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Synthesis of intrinsically soluble terpolymers with conjugated rigid block alternating with hexane-1,6-dioxy soft block

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Abstract

Intrinsically soluble terpolymers with alternating conjugated chromophoric units with inert hexane-1,6-dioxy units were synthesized using the Wittig reaction. The terpolymers were characterized with FTIR, ^{1}H NMR, UV–vis and fluorescence techniques. The thermal properties were investigated with DSC and TGA under nitrogen atmosphere. The photoluminescence of the terpolymer films was found to have emissive region and emission maxima, λ_{em}, similar to that of poly(2,5-dimethoxy-1,4-phenylenevinylene) films prepared via the Wessling method. A forward bias current was obtained and the devices showed typical diode behaviour. The photodegradation of the terpolymer films was studied by applying low-intensity irradiation at a fixed wavelength to the film. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The main driving force for the continued interest in conjugated polymers is the discovery that they can be used as light-emitting diodes (LEDs) [1]. Poly(1,4-phenylenevinylene) (PPV) and its derivatives, and more recently, polyfluorenes have in particular emerged as promising new materials for this purpose [1–10]. Conjugated polymers are designed in such a way that they are either soluble in their conjugated form or are produced in an insoluble form via a precursor polymer [11]. The former route has the advantage that syntheses are generally easier and processing is straightforward whilst the latter route has the advantage that multilayer LEDs can be easily produced. However, the drawbacks of the conjugated polymers prepared via the precursor route are the tendencies towards thermal decomposition and oxidation when the precursor polymers are heated at elevated temperature during the thermal conversion process [12].

We have reported earlier on the synthesis of an intrinsically soluble co-polymer consisting of alternating substituted 2 1/2 *p*-phenylenevinylene (2 1/2 PV) and hexane-1,6-dioxy blocks [13]. In this paper we will discuss the synthesis of some terpolymers via the Wittig condensation reaction by using the phosphonium salt, a fully conjugated dialdehyde and a dialdehyde interspaced with an inert hexanedioxy soft block as shown in Scheme 1 (schematic routes for the preparation of co-polymer and terpolymers with various dialdehyde feed mole ratios). It is expected that the dialdehydes will compete with each other for the reaction with the ylide in the Wittig reaction. Further, since terephthaldehyde is a fully conjugated dialdehyde, an extension in the conjugation length in the chromophoric blocks in the terpolymer is anticipated. The properties of the various terpolymers prepared from different feed mole ratios of dialdehydes will be discussed. These include photoluminescence (PL), thermal stability, photostability and the electrical characteristics of the LED devices fabricated.

2. Experimental

2.1. Synthesis

2.1.1. The monomers

1,4-Terephthaldehyde (**1**) (TCI) was used as received. The syntheses of 1,6-bis(4-formyl-2-methoxyphenoxy)hexane (**2**) and 1,4-bis(triphenylphosphoniomethyl)-2,5-dimethoxybenzene dichloride (**3**) have been described previously [13].

2.1.2. The terpolymers

The experimental route for the synthesis of the

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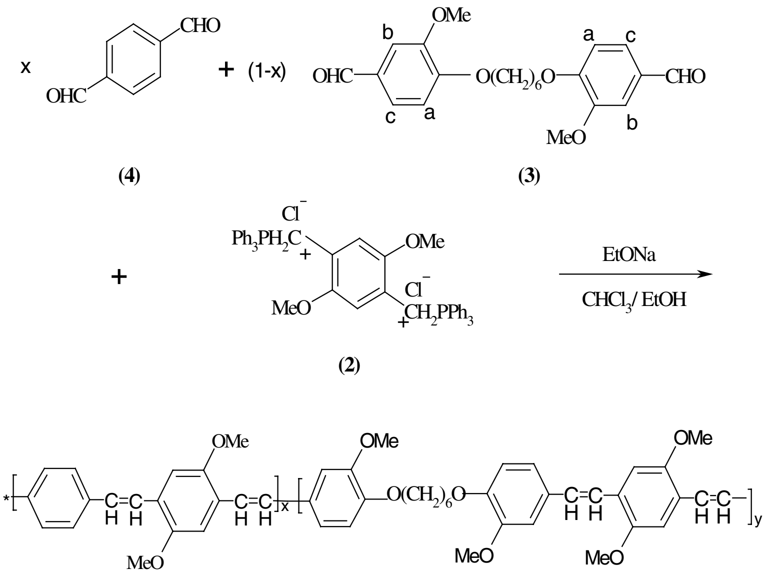

$Y = 1 - x$

01cp, when x = 0
28cp, when x = 0.2
46cp, when x = 0.4
64cp, when x = 0.6
82cp, when x = 0.8

Scheme 1.

terpolymers is shown in Scheme 1. For example, the synthesis of **28cp** is described as follows: ten millilitres of sodium ethoxide solution (prepared by dissolving approximately 0.15 g of freshly cleaned sodium metal in “superdry” ethanol) was added dropwise to a stirred solution of **2** (0.547 g, 1.42 mmol), **1** (0.0475 g, 0.35 mmol) and **3** (1.346 g, 1.773 mmol) in 30 ml of chloroform. The reaction was carried out at ambient temperature under nitrogen atmosphere. The mixture was stirred for 24 h after addition. A yellow solid was collected at the end of the condensation reaction. The crude polymeric product was filtered, followed by washing with ethanol/water (3:1) to remove the byproducts triphenylphosphine oxide and NaCl. The washed product was subsequently dissolved in chloroform and dried with anhydrous sodium sulphate. The solution was then filtered and the solvent was completely evaporated under reduced pressure. Low molecular weight compounds were removed by repeated washing (four to five times) with dried acetone until the solution became almost colourless. The obtained polymer, **28cp**, was then dried in a vacuum oven at 40°C for 2 days with a yield of 0.221 g (26.7%). Terpolymers with different ratios of dialdehyde were also prepared. Table 1 summarizes the amount of the various chemicals used and the polymer yields.

2.2. Characterization and instrumentation

FTIR spectra were obtained using a Perkin–Elmer FTIR spectrometer by casting polymer films onto the NaCl plate. ^{1}H NMR spectra were recorded using a Bruker Spectrospin 400 MHz spectrometer in $CDCl_3$ with a pulse width of 10.2 μs, and the chemical shifts were referred to TMS. UV–vis absorption spectra for both the solution and film were recorded using a Perkin–Elmer 8540 A spectrophotometer. Solution and film PL analyses were performed by using a Perkin–Elmer fluorometer equipped with a continuous xenon lamp source.

TGA measurements were carried out on an indium-calibrated Setaram TG-DTA/DSC thermal analyser. The samples were scanned at rates of 5, 10, 15 and 20 K/min

Table 1
Composition of various starting materials for polycondensation

Terpolymer (colour)	**1**	**2**	**3**	Yield
46cp (orange)	0.089 g (0.66 mmol)	0.232 g (1.00 mmol)	1.26 g (1.66 mmol)	0.134 g (19.4%)
64cp (orange)	0.122 g (0.91 mmol)	0.234 g (0.605 mmol)	1.149 g (1.51 mmol)	0.106 g (19.2%)
82cp (orange)	0.203 g (1.51 mmol)	0.146 g (0.379 mmol)	1.437 g (1.89 mmol)	0.200 g (33.6%)

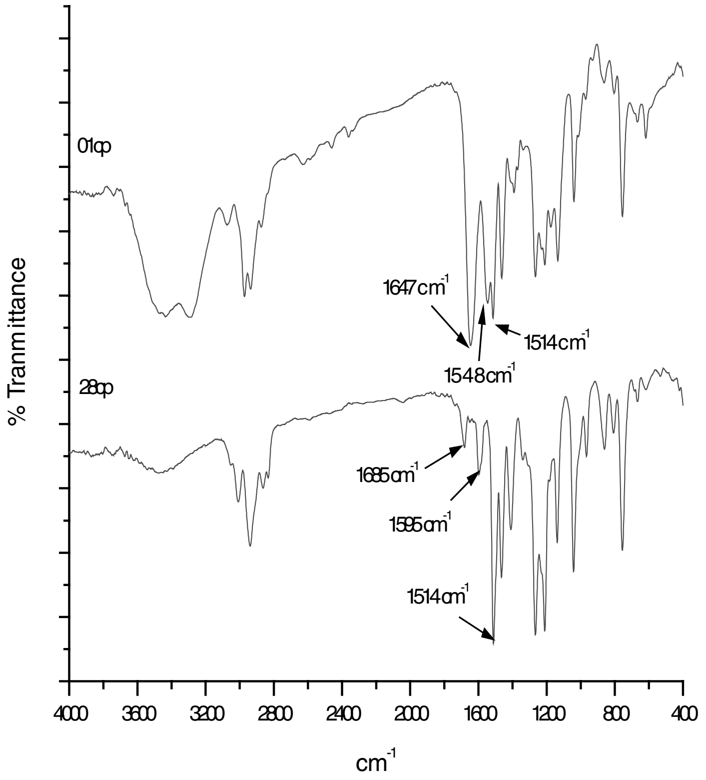

Fig. 1. FTIR spectra of **01cp** and **28cp**.

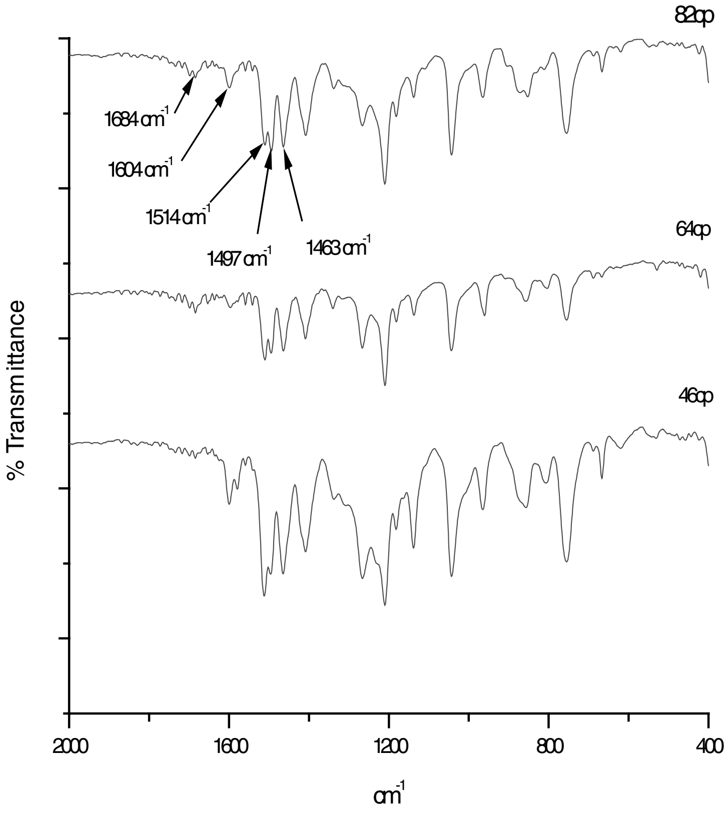

Fig. 2. FTIR spectra of **46cp**, **64cp** and **82cp**.

Table 2
Actual mole percent and feed mole percent of monomer **1** in the terpolymers

Polymer	Feed mole percent of monomer **1**	Actual mole percent of monomer **1**
28cp	20.0	25.2
46cp	40.0	50.4
64cp	60.0	64.3
82cp	80.0	68.5

under purified nitrogen atmosphere at 20 psi. DSC analyses were performed by using a Perkin–Elmer thermal analyser under purified nitrogen atmosphere at 20 psi.

2.3. Preparation of LED

An indium tin oxide (ITO) coated glass with electrical resistance of 60 Ω was cleaned by sonication. This was followed by rinsing in acetone and was dried in vacuum at room temperature for 4 h. A thin film of the polymer was spin-coated onto the ITO glass using 1% (w/v) solution in chloroform at 1000 rpm. The residual solvent was evaporated under vacuum at room temperature for 4 h. This was followed by vapour deposition of aluminium through a mask (3 mm in diameter) at a chamber pressure of at least 5×10^{-6} Torr. The top electrode, Al, was evaporated onto the polymer in a JEOL JEE-400 vacuum evaporator at a rate of 2–5 Å/s. The thickness of the Al was about 1000 Å. A typical LED was 3 mm in diameter. The effective area of the LEDs was 7.07×10^{-2} cm^2.

Basic electrical characterization involved measurement of the device current as a function of applied voltage. A HP 6282A or a HP 6212B DC power supply was used to supply the voltage across the device. The current was measured by a Keithley 238 High current source measure unit and a Keithley 614 electrometer that were connected to a computer equipped with the Interactive Characterization software. The computer recorded all the current–voltage data.

3. Results and discussion

3.1. Characterization of the terpolymers

All the terpolymers prepared were intrinsically soluble in

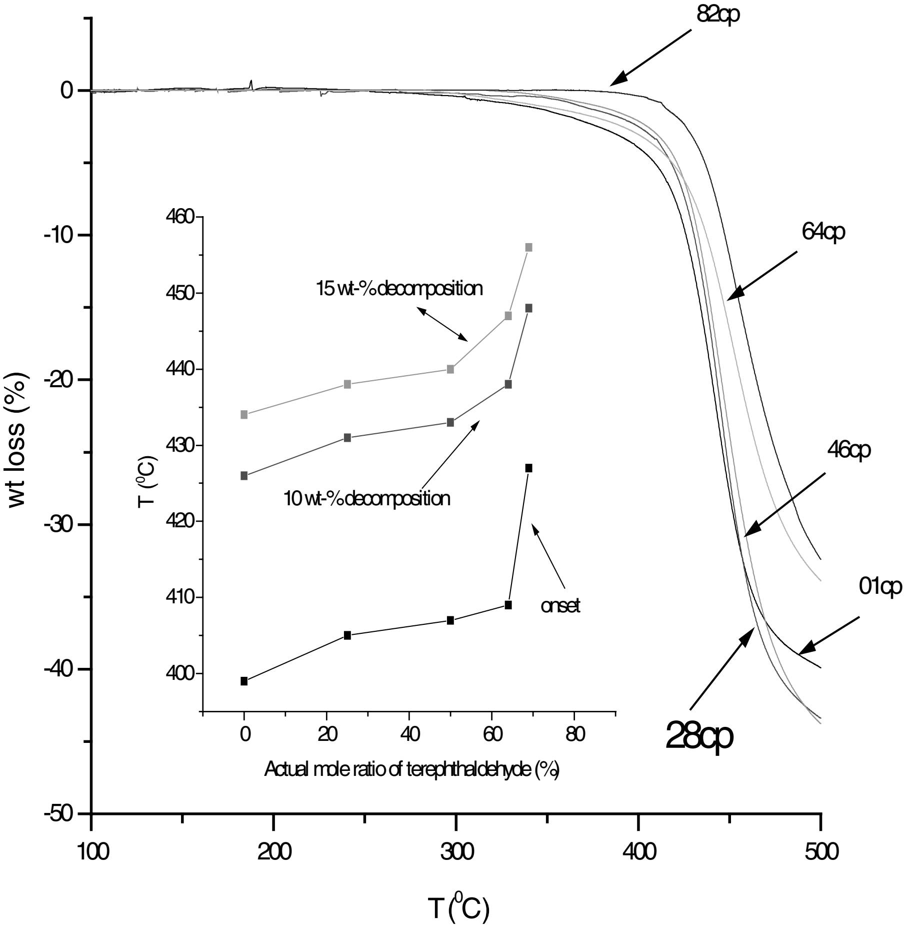

Fig. 3. TGA curves for **01cp**, **28cp**, **46cp**, **64cp** and **82cp**. Inset: decomposition temperature against mole percent of terephthaldehyde at different degrees of decomposition.

Table 3
T_g of various terpolymers

Polymer	T_g (°C)
28cp	80
46cp	116
64cp	165
82cp	–

chloroform. However, the solubility decreased from **28cp** to **82cp**. This is attributed to the increase in the rigidity of the conjugated block due to increasing terephthaldehyde content and hence the polymer is less soluble in the solvent.

The FTIR spectrum (Fig. 1) of the film of **28cp** shows a strong peak at 1514 cm^{-1} and a weak one at 1595 cm^{-1}, attributable to the –C=C bond stretching. The stretching peaks for **28cp** at this region are similar to those that belong to the fully conjugated PPV derivatives, such as MEH–PPV [14]. A weak peak that appears at 1680 cm^{-1} indicates the presence of a residual terminal aldehyde group in the polymer. It can be seen that **28cp** consists of *cis–trans* isomers, as two weak peaks are observed at 664 cm^{-1} (*cis*) and 964 cm^{-1} (*trans*).

The FTIR spectra of the three terpolymers are shown in Fig. 2. Generally the spectral pattern does not show much difference compared to that of **28cp**, except for the phenyl C=C stretch at 1514 cm^{-1}. For **28cp**, only one peak is observed at 1514 cm^{-1}, whereas two strong peaks at 1497 and 1514 cm^{-1} are observed for the other three terpolymers. This could be due to a much more complicated distribution of conjugated blocks with different conjugation lengths.

3.2. Terpolymer composition

The actual composition in mole percent of the dialdehyde co-monomers in these terpolymers was determined quantitatively using ^{1}H NMR. The results are summarized in Table 2.

3.3. Thermal gravimetric analysis

The thermal gravimetric analysis (TGA) curves in Fig. 3 show that the polymers are thermally stable up to 350°C under nitrogen atmosphere. It is noticed that the onset temperatures of the thermal decomposition for the different compositions of terephthaldehyde content (in mole percent) increases with terepthaldehyde content. This phenomenon is also evident for the 10 and 15 wt% decomposition temperatures. The results indicate an increase in thermal stability of the polymers with increasing mole ratio of the =CH–Ar–CH= unit. This is reasonable since **2** has a flexible linkage (–$OC_6H_{12}O$–), which is more prone to thermal decomposition. Hence, as the content of **1** in the polymer system increases, more and larger rigid blocks can be formed, which render the polymer thermally more stable.

Table 4
The absorption and emission maxima of the various polymers

Polymer	λ_{max} abs (nm)		λ_{em} PL (nm)	
	Solution	Film	Solution	Film
01cp	390	400	456, 480	508, 540
28cp	394	418	456, 480	532, 555 (shoulder)
46cp	404	389	512	534, 558 (shoulder)
64cp	428	427	516	532
82cp	418	404	517	534

3.4. DSC analyses of the terpolymers

Differential scanning calorimetric (DSC) experiments were run for all the terpolymers in the temperature range of 5–250°C. The T_g results are listed in Table 3. For **01cp**, we had earlier reported that $T_g = \sim 73$°C [13]. By comparing this result with those presented in Table 3, it can be noticed that the T_g increases with increase in monomer **1** content. This is because increasing the content of =CH–Ar–CH= rises the rigidity of the terpolymers and hence increases the T_g.

3.5. Absorption and PL spectra

The UV–vis absorption and PL spectra for both the film and solution were obtained. The absorption spectra for all the samples were broad and featureless. The λ_{max} and λ_{em} values are shown in Table 4.

In solution, the PL spectra of **01cp** and **28cp** consist of two peaks while those of **46cp**, **64cp** and **82cp** are broad and featureless (Fig. 4). In going from **01cp** to **82cp**, the fluorescence spectra show a significant red shift from **28cp** to **46cp**. However, λ_{em} increases very slightly from **46cp** to **82cp**. The bathochromatic shift can be accounted by the longer conjugation length in the chromophoric blocks that have been formed in the polymer. It is clear that with the lengthening of conjugation length in the chromophoric segments, the terpolymers **46cp**, **64cp** and **82cp** are now emitting in a new wavelength region different from that of **01cp** and **28cp**. The very gradual further red-shifts in λ_{em} from **46cp** to **82cp** solutions suggest that the number of conjugated double bonds are slowly achieving the maximum effective conjugation length, beyond which an increase in the mole ratio of the terephthaldehyde unit, i.e. possible increase in the conjugated double bond number, has no further effect.

The PL spectra of all the terpolymer films (Fig. 5) were red-shifted compared to their solution counterparts. This bathochromatic shift is consistent with the argument that there is an extension of effective conjugation length in the solid state [13,15]. A possible explanation to this phenomenon is that in their condensed form, the molecules are packed very closely together. The close proximity of these polymeric molecules has made interchain (or inter-chromophoric segment in the polymer chain) interactions possible [16], resulting in the lowering of transition energy.

A comparison in the emission region is also made

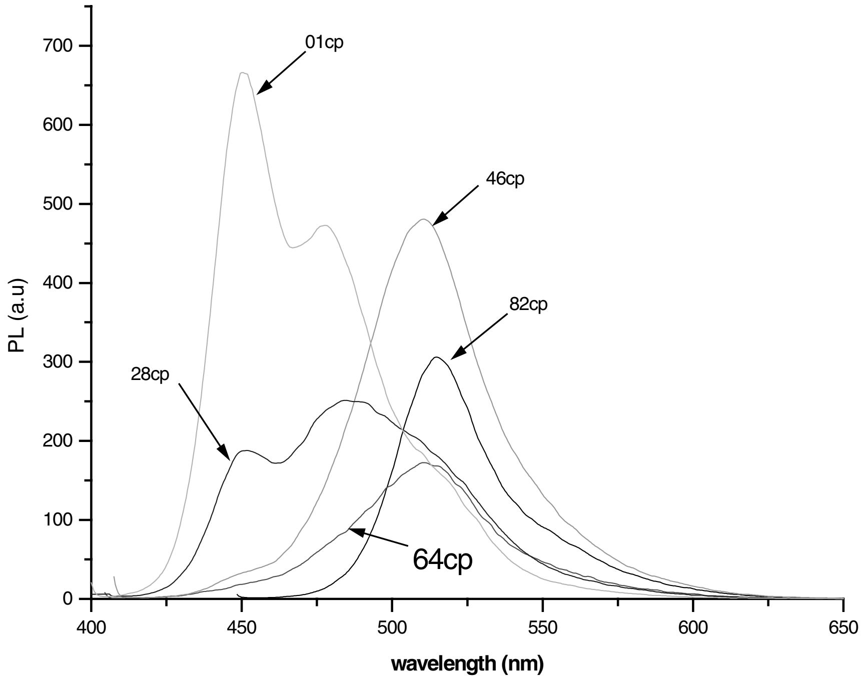

Fig. 4. PL spectra of the polymer solutions in chloroform at the concentration of 0.6 mg/l.

between the terpolymer films and the poly(2,5-dimethoxy-1,4-phenylenevinylene) (PDMoPV) films prepared via CPR and Wessling methods [17]. It is noticed that these terpolymer films have almost the same $\lambda_{em} \sim 530$ nm as that of PDMoPV film prepared via the Wessling method. This is higher than that of PDMoPV film prepared via the CPR method (with $\lambda_{em} \sim 500$ nm). In view of the fact that all the terpolymers have less number of alkoxy groups (both methoxy and hexyloxy) attached to the phenylene rings (which increase the electron density of the system) than the conjugated PDMoPV, it suggests that the effective conjugation length of the terpolymer films appears be no shorter than that of the PDMoPV film prepared via the Wessling method.

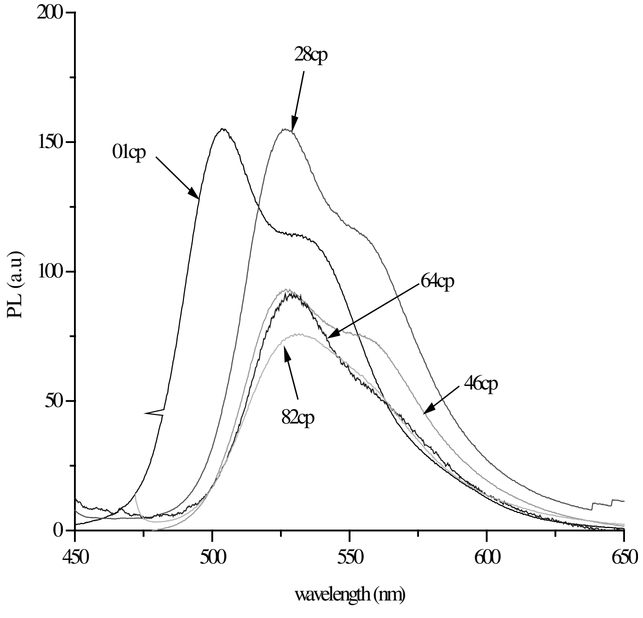

Fig. 5. PL spectra of the polymer film.

3.6. Photobleaching effect of polymers

It has already been discussed [13] that **01cp** film was prone to photobleaching even when it was under exposure to constant low-intensity irradiation. Observations also suggest that no bond scission occurs under such condition, but instead the formation of C=O and subsequently $-COO^-$ as a result of the photooxidation process may be the possible reason for the lowering in fluorescence intensity.

In order to observe the effect of low-intensity irradiation on the terpolymer films, a series of values of PL intensity against time were measured (Fig. 6). This experiment was carried out under normal atmospheric condition. The polymer film was irradiated with a low-intensity monochromatic light source in the fluorometer. The irradiation wavelength (λ_{irr}), corresponding to the peak of the excitation spectrum, was chosen such that the polymer film produced λ_{em} with the highest intensity. The PL intensity was monitored at λ_{em} over the course of the experiment. The time taken for the PL intensity to decrease by half ($t_{1/2}$) was determined. The results are presented in Table 5.

It is noticed that **01cp** is most prone to photobleaching among all these polymers. The results suggest that the incorporation of more HC–Ar–CH into the polymers increases the resistance to photodegradation. Another experiment was also carried out on the **01cp** film with $\lambda_{irr} = 420$ nm and $\lambda_{em} = 504$ nm. The $t_{1/2}$ was found to be 25 min. This

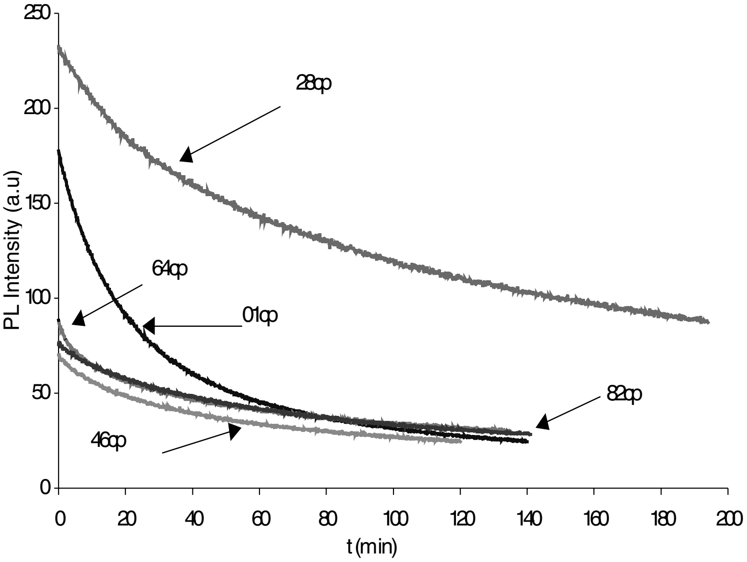

Fig. 6. PL intensity against time of the polymer films at the respective λ_{irr} and λ_{em}.

indicates that slightly different irradiation wavelengths have only a small effect on $t_{1/2}$.

3.7. Electroluminescence (EL) properties of LEDs

The current–voltage (*I*–*V*) characteristics of the devices with the configuration of ITO/**terpolymer**/Al are shown in Fig. 7. The forward bias currents were obtained when the ITO electrodes were positively biased and the Al electrodes were negatively biased. The currents increased with increasing forward bias voltage, which indicated typical diode behaviour. The devices showed relatively low turn-on voltage ranging from 4.2 to 7.0 V. The green EL could be easily observed by naked eyes for all the single-layer devices fabricated. The diode behaviour of the devices suggests that electrons and holes are injected from the Al and the ITO electrodes, respectively. Injected holes and electrons subsequently form positive and negative polarons in the bulk of the polymer. There, recombination can produce singlet molecular excitations localized at the chromophoric units of the copolymer. The radiative decay of singlet excitation is, in turn, responsible for the EL [1].

Table 5
The $t_{1/2}$ values for the polymer films measured under their respective λ_{irr} and λ_{em}

Polymer	λ_{irr} (nm)	λ_{em} (nm)	$t_{1/2}$ (min)
01cp	397	504	21.2
	420	504	25.0
28cp	420	526	106.4
46cp	425	528	54.6
64cp	433	535.6	48.9
82cp	463	533	76.1

4. Conclusions

A series of terpolymers with a rigid conjugated block interspaced with an inert hexane-1,6-dioxy spacer has been synthesized. The actual mole percent of the co-monomers were determined quantitatively by NMR spectroscopy. Thermal gravimetric analyses showed that the polymers were thermally stable up to 350°C under nitrogen atmosphere. The T_g values increased with terephthaldehyde content, which could be attributable to the increase in the rigidity of the terpolymers.

The red shifts in the PL spectra of the terpolymers are attributed to the increase in effective conjugation length in the terpolymers as compared to **01cp**. The fact that the terpolymer film showed similar λ_{em} with that of the thermally converted PDMoPV prepared via the Wessling method suggested a good way of preparing the intrinsically

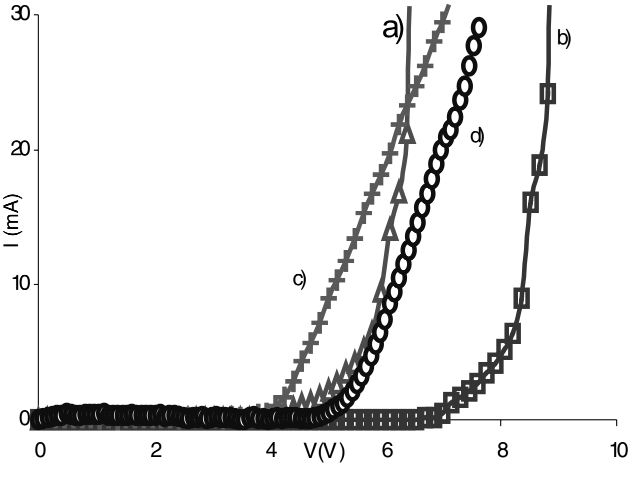

Fig. 7. The current–voltage curves of: (a) **28cp**; (b) **46cp**; (c) **64cp** and (d) **82cp**.

green-light-emitting diode materials. All these terpolymers showed a better resistance to low-intensity monochromatic light irradiation compared to **01cp**. LED devices were also fabricated and the current–voltage characteristics indicated the diode behaviour of these devices.

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