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Free Radical Polymerization of 7-Methyl-1-methylene-3-phenylindene. Copoly(methylene/7-methyl-3-phenyl-1,1-indenylene)−Excimer Photoluminescence

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ABSTRACT: The free radical polymerization of 7-methyl-1-methylene-3-phenylindene (**IV**) yields copoly(methylene/7-methyl-3-phenyl-1,1-indenylene) (**V**). This novel copolymer has an aliphatic backbone and pendant cross-conjugated 1,1-diphenylethylene chromophores. In a dilute solution of **V**, two emissions are detected at 347 and 448 nm. These have been assigned to monomer and excimer emission, respectively. A thin film of **V** shows a higher energy excimer at 390 nm, as well as monomer emission at 340 nm and excimer emission at 456 nm. 3-Phenylindene (**I**), which serves as a model compound, shows only monomer emission at 348 nm in dilute solution. Emissions from the monomer, high-energy excimer, and excimer are detected at 340, 388, and 456 nm, respectively, in a thin film of **I**. **V** has been characterized by ^{1}H NMR, ^{13}C NMR, IR, UV, and fluorescence spectroscopy, as well as by GPC and TGA.

Introduction

Polymers that contain pendant aromatic chromophores, such as poly(vinylnaphthalene), have received a great deal of attention due to their potential as light-harvesting materials.[1,2] The photochemical properties of linear poly(vinylnaphthalene),[3,4] dendrimer-linear naphthalene containing hybrid polymers,[5] and copolymers with various other aryl groups[6] have been investigated. The photoluminesence of these is dominated by emission from an excimer. This results from the ability of neighboring planar aromatic chromophores to interact through π-stacking.

While poly(arylene/1,2-vinylene) systems have been extensively studied, there are only two reports of poly(arylene/1,1-vinylene)s.[7,8] We have been interested in polymers that contain cross-conjugated units and their photoluminescence.[7] In this paper, we report the free radical polymerization of 7-methyl-1-methylene-3-phenylindene (**IV**), which has been prepared in two steps. The $RuH_2CO(PPh_3)_3$-catalyzed Murai reaction of trimethylsilylethynylbenzene and 2-methylacetophenone yields 2′-acetyl-3′-methyl-2-trimethylsilyl-1,1-diphenylethylene (**II**). This reaction involves the ruthenium-catalyzed regioselective addition of the ortho C−H bond of 2-methylacetophenone across the C−C triple bond of trimethylsilylethynylbenzene. Treatment of **II** with trimethyl orthoformate and a catalytic amount of *p*-toluenesulfonic acid gave **IV**.[9]

Benzoyl peroxide initiated free radical polymerization of **IV** results in a copolymer with a saturated backbone and pendant cross-conjugated 7-methyl-3-phenyl-1,1-indenylene units which are similar to 1,1-diphenylethylene. In dilute solution, **V** is characterized by fluorescence at 347 and 448 nm ($\tau = 1.7$ ns), which are assigned to monomer and excimer emission, respectively. A thin film of **V** shows emissions at 340, 388, and 456 nm. By comparison, a solution of **I** shows an emission at 345 nm, while a thin film shows three emissions: 340, 390, and 457 nm.

Experimental Section

^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC-250 spectrometer operating in the FT mode. Five percent w/v chloroform-*d* solutions were used to obtain NMR spectra. ^{13}C NMR spectra were run with broad-band decoupling. Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR. IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra of methylene chloride solutions were acquired on a Shimadzu UV-260 ultraviolet visible spectrometer.

Photoluminescence spectra were measured on a PTI instrument, equipped with a model A1010 xenon/mercury lamp and a model 710 photomultiplier defraction detector. Lifetime measurements (τ) were performed on a PTI fluorescence lifetime spectrometer. Spectra were obtained on methylene chloride solutions that had been degassed by bubbling argon through them for 5 min. Thin films were spin-cast on quartz slides from a $CHCl_3$ solution.

The fluorescence quantum yields (Φ_F) were measured in a CH_2Cl_2 solution using 7-(diethylamino)-4-methylcoumarin as the standard. The samples were excited at 317 nm, and the emission at 420 nm was measured.

Gel permeation chromatography (GPC) analysis of the molecular weight distribution of **V** was performed on a Waters system equipped with a 510 pump and a R401 refractive index detector. Two 7.8 mm × 300 mm Styragel columns packed with $<5\ \mu$m divinylbenzene cross-linked polystyrene, HR4 and HR2, in series were used for the analysis. The eluting solvent was toluene at a flow rate of 0.3 mL/min. The retention times were calibrated against known monodisperse polystyrene standards of M_w 929 000, 122 400, 13 700, and 690 whose polydispersity is less than 1.09.

TGA of the copolymer was measured on a Shimadzu TGA-50 instrument. The temperature program was 5 °C/min from 25 to 750 °C. The temperature was held at 750 °C for an additional 5 min.

Predictions of ^{1}H NMR chemical shifts of structures were generated using ACD/HNMR 2.5 software from Advanced Chemistry Development, Inc., Toronto, Canada.

All reactions were carried out in flame-dried glassware under an atmosphere of purified argon. 2-Methylacetophenone, trimethylsilylethynylbenzene, trimethyl orthoformate, *p*-toluenesulfonic acid, bromobenzene, magnesium powder, 1-indanone, benzoyl peroxide, and tetrahydrofuran were obtained from Aldrich and used without further purification. Benzene

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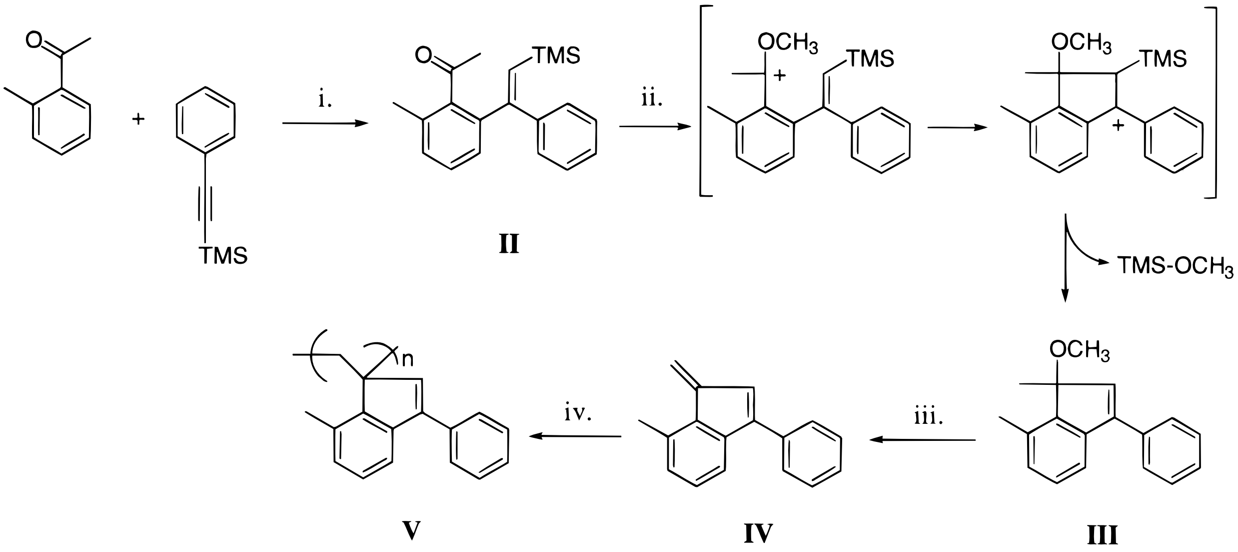


Figure 1. (i) $RuH_2CO(PPh_3)_3$, toluene, 135 °C. (ii) $(CH_3O)_3CH$, CH_3OH, *p*-toluenesulfonic acid, reflux. (iii) CH_2Cl_2, *p*-toluenesulfonic acid, reflux. (iv) Benzoyl peroxide, benzene, 100 °C.

and toluene were distilled from benzophenone ketyl. Spectral grade methylene chloride was obtained from J.T. Baker.

Dihydridocarbonyltris(triphenylphosphine)ruthenium [$RuH_2CO(PPh_3)_3$] was prepared from ruthenium trichloride hydrate (Aldrich).[10]

3-Phenylindene (I) was prepared according to literature procedure.[11]

7-Methyl-1-methylene-3-phenylindene (IV).[9] 2-Methylacetophenone (4.0 g, 29.8 mmol), trimethylsilylethynylbenzene (5.196 g, 29.8 mmol), toluene (5 mL), and $RuH_2CO(PPh_3)_3$ (300 mg) were added to a round-bottom flask equipped with a condenser and Teflon-covered magnetic stir bar. The reaction mixture was heated in an 135 °C oil bath for 24 h. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure to yield **II**.

II (3.78 g, 12.2 mmol), trimethyl orthoformate (2.62 g, 24.0 mmol), methanol (60 mL), and a few crystals of *p*-toluenesulfonic acid were added to a 250 mL round-bottom flask equipped with a condenser and Teflon-covered magnetic stir bar. The mixture was heated at reflux for 15 h. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure to yield a 1:1 mixture of 1-methoxy-1,7-dimethyl-3-phenylindene (**III**) and **IV**. These were characterized spectroscopically but were not separated. The crude mixture was taken up in CH_2Cl_2 (60 mL) in a round-bottom flask equipped with a reflux condenser and a Teflon-covered magentic stir bar. A few crystals of *p*-toluenesulfonic acid were added, and the solution was heated to reflux for 4 h. After cooling to room temperature, CH_2Cl_2 (100 mL) was added. The combined organic solution was extracted with H_2O (three times) and dried over anhydrous $MgSO_4$. In this way, a CH_2Cl_2 solution of **IV** was obtained. It was stored in the absence of light.

II has the following spectral properties.[9] ^1H NMR δ: -0.07 (s, 1.15 H), -0.02 (s, 7.85H), 2.30 (s, 3H), 2.31 (s, 3H), 5.95 (s, 0.80H), 6.41 (s, 0.20H), 6.96 (d, 1H, $J = 7.1$ Hz), 7.17 (d, 2H, $J = 7.2$ Hz), 7.25 (m, 2H), 7.35 (m, 3H).

III has the following spectral properties.[9] ^1H NMR δ: 1.74 (s, 3H), 2.54 (s, 3H), 3.11 (s, 3H), 6.23 (s, 1H), 7.06 (d, 1H, $J = 7.4$ Hz), 7.23 (d, 1H, $J = 7.5$ Hz), 7.30 (d, 1H, $J = 7.4$ Hz), 7.43 (tt, 1H, $J = 7.3$ and 1.2 Hz), 7.50 (m, 2H), 7.63 (dd, 2H, $J = 8.1$ and 1.32 Hz).

IV has the following spectral properties.[9] ^1H NMR δ: 2.65 (s, 3H), 5.95 (s, 1H), 6.17 (s, 1H), 6.62 (s, 1H), 7.12 (d, $J = 7.6$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.42 (tt, $J = 7.4$, 1.2 Hz, 1H), 7.46 (d, $J = 7.6$ Hz, 1H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.67 (dd, $J = 8.0$ Hz, $J = 1.5$ Hz, 2H).

Copoly(methylene/7-methyl-3-phenyl-1,1-indenylene) (V) was prepared via free radical polymerization of **IV**. **IV** (570 mg, 2.6 mmol), benzene (6 mL), and benzoyl peroxide (25 mg) were placed in a 25 mL round-bottom flask equipped with a reflux condenser and a Teflon-covered magnetic stir bar. The mixture was stirred at 105 °C for 3 h. After cooling to room temperature, the solvent was removed by evaporation under reduced pressure. The residue was taken up in a minimal amount of methylene chloride and was precipitated by addition of methanol. This process was repeated three times. The polymer was then precipitated three times from THF/MeOH. In this way, we obtained 420 mg, 75% yield, $M_w/M_n = 64\,700/13\,800$. ^1H NMR δ: 0.89−2.87 (br s, 5H), 4.61−5.40 (br s, 0.5H), 5.82−7.59 (br s, 8.5H). ^{13}C NMR δ: 20.35, 43.81, 57.77, 119.22, 128.09, 132.78, 135.96, 139.75, 140.63−144.49 (br), 150.64. UV λ_{nm} (ϵ): 232 (75 500), 300 (2600), $\Phi_F = 0.001$. IR ν: 3050, 2924, 2859, 1592, 1486, 1448, 1372, 1246, 1160, 1074, 1026, 972, 884, 845, 788, 755 cm^{-1}.

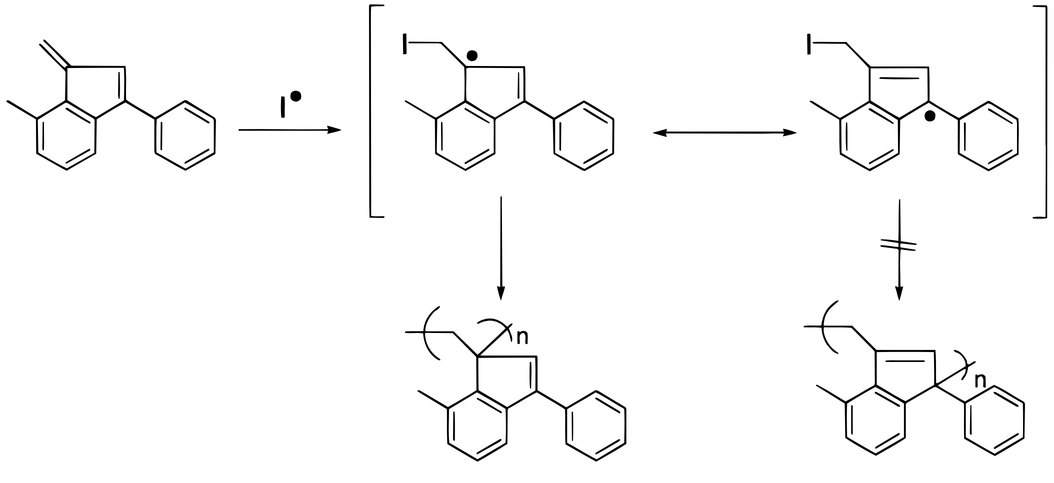
Results and Discussion

The model compound, 3-phenylindene, was prepared in two steps. Addition of the Grignard reagent, phenylmagnesium bromide, to 1-indanone gave 1-phenyl-1-indanol, which is readily dehydrated in CH_2Cl_2 by *p*-toluenesulfonic acid.[11]

Monomer and polymer synthesis is outlined in Figure 1. **II** is converted to **III** by reaction with trimethyl orthoformate and *p*-toluenesulfonic acid. This serves to convert the acetyl carbonyl to a dimethoxy ketal which reacts with *p*-toluenensulfonic acid with loss of methanol to yield a methoxy-stabilized benzylic carbocation. Intramolecular reaction of this with the vinylsilane results in electrophilic desilation[12] to yield **III**, which undergoes acid-catalyzed loss of methanol to give **IV**.

Free radical polymerization of **IV** is initiated by addition of a radical to the terminal end of the methylene group. This yields an allylic radical that is benzylic at one end and doubly benzylic at the other. Reaction at the doubly benzylic carbon with another molecule of **IV** would lead to copoly(methylene/4-methyl-1-phenyl-1,3-indenylene) (**VI**) (see Figure 2). Alternatively, reaction at the monobenzylic radical with another molecule of **IV** leads to **V**. ^1H NMR analysis indicates that the reaction occurs only at the more reactive monobenzylic end to give **V**, not the more stable doubly benzylic end. This selectivity may not be due to radical stability, however, but due to reaction at the less sterically hindered end of the allylic radical system.

^1H NMR analysis based on comparison of the experimental ^1H NMR of **V** with that calculated for structures



V **VI**

Figure 2. Free radical polymerization of **IV**.

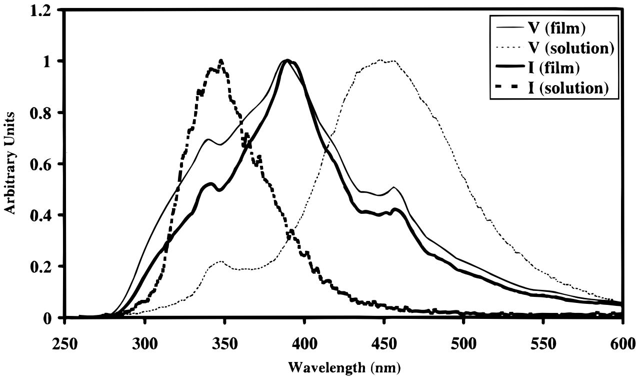


Figure 3. Fluorescence emission spectra of methylene chloride solutions and thin films of **I** and **V**.

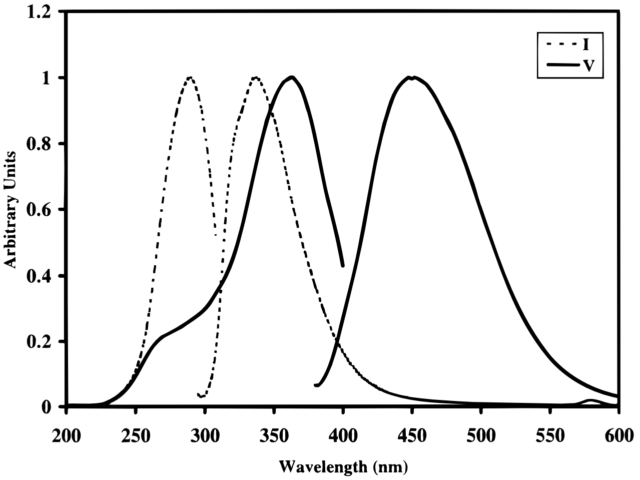


Figure 4. Excitation and emission scans of **I** and **V**.

V and **VI** confirms this assignment. According to our calculations, the most significant difference is that **VI** should have an allylic signal with a chemical shift at ~3.8 ppm. The experimental ^{1}H NMR of **V** shows three broad chemical shifts at 0.9−2.9, 4.6−5.4, and 5.8−7.6 ppm. No peak near 3.8 ppm is observed.

The monomer emission, as determined from a 0.07 mM CH_2Cl_2 solution of **I**, occurs at 345 nm. In a solution of **V**, the monomer emission is detected at 347 nm, although the predominant emission comes at 448 nm (see Figure 3). This is likely due to the formation of an excimer, resulting from the close proximity of intramolecular neighboring chromophores. Thin films of both **I** and **V** show a third, predominant emission around 390 nm, an energy level approximately halfway between the monomer and excimer. This emission may arise from intermolecular chromophore interactions, thus providing a high-energy trapping mechanism. Examples of “second excimer” luminescence have been previously reported for derivatives of poly(vinylnaphthalene) and related systems.[4]

The fluorescence quantum yield (Φ_F) of the excimer measured in a methylene chloride solution of **V** is 0.001. Such low quantum efficiencies are characteristic of systems with pendant aromatic chromophores, due to the numerous mechanisms by which nonradiative decay can occur.[13]

The excitation and emission spectra of both **I** and **V** in methylene chloride are shown in Figure 4. When the emission is monitored at 330 nm, the model compound **I** shows one peak in the excitation spectra at 290 nm. In comparison, the absorption spectrum shows an absorbance at 255 nm with a tail out to 340 nm.

By comparison, the polymer, **V**, shows two absorptions in the excitation spectrum, a weak absorption at 275 nm and a stronger absorption at 362 nm, when monitored at 452 nm. The UV absorption spectrum shows a maximum absorbance at 250 nm with a tail out to 375 nm. A similar phenomenon has been previously reported for PPV-type polymers.[14]

Interestingly, when the methylene chloride solution of **V** is excited at 260 nm, the intensity of emission at 450 nm is approximately 5 times less than when the sample is excited at 362 nm. This suggests that more efficient emission is obtained by excitation at 362 nm because energy is lost to nonradiative processes when excited at 260 nm. However, the UV absorption spectrum of the same sample shows a λ_{max} at 250 nm and only weak absorption at 362 nm. It has been found that, in contrast, maximum luminescence of the thin films of **I** and **V** is obtained by excitation at 245 nm.

The TGA of **V** shows no weight loss to 185 °C. Between 185 and 260 °C there is 9% weight loss. Above 275 °C, catastrophic linear weight loss occurs. At 470 °C only 5% of the initial sample mass remains. No

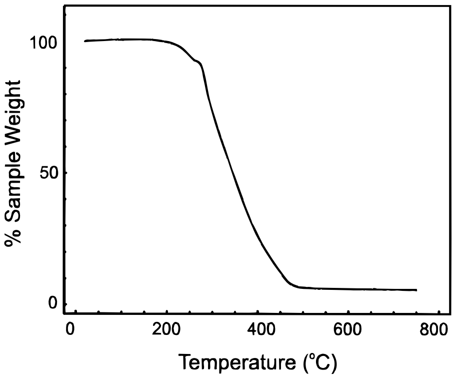


Figure 5. TGA of **V**.

further degradation is observed out to 750 °C (see Figure 5).

In conclusion, we have demonstrated a novel polymer based on 3-phenylindene repeat units. This system shows excimer formation in dilute solution, as well as a second excimer formation in a thin film. Current efforts are underway to study the photophysics of **V** in solution and film.

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