

FULLERENE POLYMERS WITH TUNABLE OPTICAL PROPERTIES

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ABSTRACT

Light transmission spectra of THF solutions of poly (C_{60} -co-methyl methacrylate)s and poly(C_{60} -co-styrene)s continuously red-shift with increasing concentration. Formation of fullerene nanoclusters may be responsible for the unusual spectral shift with concentration. It has long been scientists' dream to "tune" material's properties by simple means, and the C_{60} -containing polymers represent such a group of novel materials whose optical properties are predictably and reversibly tunable by a simple change in concentration.

INTRODUCTION

Buckminsterfullerene is a wonder molecule that possesses a range of exotic properties including superconductivity^[1], ferromagnetism^[2], and anti-HIV bioactivity^[3]. Noting that C_{60} has a three-dimensional conjugated molecular structure, we envision that it may exhibit unique optical properties. Photochromism, thermochromism, solvatochromism, ionochromism, and biochromism have been discovered in some conjugated polymer systems^[4-10]. We here report novel concentratochromism in C_{60} -containing polymer systems. We demonstrate that light transmission spectra of C_{60} -containing polymer solutions can be easily tuned by simply changing their concentrations.

EXPERIMENTAL

Highly pure C_{60} (> 99.9%) was purchased from MER (USA) and stored in a dark place before use. Methyl methacrylate (MMA) and styrene monomers (both

* This work was in part supported by a grant from the Hong Kong Government Research Grants Council (DAG96/97. SC11).

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Received February 23, 1997

Aldrich, USA) were purified by distillation. 2, 2'-Azobisisobutyronitrile (AIBN) were purchased from Acros (Belgium). Copolymerizations of C₆₀ were carried out in neat MMA or styrene using AIBN as an initiator according to published procedures^[11-16]. Results of the copolymerizations are summarized in Table 1. The C₆₀-MMA and C₆₀-styrene copolymers were purified by repeated precipitation of their THF solutions into methanol and then hexane.

Table 1 Copolymerizations of C₆₀ with MMA or styrene^{a)}

C ₆₀ (mg)	C ₆₀ /comonomer (wt%)	Yield (%)	Polymer			
			$M_w^b)$	$M_w/M_n^b)$	C ₆₀ content	
					(mg/g) ^{c)}	(No./chain) ^{d)}
MMA (4.8 ml)						
25.6	0.570	68.1	147400	3.4	8.40	0.51
35.3	0.786	81.3	130100	2.5	9.68	0.70
styrene (4.8 ml)						
11.6	0.266	46.0	96900	2.4	5.80	0.33
20.0	0.459	55.7	103300	2.4	8.26	0.50
24.1	0.553	48.6	117700	2.7	11.39	0.69

^{a)} Polymerized under nitrogen at 70°C for 24 h using AIBN (1% of MMA or 0.57% of styrene) as an initiator.

^{b)} Measured by GPC on the basis of a polystyrene calibration.

^{c)} Estimated from mass ratio of reacted C₆₀ and comonomer.

^{d)} Estimated from M_n .

THF solutions of poly (C₆₀-co-MMA)s and poly (C₆₀-co-styrene)s were prepared by dissolving accurately-weighed amounts of the copolymers in spectroscopic grade of THF (Aldrich) in volumetric flasks. Light transmission spectra of the polymer solutions were recorded at room temperature on a Milton-Roy Spectronic 3000 Array Spectrophotometer in a 1-cm square quartz cell, unless otherwise specified. The digitized transmittance data were treated on a Porro PC.

RESULTS AND DISCUSSION

In our pursuit of developing C₆₀-based optical limiters^[11,15], we had the need to check optical transmittance of the fullerene materials using a UV-vis spectrophotometer. We astonishingly found that their light transmission spectra continuously red-shift with increasing concentration, an example of which is given in Fig. 1. When the concentration of the poly (C₆₀-co-MMA) solution increases, its transmission spectrum red-shifts. A cut-off wavelength (λ_c) may be defined as the wavelength at which light transmittance is 0.1%. When the concentration of the THF solution

of poly(C₆₀-co-MMA) changes from 2.95 to 82.57 mg/ml, λ_c shifts from 259.02 to 501.13 nm. It is truly remarkable that a simple change in concentration shifts λ_c over such a wide spectral range.

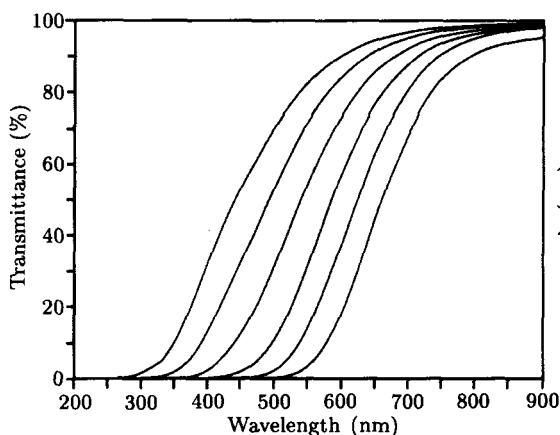


Fig. 1 Light transmission spectra of THF solutions of a poly(C₆₀-co-MMA) (C₆₀ content: 9.68 mg/g). Concentration (from left to right): 2.95, 5.90, 11.80, 23.59, 47.18, 82.57 mg/ml. Pathlength: 1 cm

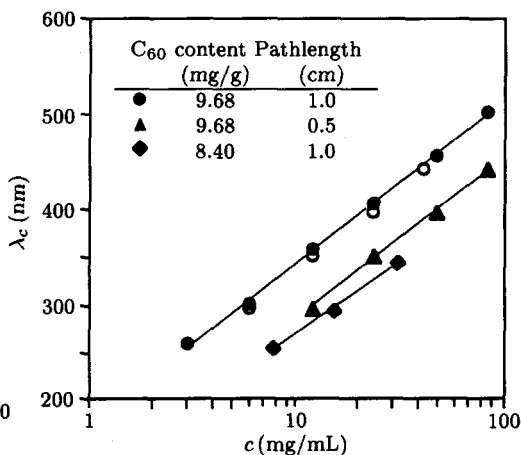


Fig. 2 Concentration (c) dependence of cut-off wavelength (λ_c) of THF solutions of poly(C₆₀-co-MMA)s with different C₆₀ contents. Data points represented by open circles are calculated by multiplying the concentrations in the short-path experiment by the pathlength of 0.5 cm

Fig. 2 shows concentration (c) dependence of λ_c for the THF solutions of poly(C₆₀-co-MMA)s. The λ_c - c plots for the polymer solutions well follow a semilogarithmic relationship; that is, their λ_c values increase linearly with $\log_{10} c$. When the C₆₀ content of the copolymer decreases from 9.68 to 8.40 mg/g, the λ_c - c plot blue-shifts, implying that C₆₀ is responsible for the unusual light transmission phenomenon. We have also studied pathlength (b) effect on λ_c by measuring the transmission spectra of the same polymer solutions using two quartz cells with different pathlengths. Data points represented by the solid triangles in Fig. 2 are those obtained from the short-path (0.5 cm) experiment. Multiplying the concentrations by the pathlength of 0.5 gives the data points represented by the open circles, which well fit the λ_c - c line for the "standard" long-path ($b = 1.0$ cm) data. Thus the experimental data in Fig. 2 suggest a light transmission relationship of

$$\lambda_c = \alpha \log_{10}(bc) + k \quad (1)$$

where α and k are constants. As can be seen from Fig. 3, Eq. 1 also holds for light transmission in the poly(C₆₀-co-styrene) solutions. Here again, the λ_c - c plot blue-

shifts with decreasing the C_{60} content.

We checked light transmission behavior of some common aromatic compounds. One example is given in Fig. 4. A change in concentration as large as 480 times caused little shift in the transmission spectra, and the $\lambda_c - c$ plot shown in Fig. 4B clearly demonstrates that λ_c is virtually independent of concentration of the THF solutions of the aromatic compound (1-methylnaphthalene). Similarly, no pronounced concentration effects were observed in the solutions of other common aromatic compounds such as toluene, 1, 2-dichlorobenzene, and 1-chloronaphthalene. We also checked light transmission behavior of THF

solutions of (pure) PMMA and polystyrene and found that their transmission spectra hardly shift over a wide concentration range (30.00–345.28 mg/ml). Thus the spectral shift with concentration is a unique property of the C_{60} -containing polymer solutions.

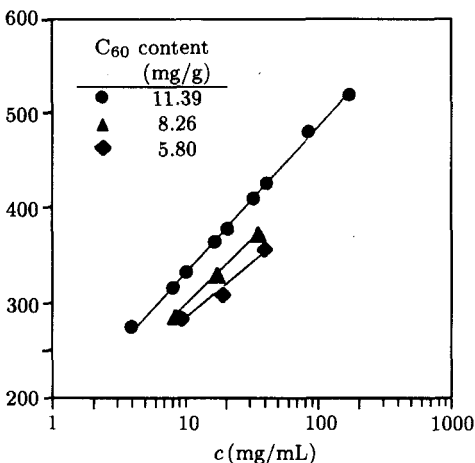
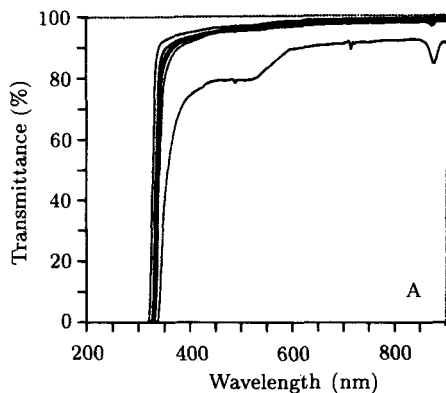


Fig. 3 Concentration (c) dependence of cut-off wavelength (λ_c) of THF solutions of poly(C_{60} -co-styrene)s with different C_{60} contents. Pathlength: 1 cm

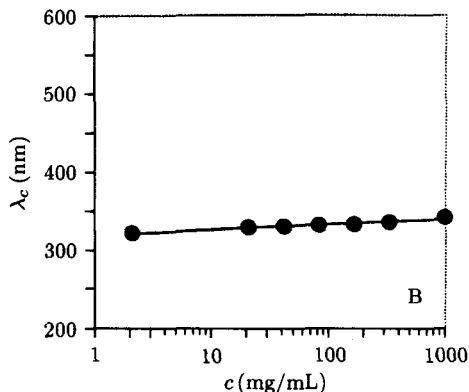


Fig. 4 Light transmission spectra (A) and concentration (c) dependence of cut-off wavelength (λ_c) (B) of THF solutions of 1-methylnaphthalene. Concentration (in A from left to right): 2.09, 20.85, 41.71, 83.42, 166.83, 333.67, 1001 (neat) mg/ml. Pathlength: 1 cm

Fullerene molecules have been found to pack together to form clusters of $(C_{60})_n$

with different sizes ($n = 13, 19, 23, 35, \dots$) in the solid state^[17], and to aggregate in aqueous micellar solutions of surfactants^[18] or in solvent mixtures like toluene/acetonitrile^[19]. Apparently there are strong attractive $\pi - \pi$ interactions among C_{60} molecules. While THF is a good solvent of PMMA, C_{60} is completely insoluble in THF^[20]. Although the THF solutions of poly(C_{60} -co-MMA)s are macroscopically homogeneous, micelle-like nanoclusters may form in the seemingly "true" solutions, in which the PMMA chains are sticking into the THF phase while the C_{60} buckyballs are filling the interior of the clusters. When the concentration of the polymer increases, more C_{60} molecules may enter one cluster and thus the size of the clusters may increase. This in turn may increase the conjugation degree of the system through $\pi - \pi$ interactions among the contacting C_{60} molecules within the clusters, hence red-shifting the optical transitions. Spectral shift with concentration in the poly(C_{60} -co-styrene) solutions may follow the same mechanism, though further experimental evidence to support the nanocluster hypothesis is needed.

It is noteworthy that the concentration dependence of light transmission in the poly(C_{60} -co-MMA) and poly(C_{60} -co-styrene) solutions well follows a semilogarithmic relationship (cf. Eq. 1). In other words, the optical property of the polymer solutions is predictably tunable by simply varying their concentrations. We have confirmed that the spectral shift is reversible with excellent reproducibility: Regardless of the order of the concentration change (thinning by adding solvent or thickening by adding solute), the transmission spectra measured at different time over one week were virtually identical. It has long been scientists' dream to tune material's properties by simple means in a predictable and programmable manner. The novel concentratochromism we discovered here may trigger intensive research efforts in developing new specialty materials with tunable optical properties, and the C_{60} -containing optical polymers may find a wide range of potential applications as optical filters, optical switches, optical limiters, etc. in the optics-related industries.

Keywords:

Fullerene polymers; C_{60} -styrene copolymers; C_{60} -MMA copolymers; Optical polymers; Light transmission; Chromic effects.

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