Photoluminescence behavior of poly(quinoline)s in silica glasses via the sol–gel process

W. Y. Huang, S. W. Ho, T. K. Kwei, and Y. Okamoto
Polymer Research Institute, Polytechnic University, 6 MetroTech Center, Brooklyn, New York 11201

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A full color display with its spectra covering the entire visible color range using a single polymer is presented here. Different concentrations of poly(2,6-[4-phenylquinoline]) and poly(2,6-[p-phenylene]-4-phenylquinoline) were incorporated into silica gels via the sol–gel technique. At high concentrations, the conjugated polymers form multiple excimers in the channels within the silica network, leading to the emission of red light (~600 nm). At low concentrations, the polymer chains are isolated and being trapped individually in the silica domain, which results in the emission of blue light (~400 nm). For concentrations in-between, moderate extensive chain interaction leads to the emission of green, yellow, and orange colors. Therefore, the color tunability can be achieved simply by varying the concentration of quinoline polymers in the silica glasses.

Conjugated rigid poly(quinoline)s have been extensively investigated as thermally stable, photoconductive, photoluminescent, and nonlinear polymeric materials. A large number of organic–inorganic functionalized nanocomposites have been synthesized by performing sol–gel condensation. Here we show that the luminescence spectrum from some poly(quinoline)s in silica glasses via the sol–gel process could be varied to cover the entire visible range of color when excited by ultraviolet radiation. The color spectrum is controlled simply by varying the concentration of polymer in silica glasses.

We have synthesized two poly(quinoline)s, poly(2,6-[4-phenylquinoline]) (PPQ) and poly(2,6-[p-phenylene]-4-phenylquinoline) (PPPQ). These structures are shown in Fig. 1. These poly(quinoline)s were readily dissolved in acids such as formic and dichloroacetic acids. The polymer solutions were characterized on a Shimadzu ultraviolet UV-vis, UV 2401, Spectrometer and a Perkin–Elmer LS-50B luminescence spectrophotometer with 0.1 cm quartz cells. The photoluminescence was performed in the 30/60° geometry. The UV absorption maxima shifted to shorter wavelengths upon dilution from 385 to 375 nm, and the fluorescence emission peak positions also varied with the concentration.

The solution emission spectra are shown in Fig. 2. The concentrated solutions of these polymers showed broad featureless emission peaks at 550 nm when they were excited at 380 nm. As the concentration decreased, the peaks shifted to a shorter wavelength about 450 nm. The emission spectra became narrow and the intensity increased greatly with decreasing concentration. These results suggest that poly(quinoline)s form aggregates/excimers in concentrated solutions, resulting in decreased emission intensity. The gradual disappearance of the emission band around 550 nm is due to polymer chains now being apart from each other and the lessening of intermolecular photophysical interaction upon dilution. The spectra (~480 nm) of diluted solutions of these polymers may be considered as that of the excited state of isolated polymer chains. The emission spectra did not change over 2 h under UV radiation at 365 nm at room temperature.

A similar dilution effect was observed when poly(quinoline)s were blended with nonfluorescent polymers such as poly(vinyl alcohol) (PVA). Although these two polymers were not completely miscible over a wide range of the concentration ratios, visually clear thin films were obtained for many compositions by spin coating. Typical fluorescence spectra of PPPQ/PVA blend systems are shown in Fig. 3. At high concentrations (>50 wt. %), broad emission peaks around 550–600 nm were seen, whereas at concentrations of 5 wt. % or less, the emission peaks shifted to a shorter wavelength (~450 nm). This also suggests that PPPQ chains in a dilute PVA blend are separated from each other by the intervention of PVA, resulting in decreasing aggregation/excimer formation and shifting of the emission peak to the blue region. However, no intermediate peak was obtained.

Recently a large number of organic–inorganic nanocomposites have been successfully synthesized by performing sol–gel condensation in organic polymers that are inert or reactive with respect to the sol–gel chemistry. Prasad and his co-workers reported a π-conjugated optically active polymer, poly(p-phenylene vinylene), incorporated in silica glass via the sol–gel process. The resulting glass was porous...
though the average pore diameter was typically much smaller (1.5–10 nm) than the wavelength of near UV or visible radiations. Thus the composite exhibited low scattering, good optical quality, chemical, and thermal stability.\textsuperscript{11}

We employed the sol–gel technique for the preparation of a composite material of polyquinoline\textsubscript{s} and silica. In this process, various concentrations of solutions of quinoline polymers in aqueous acids such as formic and dichloroacetic acids were mixed with tetraethyl orthosilicate (TEOS) at room temperature. TEOS was purchased from Aldrich and used as received. The gelation of the solutions occurred rapidly (<15 min in most cases). Then the gels were heated at 40–50 °C to complete the polymerization of TEOS. When the resulting composite materials were excited by ultraviolet radiation, colored emissions spanning nearly the entire visible range with high photoluminescence intensities were observed. The typical colored emissions under UV of PPQ are shown in Fig. 4 and the fluorescence spectra in Fig. 5. Similar results were obtained for PPPQ. The exact cause for the display of various color emissions is not clear at this time; however, we may speculate as follows.

Excimer formations among small molecules are often reported as the interaction of any excited chromophore $A^*$ with an unexcited chromophore $A$.

$$A^* + A \rightarrow (AA)^*.$$ Such an excited couple is stable as a resonance contribution, resulting in the shifting of the emission peak to the red region.

\pi-conjugated polymers such as poly(quinoline)s are generally stiff chain molecules with relatively planar geometries and very strong intermolecular interactions. It is therefore reasonable to expect that excimers might efficiently form among quinoline polymer chains. The possibility may also exist that multiple excimers, $(RRRn)^*$ form among the trapped polymers in silica channels

$$R \rightarrow R^*,$$

$$R^* + R \rightarrow (RR)^*,$$

$$(RR)^* + Rn \rightarrow (RRRn)^* \quad (n = 1,2,3,\ldots).$$
where \( R \) is a polymer chain; \( R^* \) an excited polymer chain; \( (RR)^* \) an excimer, and \( (RRRn)^* \) a multiple excimer.

The interaction among these polymer chains results in the shift of emission peaks progressively to longer wavelengths with increasing concentration. When the amount of the polymers in the sol–gel solutions is small, \(< 10^{-3}\) wt. %, the majority of the chains in solution are in the “isolated” state. The isolated polymer chains may be trapped individually in a channel of the silica domains upon gel formation, resulting in the emission of a blue color (~440 nm) upon UV radiation. At a higher concentration (~5 wt. %), the emission peak is around 600 nm and the red emitting color is indicative of possibly a high degree of cofacial chain interaction and stacking of the chromophores. For concentrations in-between, less extensive cofacial chain interaction and fewer multiple excimers trapped inside the silica domains than those at 5 wt. % lead to the emission of green, yellow, and orange colors. Thus the color can be controlled simply by varying the concentration of quinoline polymers in the sol–gel composites.

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