Novel Polymers Containing Fluorescein Moieties

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ABSTRACT: Novel fluorescein-containing polymers and copolymers derived from novel fluorescein-containing bis-acetylene **3** were synthesized by oxidative coupling. A novel fluorescein-containing polyester was obtained by the direct polycondensation of fluorescein. All polymers synthesized were semicrystalline as observed from X-ray diffractometry but formed films of good optical quality when cast from solution. All the polymers synthesized showed luminescence both in solution and the solid state and exhibited third order nonlineal optical susceptibility of the order 10^{-10} esu.

KEY WORDS   Luminescence / Fluorescein / Diacetylene-Containing Polymers.

Various fluorescent polymers have been investigated in recent years. These polymers include pendent chromophore functionalized polymers and polymers having chromophores in their backbone. In particular, polymers having pendent chromophores such as poly-(N-vinylcarbazole) have been extensively studied.[1–3] Such polymers have been used as photoconductive resins. Polymers, containing photoactive moieties also find applications as fluorescent labels, scintillators and photon harvesters.[4–7] These "plastic scintillators" which are conveniently processed into plates or fibers have faster response times than solid scintillators based on inorganic compounds and are thus useful in applications requiring high rates of energy analysis, such as particle accelerator. Dharia et al.[8] and Matsuo et al.[9] reported the synthesis and characterization of wavelength-shifting polymers based on 3-hydroxyflavone and new fluorescent poly-(arylene ether)s, respectively. Hargreaves and Webber studied intracoil energy transfer in antril- and fluorescein-tagged poly(vinylpyrrolidone).[10]

An alternative technique introducing for a fluorescent dye within the polymer entails dissolving the dye in the pure monomer and polymerizing the mixture under a slow temperature ramp. The dye is thus physically dispersed throughout the polymer. Solubility limitations constrain the concentration of the dye to several wt%. Any supersaturated concentration of dye is likely to result in migration and phase separation.

Thus, inorganic glass filled with fluorescein show a large third order nonlinear optical susceptibility ($\chi^{(3)}$) of 1 esu which makes fluorescein containing materials promising candidates for nonlinear optics.[11] However, the optical quality of these materials is very poor because of a low solubility and miscibility of fluorescein. Making fluorescent dye an integral part of the polymer through covalent binding is an important step in the design of fluorescent materials.

The chemical structure of fluorescein (**1**) is shown below:

1
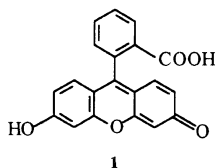
Two different synthetic approaches were employed to obtain fluorescein-containing polymers. The first is the direct polycondensation of fluorescein molecules as a monomer: using its hydroxy and carboxy groups which can be used to prepare a flourescein-containing polyester (**2**) (Scheme 1). The second synthesis of the polymer starts from fluorescein. The reaction of fluorescein with propargyl bromide gives fluorescein-containing bis-acetylene (**3**), which can be polymerized by oxidative coupling to give fluorescein-containing polymers (Scheme 2).

Scheme 1.

Scheme 2.
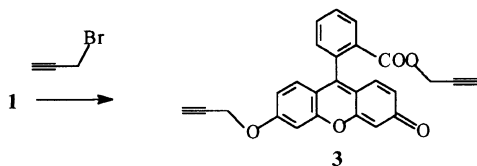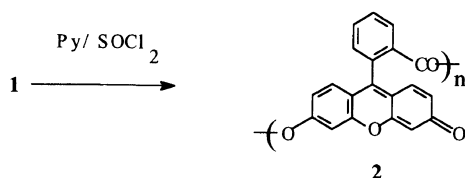
This paper, presents the synthesis and characterization of these new luminescent polymers.

EXPERIMENTAL

Materials

Pyridine (Aldrich) was distilled over CaH_2. Thionyl chloride (Fluka), *o*-dichlorobenzene (ODCB) (Aldrich) and *N,N,N',N'*-tetramethyl-ethylenediamine (TMDA) were distilled before use. Fluorescein (Aldrich Co.) was recrystallized from pyridine. Other reagents were used as received (Aldrich Co.).

Monomer synthesis

Monomer **3**: To a solution of 0.05 mol fluorescein (**1**) in 150 ml *N*-methylpyrrolidone 0.1 mol anhydrous K_2CO_3 and 0.15 mol propargyl bromide were added and the reaction mixture was stirred at 80—90°C for 48 hours. The reaction mixture was cooled and poured into water. The precipitate formed was filtered off, washed with water and recrystallized twice from 2-propanol to give compound **3** with a yield of 83%. $T_m = 189$°C. IR (cm^{-1}) 3290, 3190 ($\equiv$C–H), 3080—3030 (=C–H, C–H arom), 2950 (C–H aliph.), 2120, 2110 (C$\equiv$CH), 1740 (C=O ester), 1643 (C=O ketone), 1597, 1510 (C=C, arom). ^{1}H NMR, (CDCl$_3$), 2.27 (t, 1H, HC$\equiv$C–CH$_2$–OAr), 2.55 (t, 1H, HC$\equiv$C–CH$_2$–OOC), 4.52 (d, 2H, HC$\equiv$C–CH$_2$–OAr), 4.54 (d, 2H, HC$\equiv$C–CH$_2$–OOC), 6.38—8.32 (m, 10H, olefin., arom.). ^{13}C NMR (CDCl$_3$), 52.86 (HC$\equiv$C–CH$_2$–OAr), 56.13 (HC$\equiv$C–CH$_2$–OOC), 75.35 (HC$\equiv$C–CH$_2$–OAr), 76.18 (HC$\equiv$C–CH$_2$–OOC), 77.22 (HC$\equiv$ C–CH$_2$–OAr), 77.47 (HC$\equiv$C–CH$_2$–OOC), 101.71, 102.23, 105.98, 113.73, 115.55, 118.29, 126.32, 128.99, 129.88, 130.25, 130.74, 131.48, 133.17, 134.68, 149.41, 154.12, 158.97, 161.81 (all ring carbons), 164.57 (ester carbonyl), 185.86 (ketone carbonyl). Visible spectra (λ_{max}, nm) 509, 460, 435. *Elemental Analysis.* Calcd for $C_{26}H_{16}O_5$: C, 76.46%; H, 3.95 %. Found: C, 75.96%; H, 4.01%.

Monomer **4** (scheme 3) was prepared according to the literature[12] with 68% yield $T_m = 41$°C.

Polymerization

Polymer **2**. To 1.2 g (10 mmol) of freshly distilled SOCl$_2$ 15 ml pyridine were added at room temperature under nitrogen flow. After 20 min stirring 3 g (9.3 mmol) fluorescein dissolved in 15 ml pyridine were added to the

Scheme 3.

Copolymer	X	Y
5a	0.02	0.98
5b	0.1	0.90
5c	0.50	0.50
5d	0.70	0.30
5e	1.00	0
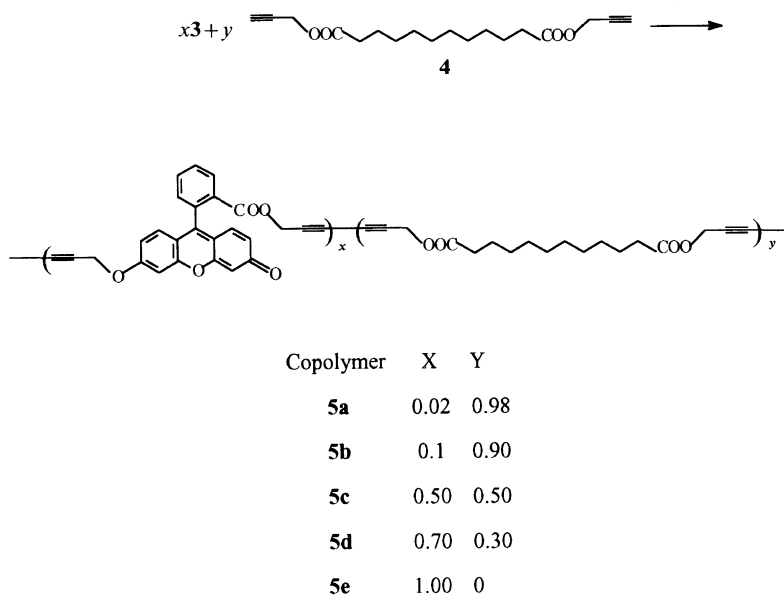
solution and the reaction mixture was stirred for 6 hours under nitrogen. After cooling, the reaction mixture was poured into acidified MeOH, the polymer precipitated was filtered off, washed with MeOH and dried in vacuum at room temperature. Yield 85%. IR (cm^{-1}) 3085—3020 ($=$C–H, C–H arom), 1740 (C$=$O ester), 1639 (C$=$O ketone), 1587, 1510 (C$=$C, arom). ^{13}C NMR, (dimethyl sulfoxide-d_6 (DMSO-d_6) 102.21, 102.83, 106.08, 114.65, 115.50, 117.99, 126.30, 128.00, 130.76, 130.25, 130.67, 131.12, 132.91, 134.68, 150.01, 159.08, 162.11, (all ring carbons), 166.77 (ester carbonyl), 185.96 (ketone carbonyl). Visible spectra (λ_{max}, nm) 510, 460, 435. *Elemental Analysis.* Calcd for $(C_{20}H_{10}O_5)_n$: C, 72.73%; H, 3.05%. Found: C, 73.06; H, 3.06%.

The copolymers **5a, 5b, 5c, 5d,** and **5e** were prepared by oxidative coupling reactions of monomers **3** and **4**. A typical example of copolymerization is shown below.

The mixture (10 mmol) of monomers **3** and **4** was dissolved in 10 ml ODCB at 70°C, 0.05 g of CuCl and 0.5 ml of TMDA were added, and the mixture was stirred for 2 hours at 70—75°C

under an oxygen atmosphere. The reaction mixture was poured into methanol acidified with HCl. The precipitate was filtered off, washed with methanol, water and dried until constant weight at room temperature under vacuum. IR (cm^{-1}) 3080—3020 ($=$C–H, C–H arom), 2950—2850 (C–H aliph., except **5e**), 2220, 2160 (C$\equiv$C–C$\equiv$C–), 1740 (C$=$O ester), 1640 (C$=$O ketone), 1600, 1510 (C$=$C, arom). Elemental analysis and inherent viscosity data of the copolymers are presented in Table I.

Measurements. Inherent viscosities were measured at 25°C either in CDCl$_3$ or pyridine (in the case of **2**). DSC measurements were performed at a heating rate of 20°C min^{-1} under nitrogen with a du Pont 2100. FT-IR-spectra were taken using a Nikolet 510p spectrometer. UV-visible spectra were taken using a UV-260 Shimadzu in chloroform or in the solid films. ^{1}H NMR and ^{13}C NMR spectroscopy were performed with a Varian at 300 and 75.5 MHz respectively in CDCl$_3$ or DMSO-d_6 with TMS as the internal standard. X-Ray diffractometry was performed using a Siemens D-500 diffractometer with Cu-K_α radiation of

Table I. Elemental analysis and inherent viscosity data (η_{inh}) data of copolymers **5a**—**5e**

Copolymer	Calcd for x-$(C_{26}H_{14}O_5)$-y-$(C_{18}H_{24}O_4)$		(η_{inh}) in dl g^{-1}	Found
5a	$x = 0.02, y = 0.98$	C, 71.07%; H, 7.86%	0.67	C, 70.98%; H, 7.83%
5b	$x = 0.10, y = 0.90$	C, 71.77%; H, 7.37%	0.59	C, 71.93%; H, 7.21%
5c	$x = 0.50, y = 0.50$	C, 74.35%; H, 5.39%	0.51	C, 73.99%; H, 5.41%
5d	$x = 0.70, y = 0.30$	C, 75.43%; H, 4.56%	—	C, 75.81%; H, 4.33%
5e	$x = 1.00, y = 0$	C, 76.84%; H, 3.47%	—	C, 76.88%; H, 3.27%

1.540 Å. The degree of crystallinity was calculated using program SOCABIM V. 3.0. This program gave the best-fit smooth curve to the diffractogram corresponding to the curve of the diffractogram of amorphous part of the sample, and therefore the ratio of the area under the calculated smooth curve to the area under experimental diffractogram was considered the proportion of the amorphous part of the sample. Photoluminescence was measured using a Perkin-Elmer LS-2 fluorimeter in CHCl$_3$ solution or in solid film with excitation at 310 nm.

RESULTS AND DISCUSSION

The direct polycondensation technique[13] was used to prepare polymers directly from fluorescein under mild conditions (scheme 1). Polymer **2** had a rather poor solubility because of its rigid structure and was "reasonably" soluble only in pyridine and DMSO. The inherent viscosity of polymer **2** was found 0.39 dl g^{-1} suggesting that the molecular weight is not high. This may be due to the presence of a small amount of tautomer **6** in fluorescein which terminates the polycondensation.

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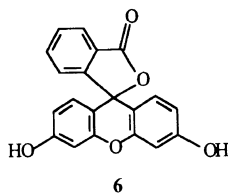
However, good quality transparent films could be cast from the pyridine solution. They were somewhat brittle when removed from the support. The IR spectra of polymer **2** contained absorption bands at 1740 and 1640 cm^{-1} corresponding to the ester and ketone carbonyl, respectively. The ^{13}C NMR spectra showed peaks at 166.77 and 185.96 ppm corresponding to ester and ketone carbons, respectively. The visible spectra of the polymer **2** matched that of fluorescein, thus confirming that the chromophore in both cases should be the same.

Scheme 2 shows the synthesis of monomer **3**. This is a one step reaction which gives the monomer in high yield. The structure of the monomer was confirmed by IR, ^{1}H NMR, ^{13}C NMR, visible spectra, and elemental analysis data. Similar to polymer **2**, the visible spectrum of monomer **3** matched that of fluorescein. The oxidative polymerization of monomer **3** (Scheme 3) was carried out at 70—75°C in ODCB in the presence of the CuCl–TMDA complex which is known to give good results for nonpolar bis-acetylenes.[14] However, in the case of the homopolymerization of monomer **3**, the polymer started to precipitate in a few minutes after starting polymerization. The resulting polymer **5e** was insoluble in common solvents because of its rigid structure. Therefore, the copolymerization of monomer **3** with the more flexible monomer **4** was carried out to improve the solubility of fluorescein-containing polymers. Copolymers with different ratios of the flexible monomer **3** were synthesized (Scheme 3). Copolymers containing up to 50 mol% of monomer **3** (**5a**, **5b**, and **5c**) were soluble in chloroform. Copolymer **5d** containing 70 mol% of monomer **3** was
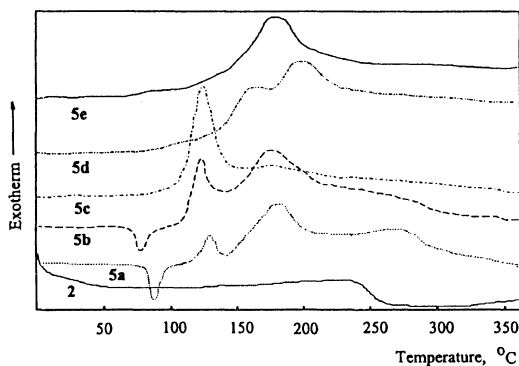
Figure 1. DSC curves of polymer 2 and copolymers 5a—5e.

Scheme 4.

insoluble in common solvents.

Figure 1 shows the DSC curves of polymers synthesized. Polymer 2 showed T_g around 250°C. Copolymers 5a—5d showed more complicated DSC curves. Copolymers 5a, and 5b, exhibited endotherms corresponding to the melting transition at 81.6 and 74.2°C, respectively. Copolymers 5c, 5d, and 5e showed no melting transition any more because the high concentration of the rigid comonomer 3 increased T_m of the copolymers above the temperature at the beginning of cross-linking. It is noteworthy that the homopolymer from monomer 4 had a melting transition at 84°C,[12] higher than those of copolymers 5a and 5b which suggests a random structure of the copolymers. All copolymers, except 5e, showed two exotherms with maxima around 135—170°C and 190—210°C (polymer 5e showed only one exotherm with a maximum around 210°C). The origin of the low temperature exotherm was studied by FT-IR spectroscopy using copolymer 5c where the exotherm was most pronounced. When heated to 150°C (the region between two exotherms) the absorption bands at 2220 and 2160 cm^{-1} corresponding to diacetylenic stretching almost disappeared. Similar to diacetylenic stretching, the absorption band at 750 cm^{-1} corresponding to the out of plane = CH deformation vibrations of cis-substituted double bond of the fluorescein
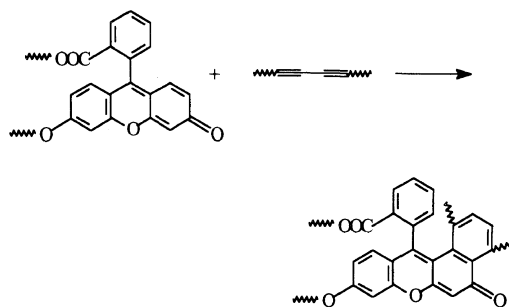
moiety also completely disappeared after thermal treatment. At the same time, increase in the intensity of C–H aromatic stretching around 3050 cm^{-1} was observed. Considering these results, it may be assumed that cyclization reaction takes place, as shown in Scheme 4, which corresponds to the low temperature exotherm. With further heating to 210°C the absorption bands at 2220 and 2160 cm^{-1} due to stretching of diacetylenic groups, completely disappeared. Therefore, the high temperature exotherm may be due to thermal cross-polymerization of the rest of the diacetylenic groups. The peak maximum of the low temperature exotherm shifted to high temperature with the comonomer 3 content, and in the case of polymer 5e, the low temperature exotherm coincided with the high temperature one. The reason for this may be increase in the rigidity of the polymer chain with the ratio of comonomer 3.

According to X-ray diffraction data, polymer 2 was almost totally amorphous. The calculated degree of crystallinity was 3.3%. Diacetylene-containing copolymers were more crystalline, the calculated degrees of crystallinity being 33.2, 32.5, 11.9, 24.3, and 14.7% for copolymers 5a, 5b, 5c, 5d, and 5e, respectively. The degree of crystallinity decreased as ratio of comonomers became equimolar; this is characteristic random copolymers. However, this was not observed in the case of 5d due to large difference in the rigidity between comonomers 3 and 4.
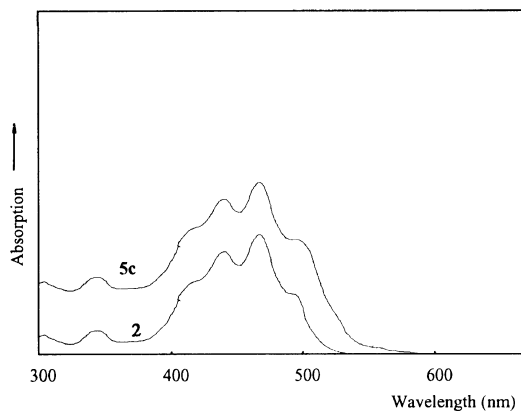
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Figure 2. Solution visible absorption spectra of polymer 2 and copolymer **5c**.
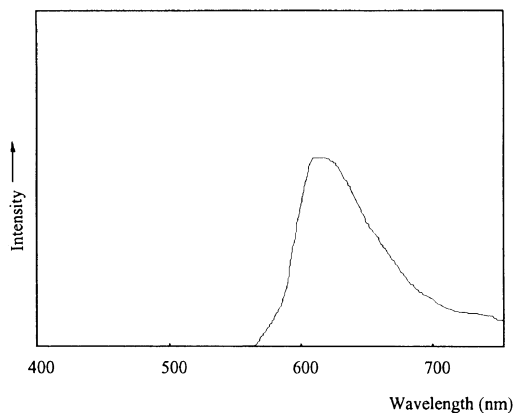

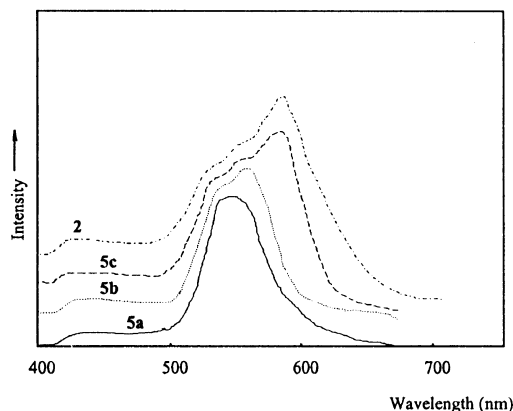**Figure 4.** Luminescence spectra of the solid film of copolymer **5c**.

Figure 3. Luminescence spectra of polymer 2 and copolymers **5a**—**5e**.

All polymers showed identical absorption bands in the visible region due to fluorescein chromophore. Apparently, the position of the absorption maxima does not depend on the fluorescein ratio in the polymers. Examples of visible absorption spectra of chloroform solutions of polymer 2 and of copolymer **5c** are shown in Figure 2.

Figure 3 shows the spectra of luminescence of diluted (10^{-3} mol l^{-1}) chloroform solutions of polymer 2 and copolymers **5a**, **5b**, and **5c**. In the region of the 400—500 nm a shoulder could be seen due to reabsorption of emitted light by fluorescein moieties. The appearance

of luminescence spectra depends on the concentrations of fluorescein moieties in the polymer chain. Thus, the spectra of copolymer **5a** which contains 2 mol% fluorescein moieties showed the only maximum at 544 nm, whereas the spectra of copolymers **5b** and **5c** showed additional maxima in the long-wavelength region, at 560, 568, and 588 nm, respectively.

In the case of copolymer **5a**, the chromophore moieties were separated because of low concentration in the polymer chain and the luminescence spectrum resembled that of the isolated chromophore. In the cases of copolymers **5b** and especially **5c** which have high concentrations of chromophore groups, the fluorescein moieties may interact with each other within one polymer chain. The long-wavelength bands in the luminescent spectra of the copolymers **5b** and **5c** may probably be of excimer origin. When excited, the chromophore moiety (A*) may form an excimer (AA)* with a cromophore moiety of the same chain in the ground state (A) which emits light at a longer wavelength than the separated chromophores moiety (A*).

The luminescence spectra of solid films of polymer 2 and copolymers **5a**—**5c** were measured. The maxima in the luminescent spectra of the solid films shift by 30—50 nm to longwave region as compared to polymer

solutions and the position of the maxima does not depend on polymer composition. All polymers had luminescence maxima around 610 nm. An example of luminescent spectra of the solid film of copolymer **5c** is shown in Figure 4. This long wavelength shift may come from difference in polarization energy of S_0 and S_1 state of the fluorescein moiety in the solid state. This means that magnitude of stabilization of S_1 in the solid state is greater than that of S_0 because in the former case, polarizability is higher. Therefore the transition energy $S_0 \leftrightarrow S_1$ decreases causing a long-wavelength shift of luminescence maxima.

Preliminary $(\chi^{(3)})$ values of polymer films were obtained using the picosecond laser consisting of a mode locked Quantel Nd: YAG laser with frequency doubled to 532 nm. $(\chi^{(3)})$ Values of copolymers increased with the fluorescein ratio and reached 3×10^{-10} esu for copolymer **5c**.

Detailed studies on the luminescent and nonlinear optical properties of these polymers as well as of other new luminescent polymers which are being synthesized in our laboratory, will be published in the future.

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