Nanocomposites and nanomaterials

Fluorescence relaxation kinetics of poly(methylphenylsilane) film and nanocomposites

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A comparative study of fluorescence relaxation kinetics of σ-conjugated poly (methylphenylsilane)-PMPS polymer film and nanocomposites has been carried out by ultrafast time-gated fluorescence (FL) measurements depending on excitation wavelength (254 nm and 343 nm) and temperature (15-320 K). It is shown that FL spectra and dynamics of excitons in the polymer films and nanocomposites differ significantly and are associated with confinement effect.

Stationary FL spectrum of the PMPS film at 5 K and λ_{ex} = 313 nm shows a narrow exciton band and a wide band, which correspond to the σ-σ* transitions in the polymer chain and to the charge-transfer (CT) states, respectively. It is found that at short times (20-80 ps) exciton band in the FL spectra of the polymer has doublet structure. At shorter, or longer times one of the components is observed, short-wavelength band or long-wavelength one, respectively. FL lifetimes for these components are 77 ps and 167 ps, respectively. Distance between the doublets depends on temperature and reaches 12 nm. Similar structure is observed also in the stationary FL spectra (10 K, λ= 313 nm) of PMPS solutions with low polymer concentration. We attribute this doublet structure to the existence of spatially independent fluorescence centers, which correspond to the polymer chains with different distribution of short and long segments. It is found that exciton energy migration between these centers takes 20-50 ps.

The study of PMPS nanocomposites with polymer incorporated into nanoporous silica of different diameters (2.8 and 9 nm) has shown that the exciton bands in the FL spectra are shifted to the short-wavelength side comparing to the polymer exciton band. FL lifetimes for individual macromolecules and clusters are much larger than those in the polymer film and are 0.08 ns and 0.1 ns, respectively. It is explained by restricted exciton migration in the confined volume. The same effect explains appearance of the CT band in the FL spectrum of composites only

as time-gated emission increases up to 900 ps. FL lifetime of these states is of about 6.7 ns.