Fullerene–Styrene Random Copolymers. Novel Optical Properties

Christopher E. Bunker, Glenn E. Lawson, and Ya-Ping Sun*

Department of Chemistry, Howard L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-1905

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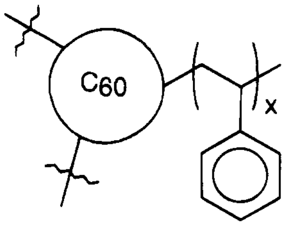
Since the development of methods for mass production of fullerenes, there has been great interest in fullerene-containing polymeric materials.[1–12] The available and proposed materials can be roughly divided into two categories. One category consists of polymers of covalently linked fullerenes,[2–6] and the other includes copolymers in which fullerenes are part of the polymer structure.[7–12] For styrene-based copolymers, there was a brief paper[10] on the preparation of a highly cross-linked fullerenated polystyrene using a Friedel–Crafts type reaction. A starlike polymer with polystyrene units attached to a C_{60} center has also been reported.[7a] Very recently, a "charm-bracelet" type styrene–C_{60} copolymer was prepared using a "buckyball-fishing" method, and the copolymer was characterized by several methods including NMR, thermal gravimetric analysis, and differential scanning calorimetry.[12] In the search for fullerene-containing polymeric materials with novel electric and optical properties, we have prepared C_{60}–styrene random copolymers with different C_{60} contents using bulk and solution polymerization methods. These copolymers have significantly different spectroscopic properties from both polystyrene and C_{60}.

In a bulk polymerization, 30 mg of C_{60} (purity 99.99%) is dissolved in 15 mL of distilled styrene. The polymerization reaction can be initiated either thermally at a temperature higher than 130 °C or by using a radical initiator. The copolymers from the two different methods have similar physical appearances but somewhat different molecular weight distributions. However, there is a reaction between C_{60} and styrene at temperatures higher than 80 °C prior to the initiation of polymerization.[13] In order to avoid unnecessary complications, the C_{60}–styrene copolymers used in this study are prepared using benzoyl peroxide as a radical initiator.[14] The polymerization reaction is carried out at 65 °C for 32 h, which yields a dark brown glasslike plug. It is dissolved in 30 mL of hot toluene, then cooled to room temperature, and precipitated with 100 mL of methanol in a blender. The precipitant is filtered and dried in an oven, yielding a reddish brown C_{60}–styrene copolymer. The yield of the polymerization reaction is ~55%, and C_{60} weight percent in the copolymer is ~0.4% (estimated from the mass ratio of reacted styrene and C_{60}). No free C_{60} is found in the residual solution after precipitation. Polymer of neat styrene is prepared under the same conditions to be used as a reference. Gel permeation chromatography (GPC) results indicate that the materials do not contain oligomers and that the C_{60}–styrene copolymer and the polystyrene reference have almost the same molecular weight distributions (weight-average molecular weight of 62 000 and polydispersity of 4). It appears that chain cross-linking is not any more significant in the copolymer than in the polystyrene reference. Copolymers containing more C_{60}, weight percent of ~1.7% (estimated from the mass ratio of reacted styrene and C_{60}, weight-average molecular weight of 79 000 and polydispersity of 13) and weight percent of ~17%[15] (weight-average molecular weight of 17 000 and polydispersity of 2.6), are prepared in toluene solutions following the same procedure. The yield for copolymer with ~1.7% C_{60} is comparable with that in bulk copolymerization. However, the yield for copolymer with ~17% C_{60} is smaller (roughly 10% or so), and the reaction mixture contains oligomers. The polymer is isolated through repeated precipitations in toluene–methanol solvent mixtures.

The C_{60}–styrene copolymers are soluble in common organic solvents such as toluene, chloroform, and dichloromethane. The most convincing evidence for the conclusion that C_{60} is indeed a part of the polymer structure is from comparative GPC analyses using a refractive index detector (RID) and a UV detector (UVD). Because the copolymers have absorption at the longer wavelength side of the polystyrene absorption spectrum (see below), the molecular weight distribution of the species responsible for the longer wavelength absorption can be determined using a UVD at 350 nm. The GPC results with a UVD are essentially the same as those with an RID.

Structural characterizations of the copolymers are carried out using FT-IR and NMR methods. Due to overwhelming contributions of unsubstituted styrene units in the polymer structures, the spectra of the copolymers are nearly the same as those of neat polystyrene. However, for the copolymer with ~17% C_{60}, the FT-IR spectrum shows extra absorption in the 520–530 cm^{-1} region, which is typical with respect to substituted C_{60}. The proton NMR (300 MHz, CCl_3D) spectrum of the copolymer also exhibits new broad peaks shifted downfield from those of the α and β protons in unsubstituted styrene units.[7] The results could be used to support a proposed copolymer structure as follows.



Because of possible rearrangements of C_{60} radicals in the polymerization process, an assignment of the substitution pattern on the cage is not practical on the basis of our existing experimental results. Further investigations are required.

Absorption spectra of the copolymers in the visible region are very different from that of free C_{60} (Figure 1). The somewhat structured absorption band of free C_{60} is replaced by a steadily decreasing curve, typical for substituted C_{60}.[18] In the UV region, the strong absorption bands are in general agreement with those of the polystyrene reference.[19] The fluorescence spectra of the copolymers excited in the visible region have peak maxima at ~600 nm, different from that of free C_{60} (Figure 2). The emission can be attributed to the C_{60}-containing sites in the polystyrene structure. At excitation wavelengths shorter than 400 nm, fluorescence spectra are excitation wavelength independent. However, at longer excitation wavelengths, emission bands become progressively narrower (Figure 2). This kind

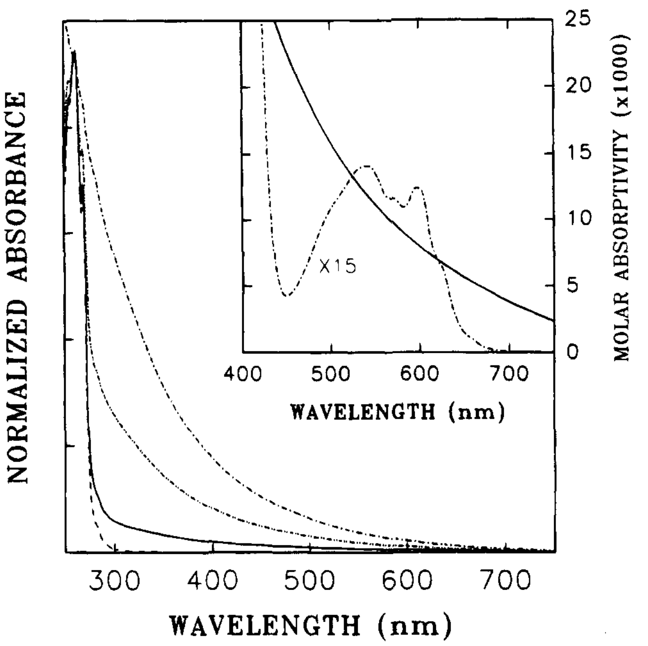


Figure 1. Absorption spectra of polystyrene reference (- - -) and C_{60}–styrene copolymers with C_{60} weight percent of ~0.4% (—), ~1.7% (-···-), and ~17% (-··-) in room-temperature dichloromethane. The inset is a comparison between the spectra of the copolymer (C_{60} weight percent of ~0.4%) in dichloromethane and C_{60} in neat styrene solution. The molar absorptivity of the copolymer is calculated with respect to the molar concentration of C_{60} in the polymer.

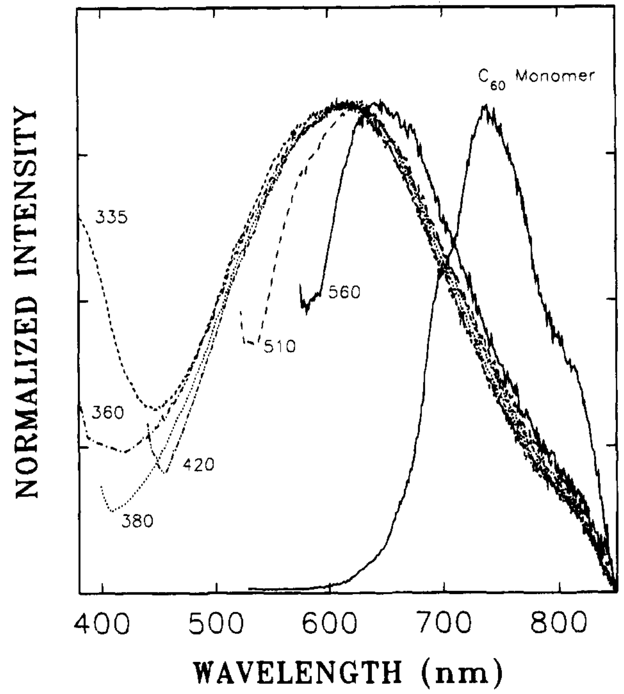


Figure 2. Fluorescence spectra of the C_{60}–styrene copolymer (C_{60} weight percent of ~0.4%) in room-temperature dichloromethane at different excitation wavelengths (as shown in the graph). The spectrum of C_{60} monomer in toluene is also shown for comparison.

of excitation wavelength dependent emission typically indicates an inhomogeneous distribution of emitting sites.[20,21] With only the band at ~600 nm taken into account, emission yields of the copolymers are much larger than that of free C_{60}.[22] For the copolymer from bulk polymerization, the fluorescence yield ratio $\Phi_{F,POLY}/\Phi_{F,C_{60}}$ is 23 at an excitation wavelength of 350 nm.

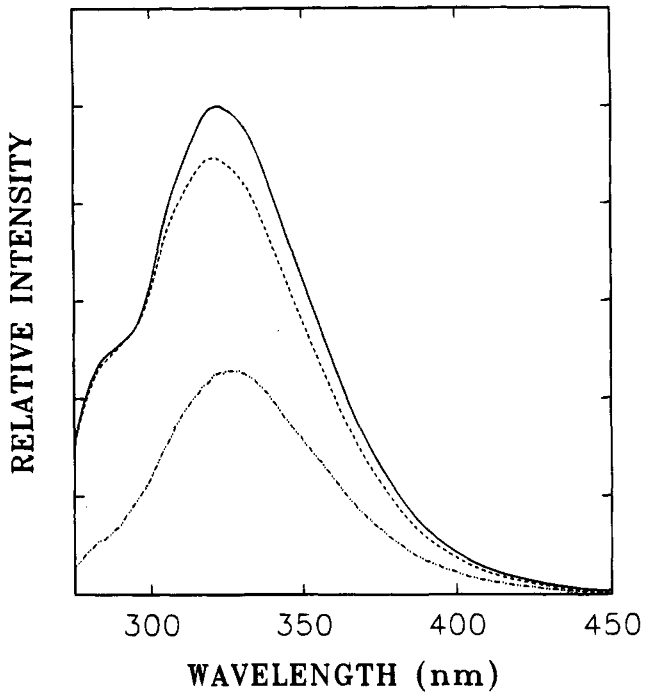


Figure 3. Fluorescence spectra of C_{60}–styrene copolymers with C_{60} weight percent of ~0.4% (- - -) and ~1.7% (-···-) and polystyrene reference (—) in room-temperature dichloromethane. The spectra are obtained with the same optical density at the excitation wavelength of 260 nm. The red fluorescence bands of the copolymers are not shown.

The absorption and fluorescence spectra and fluorescence quantum yield of C_{60} in a styrene solution are the same as those in a toluene solution. The fluorescence spectra of copolymers are also different from those of the addition products of C_{60} and styrene, which feature an emission band at ~700 nm and do not have the characteristic excitation wavelength dependence.[13]

When the copolymer solutions are excited into the intense absorption bands in the UV region, the fluorescence spectra are similar to those of the polystyrene reference. The spectra consist of emissions from both the monomeric styrene unit and the intramolecular excimer (Figure 3).[19] While the fluorescence spectral profiles are similar, the yields for the copolymers are smaller than those in neat polystyrene. The decrease of fluorescence yield in copolymers can be attributed to quenching through intramolecular excited-state energy transfer.[21,23] The C_{60}-containing sites may act as energy traps. As shown in Figure 3, the quenching of polystyrene fluorescence is more pronounced in the copolymer containing more C_{60}.

It is interesting that there are still red emissions when the copolymers are excited into the absorption bands in the UV region. This is probably consistent with the presence of intramolecular excitation energy transfer. In such a mechanism, some C_{60}-containing sites responsible for the red fluorescence band are excited through energy trapping. Further investigations for a quantitative characterization are in progress.

The enhancement in fluorescence yields is probably a result of reduced symmetry of C_{60} upon being incorporated into the polymer structure. It has been shown[24] that C_{60} could potentially be used as a third-order nonlinear optical material, and unsymmetrically perturbed C_{60} also exhibits second-order optical nonlinearity. An examination of the nonlinear optical properties of the C_{60}–styrene random copolymers should prove interesting. An advantage for these polymers is that they are soluble in common organic solvents.

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