

Photochromic cross-linked copolymer containing thermally stable fluorescing 2-indolylfulgimide

Yongchao Liang, A. S. Dvornikov and P. M. Rentzepis*

Department of Chemistry, University of California, Irvine, CA 92697, USA. E-mail: pmrentze@uni.edu

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A new photochromic cross-linked copolymer composed of PMMA and fluorescing 2-indolylfulgimide is synthesized which can be converted photochemically into two forms which are found to be thermally stable; the spectroscopic properties and quantum yields of photochemistry and fluorescence are also measured.

The increasing fast developments in new technologies associated with optoelectronics, waveguides, molecular switches, optical computer memories among others, require the design and synthesis of novel materials with properties which satisfy the specific needs of each new device.¹ Organic photochromic materials have attracted significant attention, in recent years, because of their potential application to optical devices, and in particular to switches and 3D optical storage.² One of the most promising classes of photochromic materials are fulgides because they possess excellent fatigue resistance and thermal stability in both isomeric forms.³

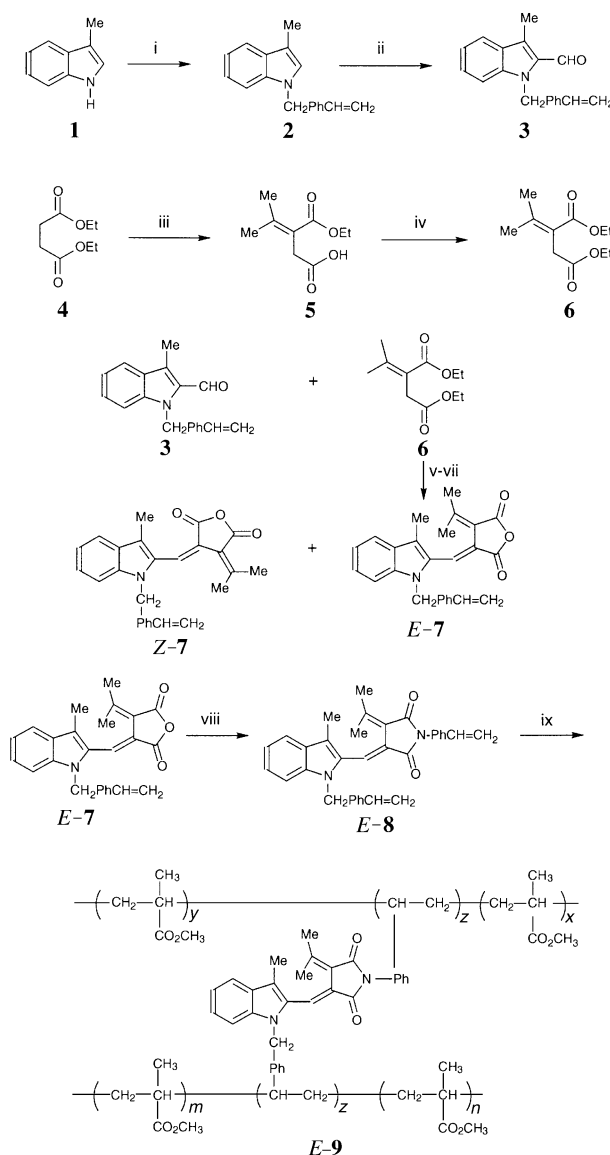
In previous papers we have reported the synthesis, photochromic and spectroscopic properties of several new thermally stable fluorescing photochromic 2-indolylfulgides and fulgimides which may be potential materials for use as media in rewritable 3D optical memory devices.^{4–6} Here we describe the synthesis and properties of a new fluorescing photochromic 2-indolylfulgimide which is attached to methyl methacrylate monomer, to form a cross-linked photochromic fluorescing polymer.

Photochromic molecules must be uniformly dispersed in a polymer matrix at relatively high concentration to be suitable for use in optical devices. The photochromic materials which have been used in 3D optical memory devices, based on two-photon absorption, require concentrations of 10^{-1} M and higher in order to record a sufficient number of bits of information.² The photochromic cross-linked copolymer described here is formed by attaching the photochromic molecule to the polymer chain by copolymerization with the corresponding monomer. We were able to copolymerize the methyl methacrylate monomer and the photochromic 2-indolylfulgimide (*E-8*), which we synthesized, to form an optically clear photochromic cross-linked copolymer.

Fulgimide *E-8* was readily prepared by the process shown in Scheme 1. Commercially available 3-methylindole (**1**) was converted to **2** by reacting it with vinyl benzyl chloride in potassium hydroxide DMSO solution (78% yield). Product **2** was then converted to **3** using the Vilsmeier-Haack formylation reaction (42% yield).⁷ Diethyl isopropylidene succinate (**6**) was prepared by Stobbe condensation (86% yield).⁸ Stobbe condensation of indole-2-carbaldehyde (**3**) with diethyl isopropylidene succinate (**6**) followed by hydrolysis and intramolecular acid anhydride formation yields 2-indolylfulgide (*E-7* and *Z-7*) with 23% yield from **3** to **7**, where *E-7* was separated as the main product. Fulgimide *E-8* was synthesized from *E-7* by Lewis acid and hexamethyldisilazane-promoted one pot reaction (42% yield).^{9,10}

The fulgimide *E-8* was subsequently dissolved in methyl methacrylate and the initiator (AIBN) was added forming a homogenous mixture. This mixture was transferred to a glass cell and sealed under vacuum. After 24 h of polymerization, at 50 °C, a rigid optically clear polymer was formed. The structure

of this copolymer was determined by immersing it into 1,2-dichloroethane solvent for one month, in which both PMMA and fulgimide *E-8* are very soluble. We found, as expected, for cross-linked copolymers, that this immersed material was not dissolved, at all, in 1,2-dichloroethane. This indicates, strongly, that this material is a cross-linked copolymer of MMA and *E-8*. After the solid, nondissolved polymer was removed from the solution, the absorption spectra of the remaining phase were measured. The spectra showed that not



Scheme 1 Reagents and conditions: i, KOH, DMSO, 4-vinyl benzyl chloride, 0 °C to r.t., 78%; ii, POCl₃, DMF, 0 °C to r.t., 42%; iii, acetone, Bu⁺OK, Bu⁺OH, then HCl; iv, EtOH, H₂SO₄, 86% (from **4** to **6**); v, NaH, benzene; vi, KOH, EtOH, then HCl; vii, DCC, THF, 23% (from **3** to **7**); viii, 4-vinylaniline, HMDS, ZnCl₂, benzene, 43%; ix, MMA, AIBN, 50 °C.

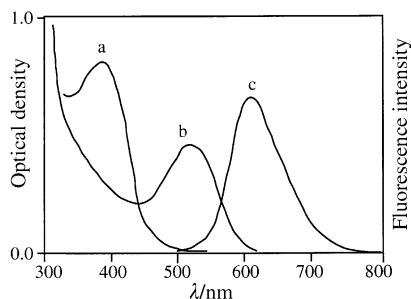
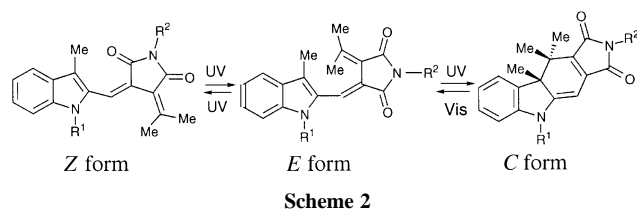


Fig. 1 Absorption and fluorescence spectra of cross-linked copolymer *E-9*. (a) absorption spectrum of the *E* form; (b) and (c) absorption and fluorescence spectra of the *C* form.

even traces of fulgimide *E-8* were present in the solution and only the spectrum of 1,2-dichloroethane solvent was recorded. To the best of our knowledge, this is the first cross-linked photochromic fulgimide copolymer ever synthesized.

The copolymer was found to possess photochromism, *i.e.* can be reversibly colored and bleached by irradiation with light of the appropriate wavelength. In addition the colored form (*C*) also fluoresces when excited with visible light which is rather seldom found in fulgimides. This is, also, the first time that a copolymer of this class has been observed. Fig. 1 shows the absorption spectra of the copolymer in its colorless and colored forms and the fluorescence spectrum of the colored form. The colored form was photoinduced by irradiating the copolymer with 400 nm light. When irradiated with visible light, $\lambda = 530$ nm, the colored form can be easily bleached back to the original colorless form, as shown in Scheme 2. The quantum efficiency of the coloration and bleaching processes were measured to be 0.13 and 0.17 respectively. These numbers are the same as the quantum efficiencies measured for pure *E-8* in ethyl acetate solution. We thought, previously, that in rigid cross-linked copolymer matrices, where the moieties of the fulgimide molecule are attached to the polymer chains, the efficiency of *E-Z* isomerization would be decreased, because of stereo constraints. In addition we had expected that because the *E-Z* isomerization competes with the ring-closure reaction, the cyclization reaction yield will increase. However, our data show that in a copolymer composed of fulgimide *E-8* and methyl methacrylate the efficiency of cyclization yield does not change. This suggests that the *E-Z* isomerization be not significantly reduced



compared to the solution, probably due to segment rotation of the polymer chain.

The colored form of the fulgimide–MMA copolymer emits red fluorescence when promoted to its first excited state. The fluorescence spectra observed are similar to the colored forms of the pure fulgimides in solution. To confirm that the recorded fluorescence is due to the colored forms of the organic photochrome rather than any impurities or other species, we measured the excitation spectra and fluorescence emission spectra intensity change as a function of bleaching/coloration cycles. The data show that the fluorescence intensity and the excitation spectra of the colored form decrease proportionally with the decrease of the absorption of the fulgimide colored form. When the material was completely bleached, *i.e.* the absorption band of the *C* form disappeared no fluorescence was detected. When the fluorescence spectrum appeared again, its intensity increased with the same rate as the rate of growth of the *C* form concentration. The fluorescence quantum yield of the colored form was found to be 5%. The method that we have used to measure the quantum efficiencies of these forms has been described previously by us.⁵

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- E-8*: mp: 149.5–150.5 °C, ¹H NMR (500 MHz, CDCl₃ TMS) δ 1.17 (s, 3H), 1.96 (s, 3H), 2.50 (s, 3H), 5.21 (d, $J = 10.9$ Hz, H), 5.31 (d, $J = 10.9$ Hz, H), 5.41 (m, 2H); 5.68 (d, $J = 17.6$ Hz, H), 5.79 (d, $J = 17.6$ Hz, H), 6.63 (dd, $J = 17.6, 10.9$ Hz, H), 6.74 (dd, $J = 17.6, 10.9$ Hz, H), 7.02 (d, $J = 8.15$ Hz, H), 7.16–7.71 (m, 10H); ¹³C NMR (500 MHz, CDCl₃, TMS) δ 11.7, 22.8, 27.2, 47.3, 109.6, 114.1, 114.9, 119.9, 124.0, 126.5, 126.7, 126.8, 136.0, 136.2, 137.4, 154.5, 167.5, 168.3; HRMS (CI) m/z calcd for C₃₄H₃₀N₂O₂ 498.2307 (M^+), found 498.2317; Anal. Calcd for C₃₄H₃₀N₂O₂: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.73; H, 6.04; N, 5.60%.