co-MAA) have been measured. No PL was detectable at the start of laser irradiation or after a few hours of laser irradiation (488 nm) in air. Furthermore, pure C<sub>60</sub> films prepared by solution spraying or vacuum vapor deposition exhibit very weak PL in its range when excited at 488 nm. Therefore, the PL from C<sub>60</sub>-doped copolymers is ascribed to the dispersed C<sub>60</sub> molecules in the continuous copolymer matrix.

Differences between the PL spectra of C<sub>60</sub>-doped P(MMA-co-EA) and P(MMA-co-MAA) at the start of laser irradiation are probably due to some differences in the state of C<sub>60</sub> dispersion within each copolymer matrix. The P(MMA-co-MAA) copolymer

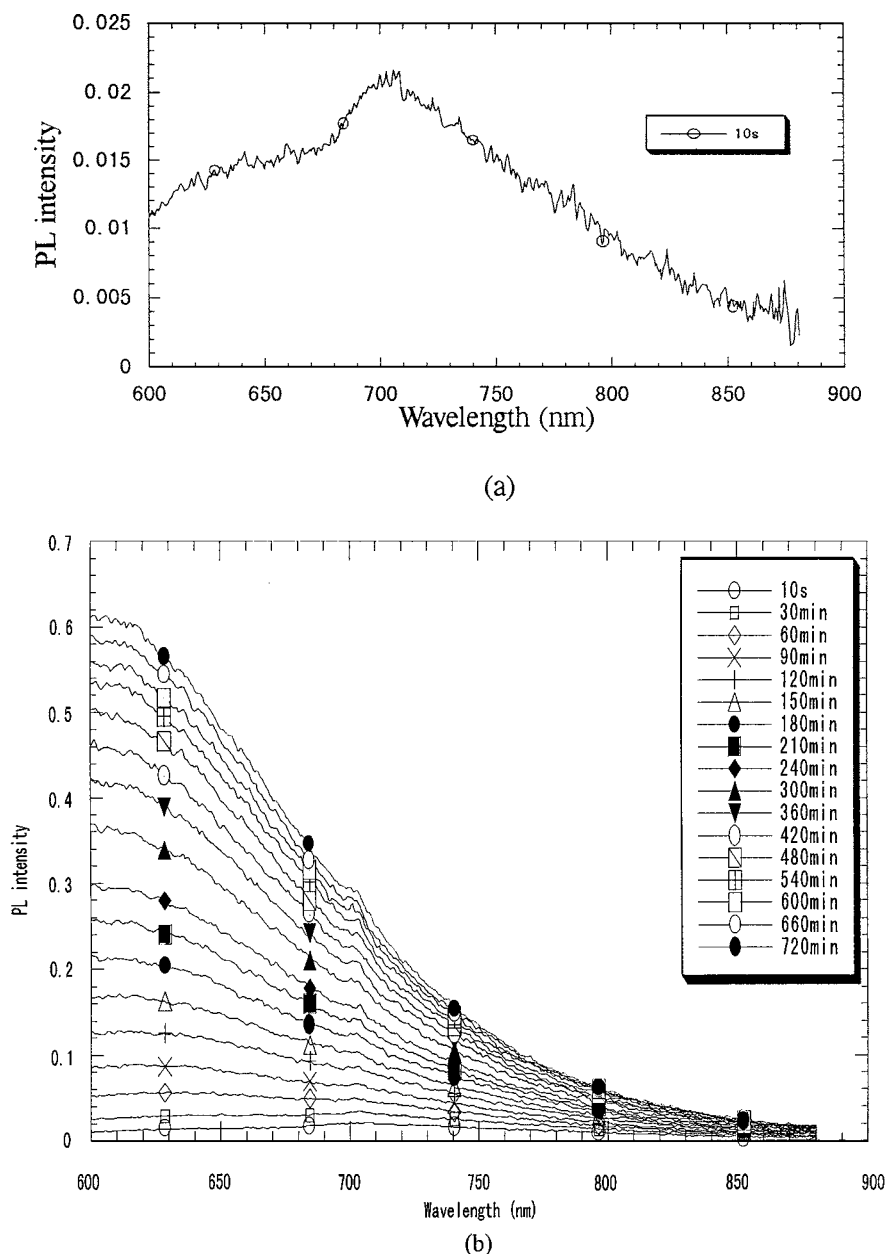


Figure 2 The enlarged photoluminescence (PL) spectrum under 10 s of laser irradiation (a) and PL spectra of a C<sub>60</sub>-doped P(MMA-co-MAA) film during laser irradiation at 488 nm (C<sub>60</sub>/P(MMA-co-MAA) composition = 1/65 wt/wt; thickness: 105 μm) (b).

contains  $\text{-COOH}$  hydroxyl groups unlike the P(MMA-co-EA) copolymer. These hydroxyl groups hydrogen-bond with carbonyl oxygens. Thus, intermolecular and intramolecular interactions among P(MMA-co-MAA) macromolecules are stronger than those among P(MMA-co-EA) macromolecules. Therefore, the fullerene miscibility in P(MMA-co-EA) is better than that in P(MMA-co-MAA). Fullerenes are easily dispersed in P(MMA-co-EA) versus P(MMA-co-MAA). These differences in the miscibility and the interactions between  $\text{C}_{60}$  and each copolymer cause differences in dispersion. Upon laser irradiation of a pure  $\text{C}_{60}$  film in air at the same conditions, the  $\text{C}_{60}$  film's weak PL intensities decrease without any change of its PL peak shape during irradiation. Thus, the PL increases for  $\text{C}_{60}$ -doped P(MMA-co-EA) and P(MMA-co-MAA) must be the result of photochemical reactions involving these copolymers.

The PL spectra of  $\text{C}_{60}$ -doped PMMA samples were measured under the same laser irradiation conditions in order to compare their rates of PL increase to those of both  $\text{C}_{60}$ -doped copolymer systems. The PL integral intensities for  $\text{C}_{60}$ -doped PMMA and the  $\text{C}_{60}$ -doped copolymers were calculated from 600 nm to 880 nm (see Fig. 3). Every symbol on the curves in Fig. 3 represents one experimental point obtained from one PL spectrum. In contrast, the symbols on the PL spectra of the fullerene-doped copolymers in Figs 1 and 2 are only used to distinguish the different curves without any further meaning. Both of the  $\text{C}_{60}$ -doped copolymers have much larger PL integral intensity increases after a few hours of laser irradiation than that for PMMA. The PL integral intensities of the  $\text{C}_{60}$ -doped copolymers increase slowly at first and then increase more quickly (Fig. 3). Finally, the rates of their PL intensity increases slow down and appear to saturate at longer laser irradiation times.

The rates at which these PL integral intensities increase for both  $\text{C}_{60}$ -doped P(MMA-co-EA) and  $\text{C}_{60}$ -doped P(MMA-co-MAA) are similar over the entire irradiation period. Furthermore, these PL intensity increases are higher than those of the  $\text{C}_{60}$ -doped PMMA. Therefore,  $\text{C}_{60}$ -doped P(MMA-co-EA) and P(MMA-

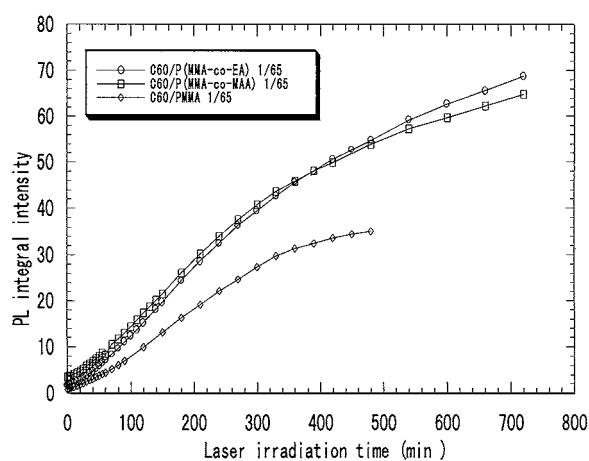


Figure 3 PL integral intensity of  $\text{C}_{60}$ -doped P(MMA-co-EA) (thickness:  $140\ \mu\text{m}$ ), P(MMA-co-MAA) (thickness:  $105\ \mu\text{m}$ ) and PMMA (thickness:  $80\ \mu\text{m}$ ) films vs. laser irradiation time.

co-MAA) are better candidates for developing novel ROM storage materials.

### 3.2. Cause of the photoluminescence increases

In order to explore the cause for the increase in PL after laser irradiation of the  $\text{C}_{60}$ -doped copolymers in air, the UV-visible absorption spectra of  $\text{C}_{60}$ -doped P(MMA-co-EA), P(MMA-co-MAA) and PMMA were studied. PMMA and its copolymers have no absorption peak in the visible light wavelength range but  $\text{C}_{60}$  has specific absorption peaks in this range. Thus, the UV-visible absorption spectra of  $\text{C}_{60}$ -doped copolymers can detect changes in the chemical structure of  $\text{C}_{60}$  upon exposure to laser irradiation. UV-visible absorption spectra of  $\text{C}_{60}$ -doped P(MMA-co-EA) (shown in Fig. 4), before laser irradiation, exhibit specific absorption peaks in the visible light region. A small peak at about 406 nm and two indistinct peaks at 540 nm and 600 nm were observed.  $\text{C}_{60}$ -doped P(MMA-co-MAA) has a UV-visible spectrum similar to  $\text{C}_{60}$ -doped P(MMA-co-EA). Its specific absorptions are similar to those exhibited by  $\text{C}_{60}$ /toluene solutions [12]. Laser irradiation of the  $\text{C}_{60}$ -doped copolymers in air for a few hours causes replacement of all three absorption peaks by a broad absorption from 400 nm to  $\sim 680$  nm. Therefore, a drastic change in the chemical structure of  $\text{C}_{60}$  molecules dispersed in the two copolymers had been induced by laser-induced photochemical reactions. The same result was obtained with  $\text{C}_{60}$ -doped PMMA. The PL spectra of  $\text{C}_{60}$ -doped PMMA induced by laser irradiation in nitrogen were almost unchanged. The PL intensity and shape remained the same. The same phenomenon was observed upon laser irradiation of  $\text{C}_{60}$ -doped polystyrene in nitrogen [9]. This contrasts sharply to irradiation in air. Clearly, oxygen must be present for PL increases to occur with  $\text{C}_{60}$ -doped PMMA or the  $\text{C}_{60}$ -doped copolymers during laser irradiation. Mass spectrometry, NMR and GPC studies of  $\text{C}_{60}$ -doped PMMA, both before and after laser irradiation in air and nitrogen, demonstrated that photochemical oxidations occurred in air, producing an unknown  $\text{C}_{60}\text{O}_n$ -PMMA product [11].

Similar  $\text{C}_{60}$ -copolymer oxidation products were formed within  $\text{C}_{60}$ -doped P(MMA-co-EA) and

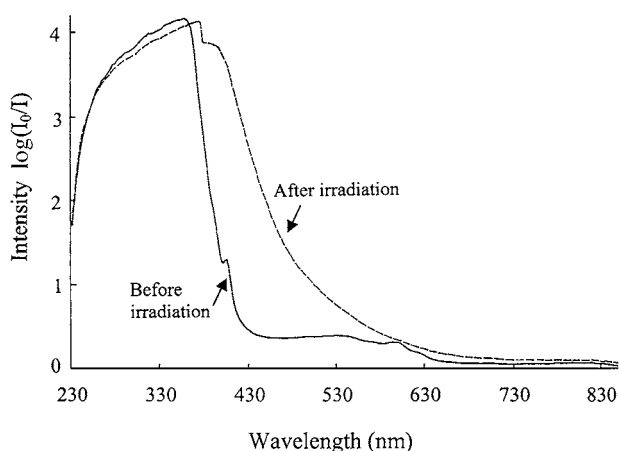
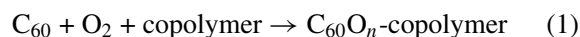


Figure 4 UV-visible absorption spectra of  $\text{C}_{60}$ -doped P(MMA-co-EA) (1/65, wt/wt) before and after laser irradiation at 488 nm.

P(MMA-co-MAA) films upon prolonged 488 nm laser irradiation in air. The laser-induced chemical oxidation among fullerene C<sub>60</sub>, oxygen and copolymer is represented, generally, in Equation 1.



The PL increase is caused by the formation of these oxidation products. The C<sub>60</sub> HOMO-LUMO transition is forbidden due to the high symmetry of the C<sub>60</sub> cage. Thus, C<sub>60</sub> has weak PL at room temperature. Laser irradiation in air causes C<sub>60</sub> photochemical reactions with molecular oxygen and copolymer to form C<sub>60</sub>O<sub>n</sub>-copolymer species of unknown structure, with oxygen atoms bonded to the fullerene cage. The lowered cage symmetry of these species, versus C<sub>60</sub>, strengthens the HOMO-LUMO transition, thereby enhancing the observed PL. The rate of the PL increase depends on the

photochemical reaction rates among C<sub>60</sub>, oxygen and each copolymer. The PL increases depend on the extent of these oxidation reactions.

### 3.3. Photoluminescence (PL) increases in C<sub>70</sub>-doped copolymers

PL spectra of C<sub>70</sub>-doped P(MMA-co-EA) upon laser irradiation in air are shown in Fig. 5. The C<sub>70</sub>-doped copolymers have much stronger PL intensities than do the C<sub>60</sub>-doped copolymers. Two PL peaks, one distinct peak at around 703 nm and another shoulder peak at around 667 nm, appear after only 10 s of laser irradiation. In contrast to C<sub>60</sub>-doped copolymers, the PL intensity of C<sub>70</sub>-doped P(MMA-co-EA) increases quickly with irradiation time and then decreases quickly upon further irradiation. This occurs without any change in the shape of the spectra (shown in Fig. 5b). Then,

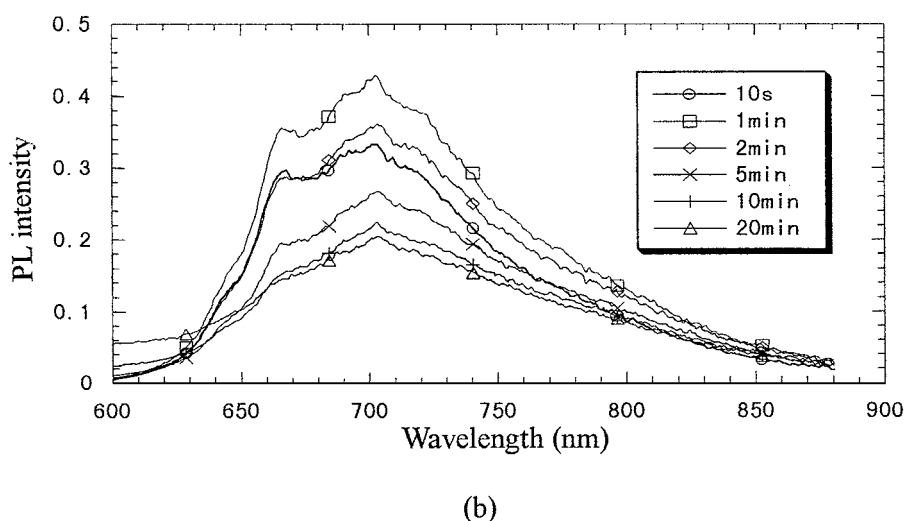
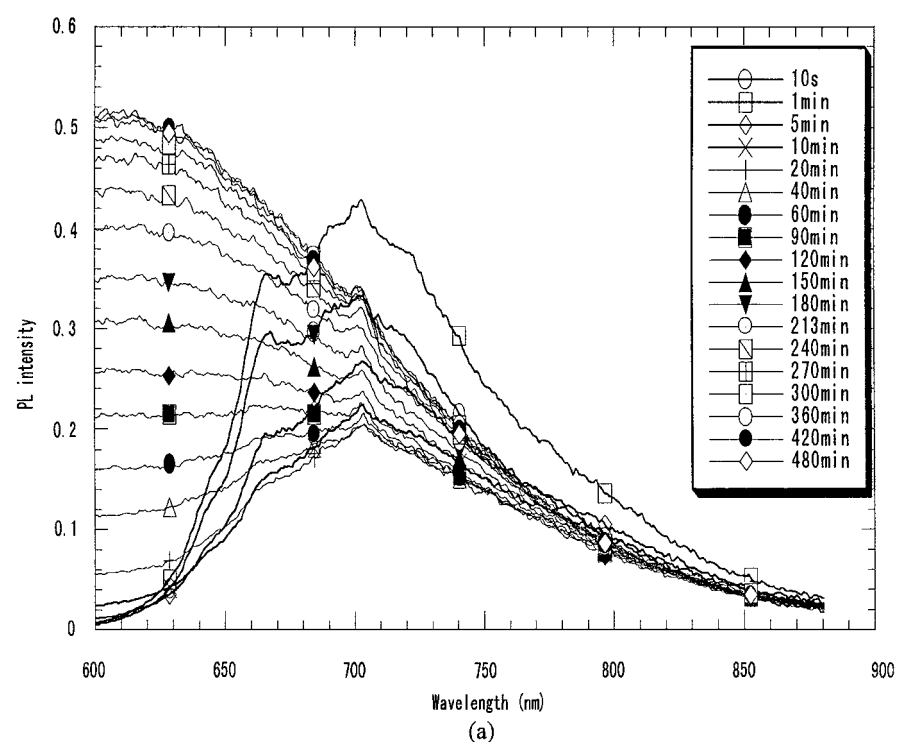


Figure 5 Photoluminescence (PL) spectra of a C<sub>70</sub>-doped P(MMA-co-EA) film during laser irradiation at 488 nm (C<sub>70</sub>/P(MMA-co-EA) composition = 1/65 wt/wt; thickness: 85 μm) (a) and the PL spectra under initial laser irradiation (b).

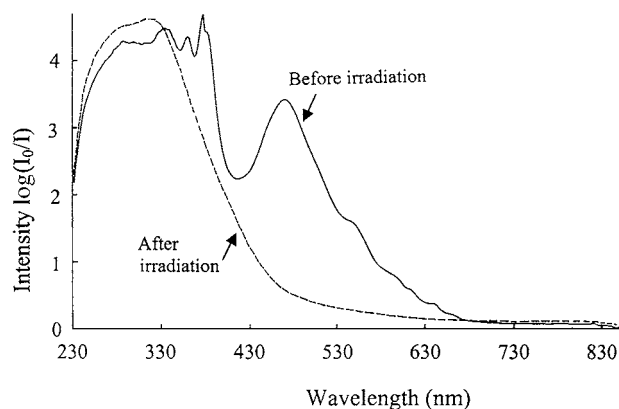


Figure 6 UV-visible absorption spectra of  $C_{70}$ -doped P(MMA-co-EA) (1/65, wt/wt) before and after laser irradiation at 488 nm.

after 20 min of irradiation, the PL intensity starts to increase again with increasing irradiation time. As this takes place, the PL peaks are simultaneously broadened and undergo a blue-shift (Fig. 5a). The exact positions of  $C_{70}$ -doped copolymers' PL peaks could not be detected after several hours of irradiation, due to the 600 nm wavelength limit for observing PL set by laser irradiation at 488 nm.  $C_{70}$ -doped P(MMA-co-MAA) exhibited the same behavior. However, the PL of  $C_{70}$ -doped PMMA initially increased with irradiation time, but, unlike  $C_{70}$ -doped P(MMA-co-EA) and P(MMA-co-MAA), it did not show a rapid intensity decrease after the initial increase. The explanation of these early irradiation period phenomena exhibited by the  $C_{70}$ -doped copolymers is unknown. On further irradiation (after 20 min of laser irradiation), the PL increases with increasing irradiation time were similar to those found for  $C_{70}$ -doped PMMA.

The UV-visible spectra for  $C_{70}$ -doped copolymers, both before and after laser irradiation, are shown in Fig. 6. Before irradiation, the UV-visible absorption spectrum of  $C_{70}$ -doped P(MMA-co-EA) exhibits one strong peak at 471 nm and indistinct shoulders at 544 nm, 590 nm, 612 nm, 638 nm and 660 nm. These are attributed to the absorptions of  $C_{70}$  molecules. The UV-visible spectrum of  $C_{70}$ -doped P(MMA-co-MAA) is similar to that of  $C_{70}$ -doped P(MMA-co-EA). However, after lengthy 488 nm laser irradiation, all of these specific absorption peaks in the visible region disappear. This is illustrated in Fig. 6 and demonstrates that a change in the chemical structure of  $C_{70}$  has occurred due to photochemical reactions.

The PL intensity increase, peak broadening and blue-shift of both  $C_{70}$ -doped P(MMA-co-EA) and  $C_{70}$ -doped P(MMA-co-MAA), which occur late during laser irradiation in air, are attributed to formation of some  $C_{70}O_n$ -copolymer complex by photochemical oxidations. This behavior is similar to that of the  $C_{60}$ -doped copolymers.

#### 4. Conclusions

The photoluminescence (PL) intensities of  $C_{60}$ -doped P(MMA-co-EA) and  $C_{60}$ -doped P(MMA-co-MAA) increase gradually during continuous laser irradiation in air. At the same time, their PL bands become broader and exhibit a blue-shift.  $C_{60}$ -doped MMA copolymers have much greater PL increases and higher rates of PL increase compared to those of  $C_{60}$ -doped PMMA. Unlike  $C_{60}$ -doped copolymers and  $C_{70}$ -doped PMMA, the PL intensities of the  $C_{70}$ -doped copolymers increase rapidly, soon after the irradiation has started. Then the PL intensities decrease quickly to a minimum after about 20 min. In this process, the PL peak shapes remain essentially unchanged. Finally, the PL intensities increase with a further increase of irradiation time, and, the PL peaks are simultaneously broadened and blue-shifted. Oxygen is required and photooxidations are associated with the PL intensity growth. Drastic changes in UV-visible absorption of fullerene-doped copolymers before and after laser irradiation demonstrate that laser-induced photochemical oxidations occurred during irradiation in air. These oxidations cause chemical and symmetry changes in the fullerenes, which enhance the intensity of their HOMO-LUMO transitions, producing larger increase in the PL intensities.

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