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Characterization and fluorescence properties of thiophene-modified π-conjugated nickel poly-yne polymers

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Abstract

Thiophene- and benzene-modified nickel poly-yne polymers **1**–**5** were characterized by gel permeation chromatography, infrared spectroscopy and X-ray photoelectron spectroscopy. The polymers, being highly soluble in common organic solvents, exhibit intense fluorescence upon excitation by ultraviolet–visible light at room temperature. The emission intensity of the polymers with thiophene-2,5-diyl is 8–277 times stronger than that of the analogous polymers without thiophene-2,5-diyl. Transient luminescence was also investigated. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Fluorescence; Nickel poly-ynes; Thiophene modification

1. Introduction

Since the first demonstration of π-conjugated organic polymer light-emitting diodes (polymer LEDs), research in this area has intensified [1–16]. Although transition metal poly-ynes, one of the partially π-conjugated polymers, were thoroughly studied for their third-order non-linearity, research into their fluorescence properties is lacking.

It has been recently reported by us that a solution of palladium containing poly-ynes exhibits strong fluorescence at the excitation of ultraviolet (UV)–visible light at room temperature [17]. The overlap of the metal $d\pi$-orbitals with the alkyne $p\pi^*$-orbitals in these polymers should give rise to a partially delocalized π-system along the polymer chain. This system imparts interesting physical properties such as non-linear optical effects and fluorescence.

We report here the characterization and steady-state fluorescence as well as transient luminescence properties of nickel poly-yne polymers containing a thiophene ring in the main chain (Scheme 1).

2. Experimental

2.1. Reagents

All reagents and solvents were purchased from commercial sources and used as received unless noted otherwise.

p-Diethynylbenzene (*p*-DEB) was prepared by the reported method [18] and purified by sublimation immediately before use in the reaction. The nickel–phosphine complexes were synthesized according to literature procedures: *trans*-bis (tri-n-butylphosphine) nickel(II) dichloride, $NiCl_2(PBu_3)_2$ [19], and *trans*-bis(triphenylphosphine) nickel(II) dichloride, $NiCl_2(PPh_3)_2$ [20]. 2,5-Diiodothiophene was prepared by modifying a reported method [21] and purified by recrystallization from ethanol. Diethylamine was distilled from calcium hydride (4–5 g/100 ml) and stored under nitrogen. Triphenylphosphine was purified by a standard method [22].

2.2. Instrumentation

Infrared (i.r.) spectra were obtained on a PE 983 infrared spectrophotometer (KBr disks). Electronic spectra were recorded on a Beckman DU-50 spectrophotometer.

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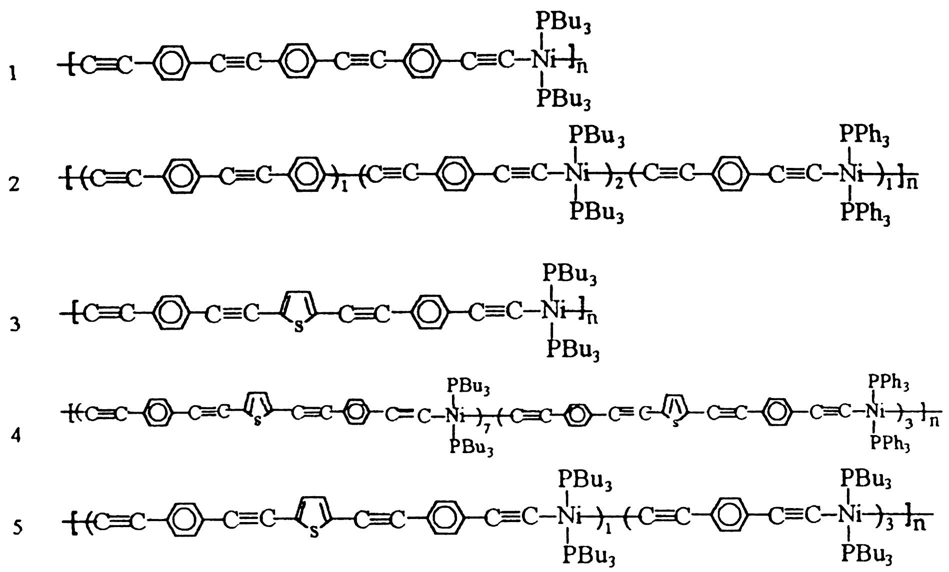


Scheme 1.

Excitation and emission spectra were measured at room temperature with a Hitachi F-300 fluorescence spectrophotometer. Transient photoluminescence (PL) was taken using the second harmonic (532 nm) of a CW mode-locked Nd:YAG laser to excite the polymers in a toluene solution. X-ray photoelectron spectroscopy (XPS) was performed at room temperature on a Kratos ES 300 spectrometer with the use of Mg K_α radiation ($h\nu = 1254$ eV). The typical X-ray operating conditions were 15 kV and 10 mA. All XPS spectra were energy-referenced to the C_{1s} photoemission peak at 284.6 eV. Molecular weights (weight-average molecular weight, $\bar{M}_w$, and number-average molecular weight, $\bar{M}_n$) as well as molecular weight distribution (MWD) determination was carried out on a Waters 208 gel permeation chromatograph (g.p.c.) versus polystyrene standards at 25°C (tetrahydrofuran (THF) was used as eluent).

2.3. Preparation of polymers

2.3.1. Preparation of polymers **1** and **3**

A mixture (I) of *p*-DEB (252.4 mg, 2.0 mmol) and *p*-diiodobenzene (329.9 mg, 1.0 mmol) or 2,5-diiodothiophene (335.9 mg, 1.0 mmol) was stirred at 25°C in 30 ml $HNEt_2$ in the presence of $PdCl_2(PPh_3)_2$ (17.6 mg, 0.025 mmol) and CuI (5.0 mg, 0.026 mmol) as catalysts under nitrogen for 2.5 h (for *p*-diiodobenzene) or 4.5 h (for 2,5-diiodothiophene) in a manner similar to the method in the literature [12,13]. Solutions of $NiCl_2(PBu_3)$ (534.1 mg, 1.0 mmol) in 25 ml $HNEt_2$ and of CuI (5.0 mg, 0.026 mmol) in 5 ml $HNEt_2$ were then injected to the reacted mixture (I) and stirred at 5–10°C for 24 h (polymer **1**) or 8 h (polymer **3**). The resulting mixture was filtered to remove insoluble residue and the filtrate was concentrated to dryness at reduced pressure. The polymers were then dissolved in 3 ml of THF and precipitated into methanol, washed with methanol, and dried under vacuum at room temperature for 24 h to give bright yellow polymer **1** and orange polymer **3** (containing thiophene rings in the main chain).

2.3.2. Preparation of polymers **2** and **4**

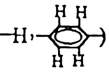
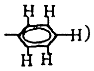
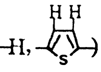
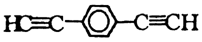
Into a reacted mixture (I) described above was injected a solution of $NiCl_2(PBu_3)_2$ (374.0 mg, 0.7 mmol) in 20 ml $HNEt_2$, and the mixture was stirred at 5–10°C for 6 h. A solution of $NiCl_2(PPh_3)_2$ (196.3 mg, 0.3 mmol) in 6 ml dimethylsulfoxide (DMSO) was then added and stirred at 5–10°C for 6 h. The other procedures are the same as described above to give orange polymers **2** and **4**.

Table 1
Elemental[a] and g.p.c. analysis data for polymers **1**–**5**

Polymer	%C	%H	%Ni	$\bar{M}_w$ (× 10^4)	MWD
1	71.91 (76.24)	7.60 (8.45)	7.76 (7.45)	0.79	1.57
2	71.99 (74.98)	7.59 (7.65)	7.77 (8.45)	1.48	1.68
3	68.55 (72.63)	7.52 (8.13)	7.00 (7.39)	0.72	2.63
4	73.86 (74.70)	7.20 (6.90)	7.53 (7.07)	1.13	1.89
5	68.49 (70.48)	8.28 (9.39)	9.55 (9.18)	0.49	1.32

[a] Calculated values in parentheses.

Table 2
I.r. data for polymers and monomers

Compound	I.r. (cm^{-1})					
	ν(≡C–H)	ν(MC≡C)	ν(ArC≡CAr)	δ (C–H, )	δ (C–H, )	δ (C–H, )
						785 (s)
		3264(s)				
	3264 (s)		2136 (w)	830 (vs)		
1	3282 (w)	2067 (vs)	2190 (w)	835 (vs)		
2	3280 (w)	2072 (vs)	2200 (w)	835 (vs)	690 (m), 740 (m)	
3	3278 (w)	2070 (s)	2195 (w)	838 (s)		795 (s)
4	3280 (w)	2068 (vs)	2180 (w)	834 (vs)	690 (m), 740 (m)	795(s)
5	3280 (w)	2072 (vs)	2180 (w)	834 (vs)		795(m)

*2.3.3. Preparation of polymer **5***

To a reacted mixture of 2,5-diiodothiphene (168.0 mg, 0.5 mmol) and *p*-DEB (126.2 mg, 1.0 mmol) described above was injected a solution of $NiCl_2(PBu_3)_2$ (534.3 mg, 1.0 mmol) in 20 ml $HNEt_2$, the mixture was stirred at 5–10°C for 10 h. Then a solution of *p*-DEB (126.2 mg, 1.0 mmol) and $NiCl_2(PBu_3)_2$ (267.0 mg, 0.5 mmol) in 10 ml $HNEt_2$ was injected, and stirring was continued at 5–10°C for 15 h. The treatment of the polymer is the same as described above. The final yellow polymer **5** was obtained.

3. Result and discussion

3.1. G.p.c., i.r. and XPS analysis

Thiophene- and benzene-modified nickel poly-yne polymers **1**–**5** were synthesized by stepwise polycondensation of *p*-diethynylbenzene and 2,5-diiodothiophene (or *p*-diiodobenzene) with dihalide complexes $NiCl_2(PR_3)_2$ (where R = Ph or n-butyl) in the presence of $PdCl_2(PPh_3)_2$ and CuI in diethylamine at 5–10°C.

The g.p.c. analysis shows that the polymers possess $\bar{M}_w$ in the range from 0.49×10^4 to 1.48×10^4 (Table 1). As shown in Table 2, the i.r. bands of the nickel poly-ynes resemble those of palladium poly-yne polymers [17] and are reasonable for their structures (Scheme 1). As a consequence of the stepwise polycondensation, the strong ethynyl ν(C–H) band of the monomer (*p*-DEB) at 3264 cm^{-1} is shifted to a higher frequency at about 3278–3282 cm^{-1} and becomes very weak (Fig. 1). The result suggests that a dehydrogenation polycondensation reaction has occurred. The i.r. spectra of polymers **1**–**5** show that the ν(C≡C) band of *p*-DEB at 2110 cm^{-1} is shifted to 2180–2200 cm^{-1}, which is consistent with a known trend that disubstituted acetylenes give rise to the ν(C≡C) band at a frequency higher than monosubstituted ones [23]. As can be seen from Fig. 1, the i.r. spectra of polymers **1**–**5** show a characteristic sharp and intense absorption peak at 2067–2072 cm^{-1}, which is attributed to the ν(MC≡C) absorption [24,25]. The result also indicates that poly-ynes containing σ-bonded metals are formed.

The i.r. spectra of polymers **3**–**5** also show a new δ(C–H) absorption of the thiophene-2,5-diyl unit at 795 cm^{-1}. Compared with that of the 2,3-diiodothiophene, the δ(C–H) absorption band of the thiophene-2,5-diyl unit of the polymers is shifted to a higher frequency region. It also can be seen from Table 2 that the i.r. absorption bands from 1,4-phenylene units of the polymers resemble those of the monomer. The i.r. spectra of polymers **2** and **4** show out-of-plane vibrations of the terminal phenyl units at 740 and 690 cm^{-1}. The results indicate the presence of triphenylphosphine in the polymers **2** and **4**.

Table 3
XPS analysis of $NiCl_2(PPh_3)_2$ and $NiCl_2(PBu_3)_2$ complexes and polymers **3**–**5**

Compound	Binding energy, E_b (eV)			Atomic ratio Ni/S (mol/mol)[b]
	Ni $2p_{3/2}$	P $2p$ [a]	S $2p$ [a]	
$NiCl_2(PBu_3)_2$	845.5	130.5		
$NiCl_2(PPh_3)_2$	854.6	130.8		
3	854.2	130.5	164.4	0.62/1.0 (1.0/1.0)
4	854.5	130.4	164.4	0.20/1.0 (1.0/1.0)
5	854.6	130.6	164.35	0.96/1.0 (4.0/1.0)

[a] Corresponding to the main signal.
[b] Calculated values are in parentheses.

As shown in Table 3, the binding energy for Ni $2p_{3/2}$ in polymers **3**–**5** is 854.2, 854.5 and 854.6 eV respectively, similar to the values obtained for the reference compounds $NiCl_2(PBu_3)_2$ and $NiCl_2(PPh_3)_2$. The difference between the P 2*p* binding energy values of $NiCl_2(PBu_3)_2/NiCl_2(PPh_3)_3$ and the polymers is also small. The results suggest that the charge on the nickel and phosphorus atoms does not change a great deal when the polymers are formed, and the Ni–C σ-bond resembles the Ni–Cl bond. It is clear that overlap of the nickel $d\pi$-orbitals with the alkyne $p\pi^*$-orbitals occurred and charge is transfered from the metal $d\pi$-orbitals to alkyne $p\pi^*$-orbitals. The overlap between the metal $d\pi$-orbitals and alkyne $p\pi^*$-orbitals provides a special, partially π-conjugated structure along the metal–poly-yne main chains and this structure may exhibit interesting optical properties. A narrow signal for Ni $2p_{3/2}$ is observed, suggesting that only one nickel species exists. The appearance of an S 2*p* XPS signal reveals the presence of the thiophene ring in the present polymers. The XPS results are in accordance with the i.r. analysis.

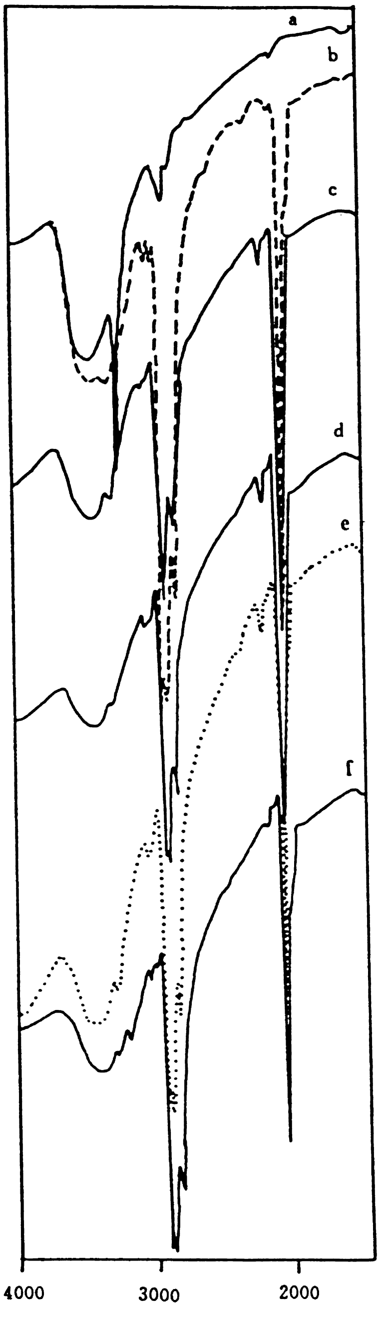


Fig. 1. I.r. spectra of monomer and polymers: (a) *p*-DEB; (b)–(f) polymers **1**–**5**.

3.2. Steady-state fluorescence

The steady-state fluorescence, as well as the excitation of a solution of the polymers in THF (0.02–0.10 mg ml^{-1}), are shown in Table 4. A solution of polymer **4** in THF (0.02 mg ml^{-1}) exhibits an emission peak at 467.0 nm when excited at 373.0 nm. The transition energy $E(\pi-\pi^*)$, estimated from the maximum absorption band of **4**, is 3.08 eV. The band gap E_g (2.67 eV) estimated from the onset position of the absorption is consistent with the emission band (2.66 eV). The result suggests that the fluorescence at 467.0 nm (2.66 eV) is attributed to the migration of electrons in the conduction band (CB) to the valence band (VB).

Fig. 2 shows the effect of concentration on the fluorescence intensity and wavelength. The emission intensity from the solution of **3** in THF is increased (0.013–0.1 mg ml^{-1}) and then decreased ($>$ 0.1 mg ml^{-1}) with the increase of concentration. This is due to the concentration quenching effect which is often observed for the fluorescence of monomeric organic molecules. The dilute THF solutions of **3** ($\leq$ 0.005 mg ml^{-1}) exhibit fluorescence at 439.6 nm (2.82 eV). The solutions (0.013, 0.020, 0.025 and 0.050 mg ml^{-1}) give rise to a main emission peak at 440.0–441.2 nm (Fig. 2(b), Fig. 2(c), Fig. 2(e)) and a subpeak at 456.0–460.7 nm. The main emission at 440.0–441.2 nm (2.82–2.81 eV) agrees with the band gap of polymer **3** (2.82 eV). As discussed above, this emission is ascribed to electron migration from CB to VB. The fluorescence at 456.0–460.7 nm may be attributed to the emission from an excimer-like adduct [9]. The fluorescence spectra from the solutions at higher concentration (0.1 and 0.2 mg ml^{-1}) exhibit a contribution from emission centered at 460 nm (Fig. 2(a), Fig. 2(d)). This fluorescence may also be attributed to emission from the excimer. Other samples of this system possess a similar fluorescence process. That is, in dilute ($\leq$ 0.005 mg ml^{-1}) THF solution, the fluorescence may be ascribed to the migration of electrons from CB to VB, this emission being connected with single polymer molecules; the fluorescence at a higher concentration ($\geq$ 0.1 mg ml^{-1}) shows bands mainly from the excimer-like adducts; and in solutions with concentration in the range 0.013–0.1 mg ml^{-1}, the fluorescence consists of emissions both from single polymer molecules and excimer-like adducts.

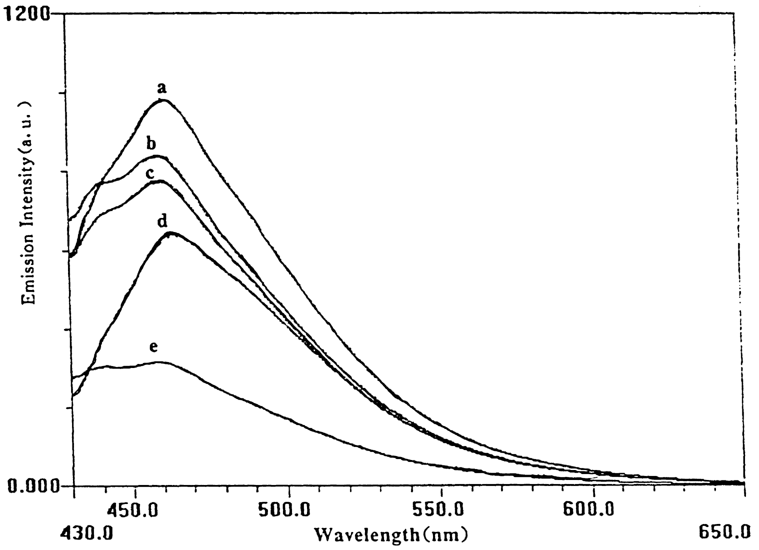


Fig. 2. Emission spectra of polymer **3** in THF at room temperature: (a) 0.1 mg ml^{-1}; (b) 0.05 mg ml^{-1}; (c) 0.025 mg ml^{-1}; (d) 0.2 mg ml^{-1}; (e) 0.0125 mg ml^{-1}.

Photoluminescence originates from the radiactive recombination of photoexcitation states. The quantum yield for photoluminescence in small conjugated polymers can be very high, but is reduced as the extent of π-electron conjugation is increased [3,26].

One approach commonly employed to prepare efficient fluorescence materials is to limit the delocalization length of the polymers by interrupting π-conjugation or synthesizing short-chain oligomers [2], but this leads to lower charge-carrier mobility and increases the bias to drive the device [12]. The ideal material therefore possesses not only an extensively π-conjugated system but also strong fluorescence intensity. Metal poly-yne, a partially π-conjugated system, seems to be one answer to this issue.

As shown in Table 4, the intensity of the emission from the solution (0.02 mg ml^{-1}) of **3** in THF is 277 times stronger than that from the solution (0.1 mg ml^{-1}) of **1** in THF. The result suggests that polymers having a thiophene ring in the main chain exhibit much stronger fluorescence and a smaller Stokes shift than those without the thiophene ring. Although the concentration may influence the emission intensity, this leads at most to a threefold change in fluorescence intensity (Fig. 2) in the concentration range from 0.013 to 0.2 mg ml^{-1}. As also can be seen by comparing polymer **3** with **5** or **4** with **2**, the fluorescence is enhanced with increasing content of thiophene-2,5-diyl in the polymer repeat unit. The results concerning palladium poly-ynes described previously [17] indicated that polymers with triphenylphosphine ligands emit stronger fluorescence than those with tri-n-butylphosphine ones. However, this is not the case with nickel poly-ynes.

3.3. Transient photoluminescence

The photoluminescence emissions from π-conjugated polymers generally show low quantum yield and very short lifetimes ranging from less than 10 ps to 200 ps. These results suggest the presence of efficient non-radiative

Table 4
Excitation, emission, E_g, $E(\pi-\pi^*)$ and apparent Stokes shift of polymers **1**–**5**

Polymer	λ_{max}^{ex} (nm)[a]	λ_{max}^{em} (nm)[b]	*I*	$E(\pi-\pi^*)$ (eV)[c]	E_g (eV)[d]	Stokes shift (eV)[e]
1	444.0	511.4 (2.42)	10.33	3.18	2.81	0.76
2	448.0	518.4 (2.39)	4.17	3.09	2.86	0.70
3	423.0	440.0 (2.82)	2603	3.18	2.82	0.36
		458.6 (2.70)	2867			
4	373.0	467.0 (2.66)	32.90	3.08	2.67	0.42
5	432.0	469.4 (2.64)	29.42	3.19	2.78	0.55
		490.3 (2.53)	25.20			

[a] Measured at λ_{max} of the emission in THF (**1**, **2** and **5**: 0.1 mg ml^{-1}; 3 and **4**: 0.02 mg ml^{-1}).

[b] Same conditions as indicated in footnote a. Measured at room temperature. Slit (ex/em): 5 nm/5 nm. Energy in eV corresponding to λ_{max}^{em} is given in parentheses.

[c] $\pi-\pi^*$ transition energy estimated from the maximum absorption.

[d] Band gap estimated from the onset position of the absorption band.

[e] Energy separation between absorption and fluorescence maxima.

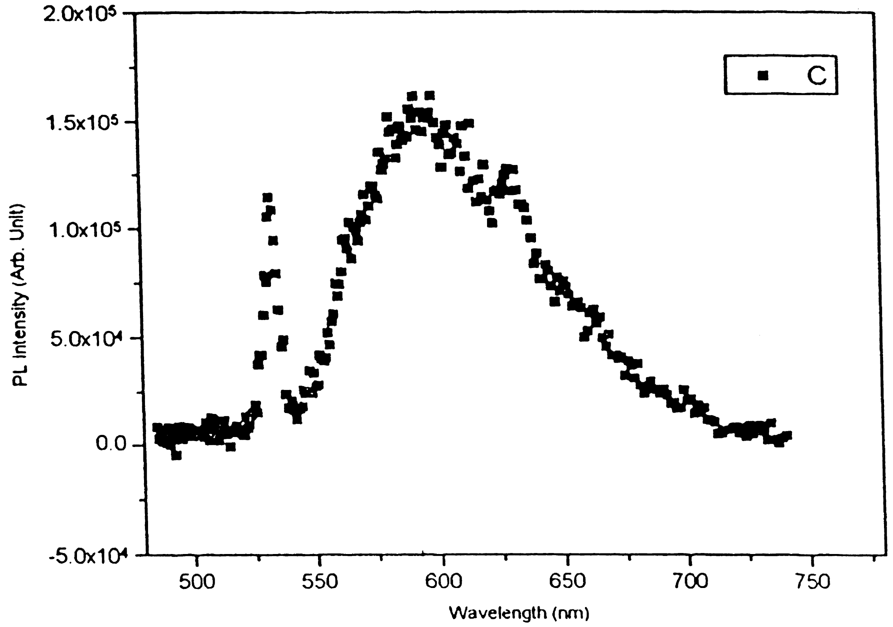


Fig. 3. Luminescence spectra of polymer **3** in toluene solution at room temperature, excited by 532 nm (2.33 eV) laser light.

decay paths [6,26–32]. We have carried out transient photoluminescence studies of polymer **3** with 532 nm (2.33 eV) pulses and 60 ps width at room temperature. Fig. 3 shows that the solution of **3** in toluene exhibits intense fluorescence at 557 nm. Inspection of the experimental curve in Fig. 4 suggests that the decay of fluorescence of polymer **3** is non-exponential. This indicates the presence of sigificant nonlinear recombination processes in addition to the linear monomolecular decay.

The luminescence of π-conjugated polymers was found to be more intense for excitation polarized perpendicular to the polymer chain ($E \perp C$) than for parallel excitation ($E \| C$) and the luminescence decay is faster for parallel ($E \| C$) than for perpendicular ($E \perp C$) excitation [26]. The decay for excitation with $E \perp C$ may be single exponential and that following $E \| C$ may be non-exponential in addition to exponential. In the case of our sample, the polymer molecules are dispersed at random among solvent molecules and a decay with complex processes is therefore expected. Other factors such as the existence of polymer molecules with different π-conjugated lengths, which may lead to different emission species, and the strong electron–lattice coupling may also result in the decay with complex processes.

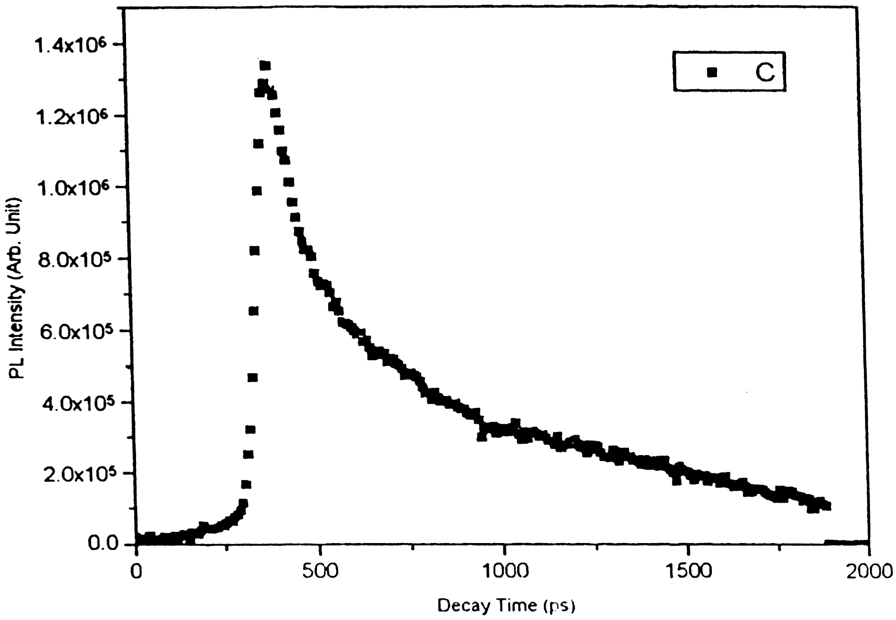


Fig. 4. Luminescence decay curves of polymer **3** excited by 532 nm (2.33 eV) laser light with 60 ps pulse in toluene solution at room temperature.

The time for the photoluminescence of **3** to decay to about 1/e of its initial value is ca. 366 ps at room temperature.

4. Conclusions

Nickel poly-yne polymers containing thiophene-2,5-diyl in the main-chain backbone possess a partially π-conjugated structure and exhibit intense fluorescence excited by UV–visible light at room temperature. Both single-molecule and excimer-like adduct emissions were observed. Insertion of thiophene-2,5-diyl into a polymer chain greatly enhances the fluorescence intensity. The decay of fluorescence of the polymers tends to be non-exponential.

Acknowledgements

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