Electron-beam patterning of photoluminescent structures in polystyrene using water vapor.

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It is known that electron irradiation transforms polystyrene (PS) from a non-luminescent polymer into a luminescent material. For example, photoluminescence (PL) from irradiated PS results from formation of polycyclic aromatic hydrocarbons (PAH) [1] or carbon dots, assumed to be composed of PAH[2]. In unrelated work, water vapor has been shown to modify chemical processes during electron-beam irradiation of Teflon AF[3] and water vapor also alters the sensitivity and contrast of PMMA in electron-beam lithography[4]. These prior efforts motivated us to study the effect of water-vapor on the e-beam induced synthesis of fluorophores in polystyrene.

Here we describe the effect of dose and water-vapor pressure on the emission spectra and photon yield of irradiated PS films on glass substrates. The films were exposed in an environmental scanning electron microscope using a 30 keV electron-beam. The water vapor pressure ranged from $<10^{-5}$ mbar (high vacuum) to 3 mbar, and the dose ranged from 1.8 to 45 mC/cm^2 as illustrated in Figure 1. Under high-vacuum, as shown in Figure 2, we found that increasing dose red-shifts the emission spectrum and increases the photon yield, which is consistent with prior work.[1,2] However, under water vapor, we found that the emission wavelength and photon yield can be tuned by both dose and water-vapor pressure (Figure 3). Importantly, water vapor significantly increased the photon yield with a maximum occurring at 1 mbar pressure (Figure 4). The emission spectra from PS exposed under water-vapor exhibit at least two peaks that are much sharper than those observed for high-vacuum exposure. Thus, localized electron-beam synthesis of fluorophores in polystyrene can be controlled by both dose and by ambient water-vapor pressure. Moreover, water vapor enhances photon-yield up to a factor of 3 compared to high-vacuum exposure. This technique could enable new approaches to photonics where fluorophores with tunable emission properties can be locally introduced by electron-beam patterning.

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[1] Lee, H. M., Kim, Y. N., Kim, B. H., Kim, S. O., & Cho, S. O. (2008). Advanced Materials, 20(11), 2094-2098.

[2] Kamura, Y., & Imura, K. (2019). ACS omega, 4(2), 3380-3384.

[3] Sultan, M. A., Lami, S. K., Ansary, A., Strachan, D. R., Brill, J. W., & Hastings, J. T. (2019). Nanotechnology, 30(30), 305301.

[4] Kumar, D., Chaudhuri, K., Brill J. W., Pham J. T., and Hastings J. T. (2023). Journal of Vacuum Science & Technology B 41, 012604. https://doi.org/10.1116/6.0002118.

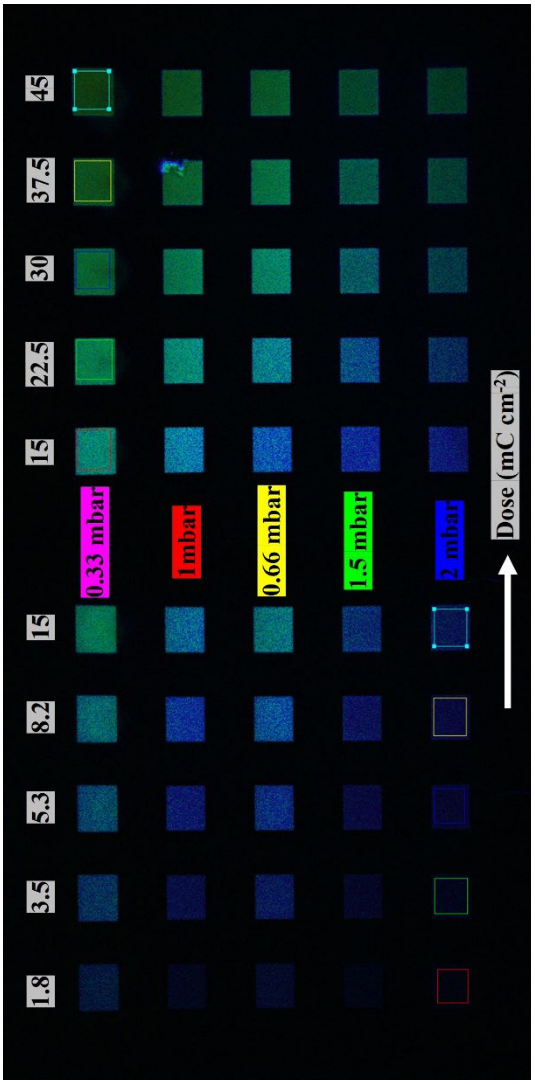

Figure 1. Photoluminescence (PL) from electron-irradiated polystyrene at different water-vapor pressures and doses. Both the intensity and color of photoluminescence can be tuned with dose and water vapor-pressure. The pressure along columns and the doses along the rows remain the same. The films were exposed in an environmental scanning electron microscope using a 30 keV electron-beam. The water vapor pressure ranged from $<10^{-5}$ mbar (high vacuum) to 3 mbar, and the dose ranged from 1.8 to 45 mC/cm^2.

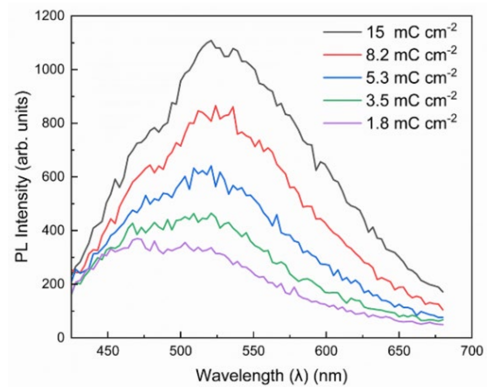

Figure 2. PL spectra from polystyrene irradiated under high vacuum at various doses. Increasing dose increases the photon yield and red-shifts the spectrum.

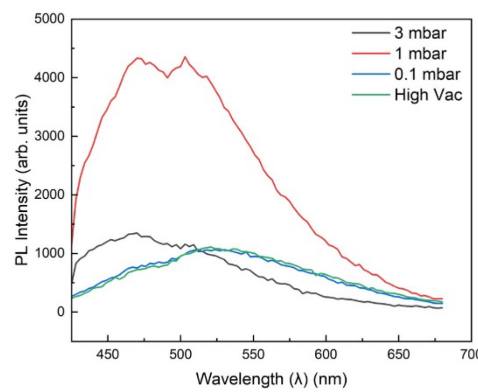

Figure 3. PL spectra from polystyrene irradiated under various water vapor pressures at 15 mC/cm^2. Increasing water vapor pressure blue-shifts the emission spectra, and the photon yield reaches a maximum near 1 mbar.

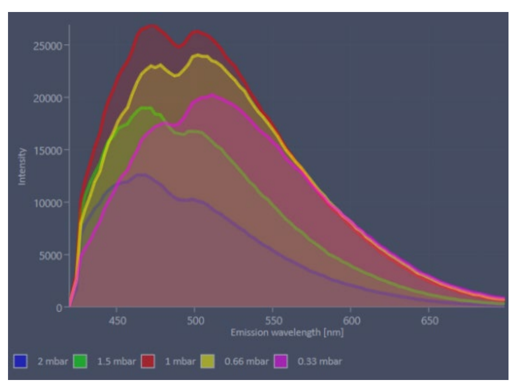

Figure 4. PL spectra from polystyrene irradiated under a narrow range of water vapor pressures at 15 mC/cm^2. Optimal photon yield is observed at 1 mbar pressure, and a clear shift from the longer wavelength to the shorter wavelength peak is observed with increasing vapor pressure.