

Synthesis and Studies of Blue Light Emitting Polymers Containing Triphenylamine-Substituted Fluorene and Diphenylanthracene Moiety

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ABSTRACT: Photoluminescent (PL) polymers containing triphenylamine-substituted fluorene and diphenylanthracene (DPA) units were synthesized by aromatic nucleophilic substitution reaction. The light emitting polymers (LEPs) contains hole-transporting triphenylamine (TPA) groups at the C-9 position of fluorene and DPA-emitting segments in the main chain. The obtained polymers were soluble in various organic solvents and thermally stable. The synthesized polymers were successfully characterized

by elemental analyses, FTIR and, ^1H NMR spectroscopy. The electrochemical measurements and optical properties of the polymers were also studied. The obtained polymers showed significant blue emission. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3483–3492, 2011

Key words: photoluminescent; triphenylamine-substituted fluorene; diphenylanthracene units; light emitting polymers

INTRODUCTION

Since the first use of photoluminescent (PL) polymers for light emitting diodes (LEDs) by Friend and coworkers, such polymers have stimulated tremendous research activity in the development of LEDs for display applications.^{1–5} The emission color of these polymer can be easily tailored by modifying the molecular design of an organic material used in the polymer structures. However, one area of ongoing research is the quest for a stable blue-emitting material because efficient, highly bright and stable blue light is necessary for full color PL display application.^{6,7}

Triphenylamine (TPA)-substituted fluorene has been selected for the backbone of many light emitting polymers (LEPs) due to its large band gap, high photoluminescence, quantum efficiency, good thermal stability as well as good solubility. Fluorene containing polymers (polyfluorenes) also have emerged as an attractive alternative to other π conjugated polymers for organic optoelectronics due to their strong blue emission, high charge mobility, and excellent chemical and thermal stability. Almost all polyfluorenes utilize side-chain substituents that improve solution processing as well as confer new

functionality. Thermal cycling of polyfluorenes results in distinct backbone and side-chain conformations that lead to improved optical and electronic properties.⁸ Numerous polyfluorenes with various co monomers have been developed with a view to obtaining stable, highly efficient, red, green, and blue emitters. Many studies of the introduction of charge transporting moieties into π conjugated polymers for efficient PLEDs have been reported.^{5–7} It is known that the hole mobilities of most emissive π conjugated polymers are generally orders of magnitude larger than their electron mobilities.⁹ It was found that the separate attention is being given to the study of diphenylanthracene (DPA) and TPA-substituted fluorene containing polymers. Therefore, it was worthwhile to synthesize the LEPs where these two areas could be combined in novel way. Hence, the LEPs containing alternate TPA-substituted fluorene and DPA segments in the backbone were synthesized. The synthesis and architecture of the polymers are based on the ether linkage in the backbone which gives the thermal stability and adjust the length of conjugation.

In this article, we focus first on the incorporation of electrochemically stable DPA, a blue light emitting segment into the polymer molecule.^{10–12} It is known that DPA has unit PL quantum yield, good electrochemical and chemiluminescence properties.^{13,14} It has also been reported that, the conjugation length of the PL polymer could be effectively tailored by incorporating the non conjugation segment or phenylene unit in the backbone.^{15–20} This

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method not only fixes the effective conjugation length but also maintains the thermal stability.

EXPERIMENTAL

Materials

All reagents and solvents were purchased from S D Fine-Chem, Mumbai and were used without any further purification.

Instrumentation

UV-Visible spectra were recorded by Shimadzu UV-2100 spectrophotometer. Fluorescence spectra were recorded on Shimadzu spectrofluorophotometer RF-5310(PC). FTIR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrophotometer in KBr discs. ^1H NMR spectra were recorded on a Bruker AMX-300 spectrometer in CDCl_3 and chemical shifts were reported in δ (ppm) values relative to the internal standard tetramethyl silane (TMS). Cyclic voltammetry study was carried out with three-electrode cell consisting of Glassy carbon as working electrode, Platinum as an auxiliary and $\text{Ag}/\text{AgCl}/\text{LiCl}_{\text{sat}}$ (EtOH)/ $\text{TMACl}_{\text{sat}}$ (DMSO) in pure DMSO (99% pure, S D Fine-Chem, Mumbai) solvent as reference electrode. Thermolysis of polymers was performed with Perkin-Elmer/Pyris Diamond TG-DTA assembly using $10^\circ\text{C}/\text{min}$ heating rate and N_2 atmosphere. Gel permeation chromatograms (GPC) were measured on a Perkin-Elmer series 200 GPC equipped with an isocratic pump, a solvent degasser, a column oven, a refractive index (RI) detector, and Chromatographic Column PLgel $10\ \mu\text{m}$ Mixed-B, $300 \times 7.5\ \text{mm}$ [tetrahydrofuran (THF) 40°C , flow rate of $1\ \text{mL}\ \text{min}^{-1}$ and polystyrene was used for calibration]. Atomic force microscopic (AFM) observations for the some polymers were carried out using tapping mode operations with Nanoscope III multimode scanning probe microscope from digital instruments (Santa Barnara, CA) using a "D" vertical engage scanner. Silicon micro-cantilever (SI-DF40 manufacturer specifications: spring constant $42\ \text{Nm}^{-1}$, resonance frequency 250–390 KHz obtained from Seiko Instrument (Japan) was used for imaging. The polymers were dissolved in double distilled acetone. The solutions were spin coated (at the rate of 500 rpm) on clean mica surfaces and AFM images were taken under tapping mode conditions. The voltammetric system used for the electrochemical studies was Electrochemical Work Station, model Autolab 30; the electrode assembly being a 663 VA stand with GPES computer software for recording and processing analyses of the voltammograms was supplied by Eco Chemie, The Netherlands. All experiments were performed with the three-electrode

cell consisting of Glassy carbon as working electrode, Platinum as an auxiliary and $\text{Ag}/\text{AgCl}/\text{LiCl}_{\text{sat}}$ (EtOH)/ $\text{TMACl}_{\text{sat}}$ (DMSO) in pure DMSO solvent. Before each measurement a stream of pure nitrogen deaerated the solution. A known volume of supporting electrolyte $0.05\ \text{mol}\ \text{L}^{-1}$ TEAP in DMSO was taken in sample cell. To this solution, a concentrated solution of the polymer (in DMSO) was added to get the desired working concentration in the cell and the cyclic voltammogram was run.

Synthesis

Preparation of 9,10-dihydroxy-9,10-di(*p*-methoxyphenyl)anthracene (a)

A *p*-methoxyphenyl bromide and magnesium was dropped into an ether solution of 9,10-anthraquinone at -5 to 10°C to obtain Grignard reagent (*p*-methoxyphenyl magnesium bromide). Thus, Grignard reaction was carried out with mechanical stirring to prevent a side reaction. Dilute HCl solution was then slowly added to acidify the reaction mixture. The crude product was extracted with diethyl ether and recrystallized with THF and hexane as solvents.

Preparation of 9,10-di(*p*-methoxyphenyl)anthracene (b)

A dehydration of 9,10-dihydroxy-9,10-di(*p*-methoxyphenyl)anthracene was carried out by using potassium iodide and $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in acetic acid for 4 hr. After refluxing, the crude product was filtered and washed with water and diethyl ether.

Preparation of 9,10-di(*p*-hydroxyphenyl)anthracene (c)

For ether cleavage reaction, a 9,10-di (*p*-methoxyphenyl)anthracene was refluxed for 24 hr in excess of HBr and acetic acid. The reaction mixture was cooled to room temperature. The crude product obtained was filtered and washed with water and acetic acid. ^1H NMR [CDCl_3 , 298K, δ (ppm)]: 3.9 (2H, $-\text{OH}$), 7–8 (16H, ArH). Elem. Anal. Found: C, 85.90; H, 4.79; O, 9.31. Elem. Anal. Cal. C, 85.96; H, 4.87; O, 9.17. (Scheme 1)

Preparation of 9,9-bis(triphenylamine)-2,7-dibromofluorene (d)

To a mixture of dibromofluorenone and TPA a methanesulfonic acid was added. The reaction mixture was then heated at 140°C under nitrogen atmosphere for 12 hr. The cooled mixture was diluted with dichloromethane and washed with aqueous sodium carbonate. The organic phase was dried over MgSO_4 and the solvent was evaporated. The crude product obtained was recrystallized with acetone. ^1H NMR [CDCl_3 , 298K, δ (ppm)]: 7–8 (34H, ArH).

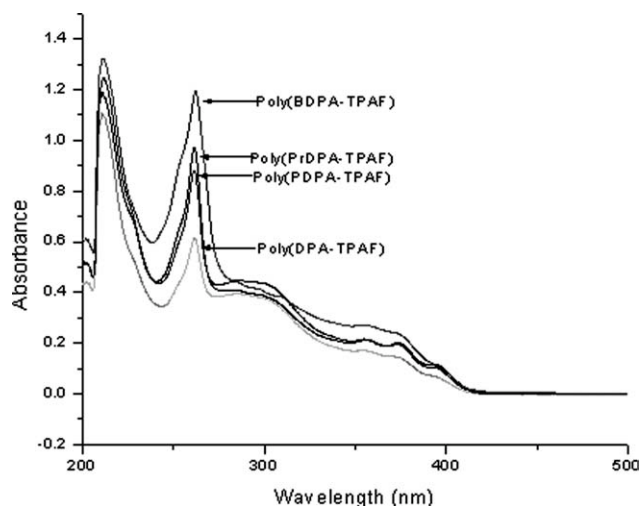


Figure 1 UV spectra of polymers in THF solution.

Elem. Anal. Found: C, 72.61; H, 4.16; N, 3.32. Elem. Anal. Cal. C, 72.70; H, 4.20; N, 3.46 (Scheme 2).

Preparation of 9,10-di(*p*-hydroxyphenyl)anthracene derivatives

The derivatives of anthraquinone were prepared by using various alkyl halides such as 1-bromopropane, 1-bromopentane, 1-bromobenzene and were used for the preparation of series of 9,10-di(*p*-hydroxyphenyl)anthracene derivatives by the method discussed earlier.

2-propyl-9,10-di(p-hydroxyphenyl)anthracene (PrDPA). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 0.9 (3H, $-\text{CH}_3$), 1.5 (2H, $-\text{CH}_2$), 1.9 (2H, $-\text{CH}_2$), 3.9 (2H, $-\text{OH}$), 7–8 (15H, ArH). Elem. Anal. Found: C, 86.01; H, 6.24; O, 7.93. Elem. Anal. Cal. C, 85.92; H, 6.17; O, 7.90.

2-pentyl-9,10-di(p-hydroxyphenyl)anthracene (PDPA). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 0.9 (3H, $-\text{CH}_3$), 1.4 (4H, $-\text{CH}_2$), 2.2 (2H, $-\text{CH}_2$), 3.4 (2H, $-\text{CH}_2$), 3.9 (2H, $-\text{OH}$), 7–8 (15H, ArH). Elem. Anal. Found: C, 85.92; H, 6.73; O, 7.25. Elem. Anal. Cal. C, 85.91; H, 6.69; O, 7.39.

2-benzyl-9,10-di(p-hydroxyphenyl)anthracene (BDPA). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 3.9 (2H, $-\text{OH}$), 7–8 (20H, ArH). Elem. Anal. Found: C, 86.54; H, 5.31; O, 7.34. Elem. Anal. Cal. C, 87.47; H, 5.23; O, 7.28.

Polymerization

A mixture of 9,9-bis(triphenylamine)-2,7-dibromofluorene, corresponding 9,10-di(*p*-hydroxyphenyl)anthracene derivative and K_2CO_3 in cosolvent (1 : 2 toluene/dioxane) were refluxed for 12 hr. After polymerization was completed, excess 9,9-bis(triphenylamine)-2,7-dibromofluorene was added for end capping of hydroxyl groups. After end capping reac-

tion, the reaction temperature was reduced to room temperature, and water was added. The polymer was precipitated in methanol after toluene solvent was evaporated and extracted with methylene dichloride. The polymer (**e**) obtained was filtered and dried in an oven (Scheme 3).

Poly[9,10-diphenylanthracene-co-9,9-bis(triphenylamine)fluorene]

Poly(DPA-TPAF). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 7–8 (50H, ArH). Elem. Anal. Found: C, 88.88; H, 5.12; N, 2.64; O, 3.36. Elem. Anal. Cal. C, 89.11; H, 4.91; N, 2.81; O, 3.17.

Poly[2-propyl-9,10-diphenylanthracene-co-9,9-bis(triphenylamine)fluorene] Poly(PrDPA-TPAF). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 0.9 (3H, $-\text{CH}_3$), 1.5 (2H, $-\text{CH}_2$), 2.0 (2H, $-\text{CH}_2$), 7–8 (49H, ArH). Elem. Anal. Found: C, 87.98; H, 5.87; N, 2.89; O, 3.26. Elem. Anal. Cal. C, 88.89; H, 5.41; N, 2.66; O, 3.04.

Poly[2-pentyl-9,10-diphenylanthracene-co-9,9-bis(triphenylamine)fluorene] Poly(PDPA-TPAF). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 0.9(3H, $-\text{CH}_3$), 1.3 (4H, $-\text{CH}_2$), 2.2 (2H, $-\text{CH}_2$), 3.5 (2H, $-\text{CH}_2$), 7–8 (49H, ArH). Elem. Anal. Found: C, 88.68; H, 5.11; N, 2.75; O, 2.46. Elem. Anal. Cal. C, 88.81; H, 5.64; N, 2.59; O, 2.96.

Poly[2-benzyl-9,10-diphenylanthracene-co-9,9-bis(triphenylamine)fluorene] Poly(BDPA-TPAF). ^1H NMR [CDCl_3 , 298K, $\delta(\text{ppm})$]: 7–8 (54H, ArH). Elem. Anal. Found: C, 89.71; H, 4.88; N, 2.31; O, 3.10. Elem. Anal. Cal. C, 89.42; H, 5.06; N, 2.58; O, 2.95.

RESULTS AND DISCUSSION

Optical properties

The absorption and PL spectra of the polymers in dilute solutions are shown in Figures 1 and 2, respectively. The UV absorption spectra of the obtained polymers had similar maxima in between

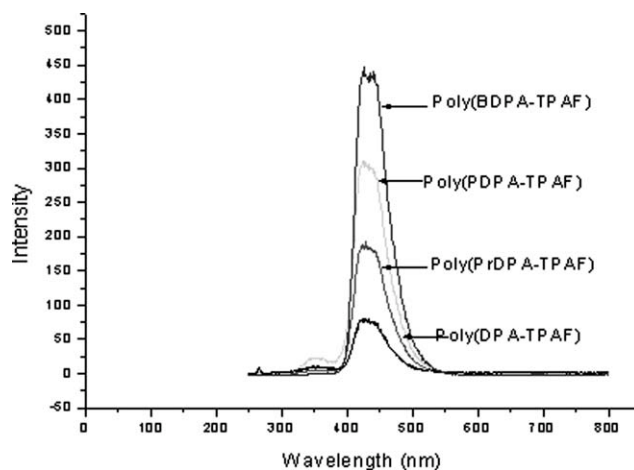


Figure 2 Emission (PL) Spectra of polymers.

TABLE I
Optical Properties of Polymers

Polymer	UV-visible λ_{\max} (nm)	PL λ_{\max} (nm)	Intensity	E_g (Band gap) eV	Quantum yield (Φ_{PL})
Poly(DPA-TPAF)	373.20	429	191.6	2.91	0.72
	261.60				
	211.20				
	203.00				
Poly(PrDPA-TPAF)	368.00	426	236.4	2.89	0.74
	262.40				
	211.00				
	203.20				
Poly(PDPA-TPAF)	373.20	424	321.5	2.92	0.77
	261.80				
	212.20				
	203.00				
Poly(BDPA-TPAF)	373.80	425	446.8	2.91	0.79
	261.00				
	212.20				
	203.60				

Solvent: THF.

261 and 262 nm which is characteristic absorption of DPA.^{21–26} The solutions also exhibited an absorption with the λ_{\max} in 368–373 nm due to $\pi \rightarrow \pi^*$ transition derived from the fluorene moiety in polymer backbone. An additional absorption bands around 211–212 nm and 203 nm were originated from absorption due to TPA pendent group. It was worth noting that no absorption bands were observed in the longer wavelength region (400–600 nm) which would corresponds to the charge transfer transition from the electron rich triphenylamine group. The characteristic band of fluorene moiety of polyfluorenes is

reported in the range of 370–388 nm.²² The four transitions observed for synthesized polymers were compared separately with DPA containing polymer as well as TPA-substituted polyfluorenes reported in the literature^{22,24} and assigned for $\pi \rightarrow \pi^*$ transitions (Table I, Fig. 1).

To study PL property, polymer solutions were added to quartz cuvettes and degassed for ~ 15 min. The PL study was carried out in various solvents such as tetrahydrofuran, dichloromethane, acetonitrile, acetone, and chloroform every time the maximum intensity peak was observed in the wavelength range

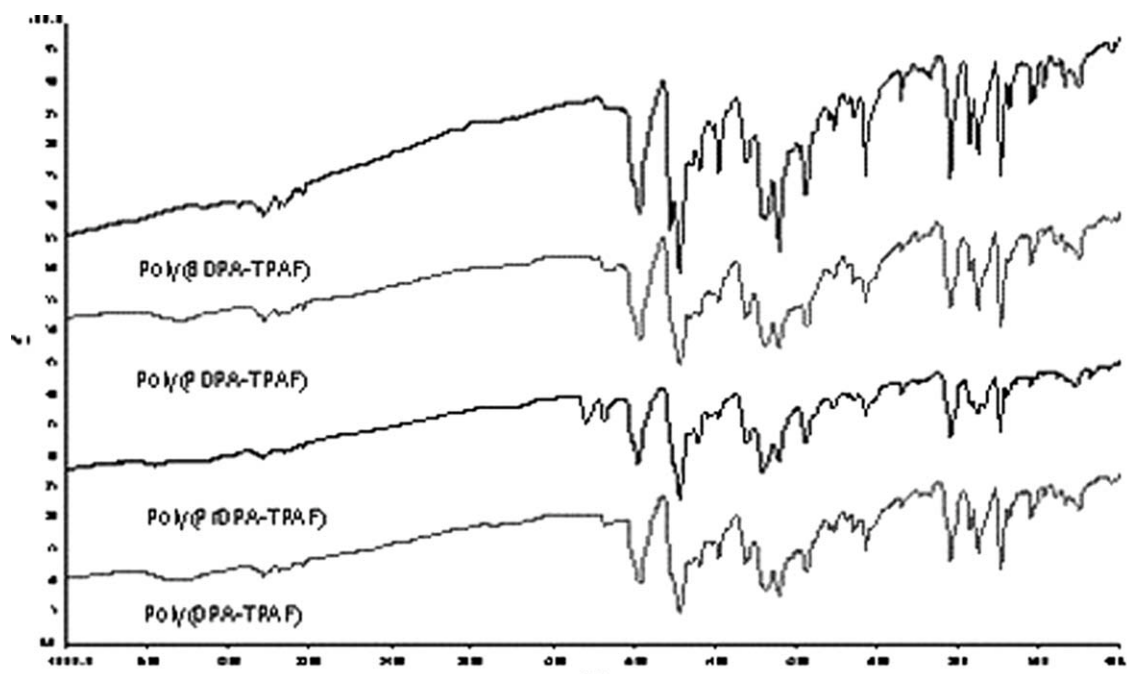


Figure 3 FTIR spectra of polymers.

TABLE II
FTIR Signals (cm^{-1}) for Polymers

Polymer	C—O—C (ether linkage)	C=C of aromatic rings	C—N of t-amine (Stretching)
Poly(DPA-TPAF)	1029.40 (s)	1586.99 (s)	1324.73 (s)
Poly(PrDPA-TPAF)	1029.40 (s)	1592.13 (s)	1321.90 (s)
Poly(PDPA-TPAF)	1029.39 (s)	1586.90 (s)	1324.77 (s)
Poly(BDPA-TPAF)	1029.84 (s)	1587.17 (s)	1325.11 (s)

s-sharp.

424–429 nm indicative of blue light emission. Literature survey also reveals that the region ~ 400 – 500 nm is reported for the blue light emission of the polymers.²⁵ On UV excitation, solution of the polymers exhibited very intense fluorescence with a maximum at 424–429 nm (Table I). The fact that the emission band was much narrower than the absorption bands and showed well-resolved vibronic bands was consistent with the emission from localized excited state. Most likely after a migration of the excitons along the main chain to segments that represented low energy state. The PL quantum yield of the polymers in THF solutions was measured to be $0.72 \pm 10\%$ upon excitation at 263 nm. The higher quantum efficiency may have resulted from intramolecular energy transfer from TPA-substituted fluorene unit which might act as electron transporting material during radioactive process.²³ The direct (optical) band gap obtained from PL data was in the range of 2.89–2.92 eV confirmed blue light emission. It was observed that an emission intensity increases with the size of substituent (R) attached on DPA moiety. Poly (BDPA-TPAF) has the highest intensity than Poly (DPA-TPAF). The PL spectra recorded in THF are shown in Figure 2.

FTIR spectral study

The first significant feature of the infrared spectra of polymers (Fig. 3) was the absence of absorption peaks in the region 3391 – 3441 cm^{-1} indicated that polymerization was completed and the terminal hydroxy group of alkyl substituted DPA monomers was terminated. Another significant feature of the spectra was absence of band at 694.56 cm^{-1} indicating the removal of Br atoms of TPA-substituted fluorene monomer during the polymerization. This

suggested that, HBr molecule was removed during the polymerization.

The strong absorption peak in the range 1029.39 – 1029.84 cm^{-1} was observed in the spectra due to C—O—C stretching vibrations of ether linkage on the main polymer backbone. This observation confirmed the formation of polymers via removal of HBr molecule.²⁶ The sharp band in the range 1586.90 – 1592.13 cm^{-1} was observed in the infrared spectra due the frequency of C=C vibration of conjugated aromatic rings. The data of the infrared studies is summarized in the Table II.

Cyclic voltammetry

All measurements were calibrated using ferrocene (Fc) value of -4.8 eV as the standard.^{27–29} In the anodic scan, the onsets of oxidation of polymers was occurred in the range 0.95 – 0.98 V, which correspond to the ionization potential (I_p) range of -5.65 to -5.68 eV, according to the empirical relationship proposed by Leeuw et al. ($I_p(\text{HOMO}) = -(E_{\text{onset,ox}} + 4.7)$ (eV), $E_a(\text{LUMO}) = -(E_{\text{onset,red}} + 4.7)$ (eV), where $E_{\text{onset,ox}}$ and $E_{\text{onset,red}}$ are the onset potentials of oxidation and reduction, respectively.³⁰ Similarly, the electron affinity (E_a) values of the polymers were obtained in the range -2.66 to -2.71 eV. From the onset potentials of the oxidation and reduction processes, electrochemical band gaps can be estimated by the equation, $E_g = E_{\text{onset,ox}} - E_{\text{onset,red}}$,^{31,32} the band gaps were obtained in the range of 2.97 – 3.03 eV, indicative of blue light emission. The electrochemical band gaps were slightly higher than the optically determined ones (Table I) this may be due to interface barrier for charge injection.^{33,34} In general, the band gaps increases with the size of substituent (R) attached on DPA moiety. This

TABLE III
Electrochemical Properties of the Polymers

Polymer	$E_{\text{onset oxidation}}$ (V)	$E_{\text{onset reduction}}$ (V)	E_{pc}	E_{pa}	$E_{1/2} = (E_{\text{pa}} + E_{\text{pc}})/2$	HOMO (I_p) (eV)	LUMO (E_a) (eV)	E_g (eV)
Poly(DPA-TPAF)	0.98	-1.99	-1.20	-0.56	-0.88	-5.68	-2.71	2.97
Poly(PrDPA-TPAF)	0.97	-2.05	-1.27	-0.35	-0.81	-5.67	-2.66	3.01
Poly(PDPA-TPAF)	0.99	-2.04	-1.04	-0.51	-0.77	-5.69	-2.66	3.03
Poly(BDPA-TPAF)	0.95	-2.04	-1.00	-0.55	-0.77	-5.65	-2.66	2.99

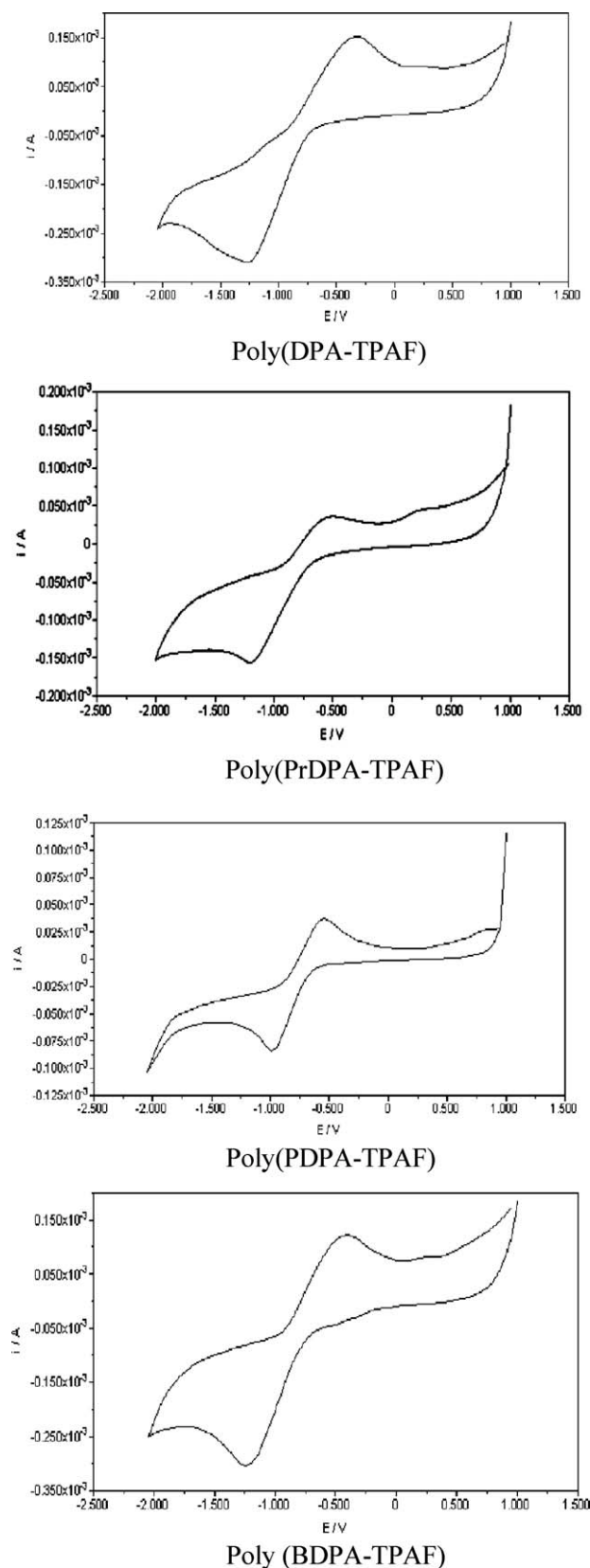


Figure 4 Cyclic voltammograms.

observation was also supported by optical band gaps obtained from photoluminescence studies discussed earlier.

The literature study reveals that the oxidation of TPA-substituted polyfluorene backbone was occurred with a peak potential around 1.10 V, which was not observed in this study.²³ This observation suggested non involvement of TPA-substituted polyfluorene backbone with the present electrode system. Therefore the fact implies that polymers may have electron-injection properties typical of DPA monomer.¹⁴ Similar cyclic voltammogram for electrochemical process of DPA was also reported in the literature.³⁵

The electrochemical data of the polymers is summarized in Table III and the voltammogram are shown in Figure 4.

Gel permeation chromatography

GPC provides the way to determine average molar mass (M_n) of the copolymers and attests an efficient formation of a link between the two constituting blocks. The data obtained from this technique, gives molar masses of polymers. The molecular weights M_n , M_w and M_z obtained for the polymers are summarized in Table IV. The number average molecular weight (M_n) was considered for the further study. The data showed that, the polymers were having varying molar masses. No uniform trend was observed in the obtained masses. The degree of polymerization (DP) was also calculated from the molar masses obtained. From weight average molecular weight (M_w) and number average molecular weight (M_n) the polydispersity index was calculated. The value obtained was less than 2 indicating uniform and one length of polymer was present.³⁶

Thermal study

The TG studies showed that the polymers were thermally more stable to varying degree. The thermograms showed the gradual loss in weight due to decomposition by fragmentation with increasing temperature. All the polymers did not showed significant weight loss below 100°C indicating absence of moisture content (free moisture or bound moisture) in the polymer chain. The polymers in general undergo three step decomposition processes. The

TABLE IV
GPC Data for Polymers

Polymer	M_n	M_w	M_z	M_w/M_n	DP
Poly(DPA-TPAF)	4225	6275	9882	1.485	4
Poly(PrDPA-TPAF)	8061	12,862	20,303	1.596	8
Poly(PDPA-TPAF)	3534	5365	7925	1.518	5
Poly(BDPA-TPAF)	4264	6808	12,015	1.597	4

Number average molecular weight (M_n), Weight average molecular weight (M_w), molecular weight (M_w), Z-average Molecular Weight (M_z), degree of polymerization (DP).

TABLE V
Thermal Analyses Data for Polymers

Polymer/M.F.	Dissociation step	DTA peak temp. (°C)	Temp. range in TG (°C)	Obs. wt loss %	Calc. wt. loss %	Moiety lost	Residue
Poly(DPA-TPAF)/C ₃₀₀ H ₂₀₀ N ₈ O ₈	I	110	40–150	3.295	4.158	C ₁₂ H ₁₀ N	C ₂₆ H ₁₆ O ₂
	II	220	150–430	36.730	36.237	C ₁₀₈ H ₈₄ N ₆	
	III	740	430–990	46.914	47.722	C ₁₅₄ H ₉₀ NO ₆	
Poly(PrDPA-TPAF)/C ₆₂₄ H ₄₅₆ N ₁₆ O ₁₆	I	80	30–160	2.608	2.661	C ₁₅ H ₃₅	C ₂₀ H ₁₂ O
	II	270	160–370	25.701	25.853	C ₁₅₃ H ₁₃₃ N ₈	
	III	390	370–1090	71.020	71.035	C ₄₃₆ H ₂₈₄ N ₈ O ₁₅	
Poly(PDPA-TPAF)/C ₂₄₀ H ₁₈₃ N ₆ O ₆	I	80	30–140	2.762	2.189	C ₅ H ₁₁	–
	II	230	140–530	47.850	47.178	C ₁₁₇ H ₁₁₉ N ₆	
	III	630	530–1090	49.388	50.632	C ₁₂₃ H ₇₀ O ₆	
Poly(BDPA-TPAF)/C ₃₂₄ H ₂₂₀ N ₈ O ₈	I	110	30–270	11.816	10.947	C ₃₆ H ₃₀ N	C ₅₈ H ₃₆ O ₅
	II	380	270–510	39.712	39.282	C ₁₁₄ H ₈₈ N ₆	
	III	580	510–1150	27.069	27.368	C ₉₈ H ₅₂ O ₃	

first step of decomposition was observed in the range 30–270°C which was accompanied by a weight loss of 2.60–11.81%. This may be attributed to the loss of substituent moiety (R) on the DPA. For poly(DPA-TPAF), this loss may be attributed to some part of TPA moiety. The second step was observed in the range 150–540°C which was accompanied by a weight loss of range 25.70–47.17%. This may corresponds to the loss of TPA moiety in the polymer chain.

The third step of decomposition process occurred in the range 370–1150°C which was accompanied by weight loss of 27.06–71.02%. This may corresponds to the loss of some part of DPA moiety. In

general, 100% weight loss was not observed except poly(PDPA-TPAF) and the residue left in the crucible may contain anthracene moiety of main polymer chain. The poly(PDPA-TPAF) showed complete decomposition indicating lower thermal stability as compared with other polymers. The values of TG temperature range, weight loss observed and calculated are summarized in the Table V, whereas Figure 5 shows thermograms of the polymers. The thermogram of poly(PrDPA-TPAF) is taken as an examples for decomposition study of the polymers. The proposed thermal decomposition mechanism for Poly(PrDPA-TPAF) is illustrated in Figure 6.

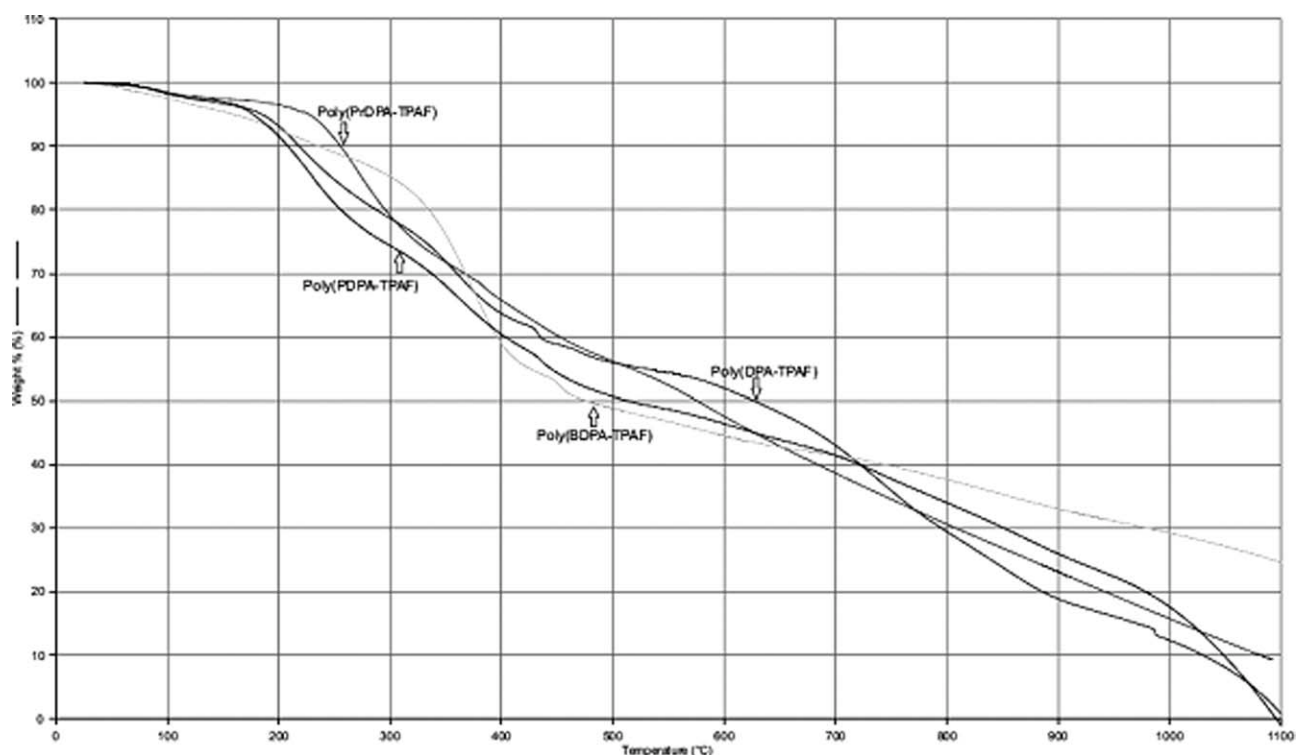


Figure 5 Thermograms of polymers.

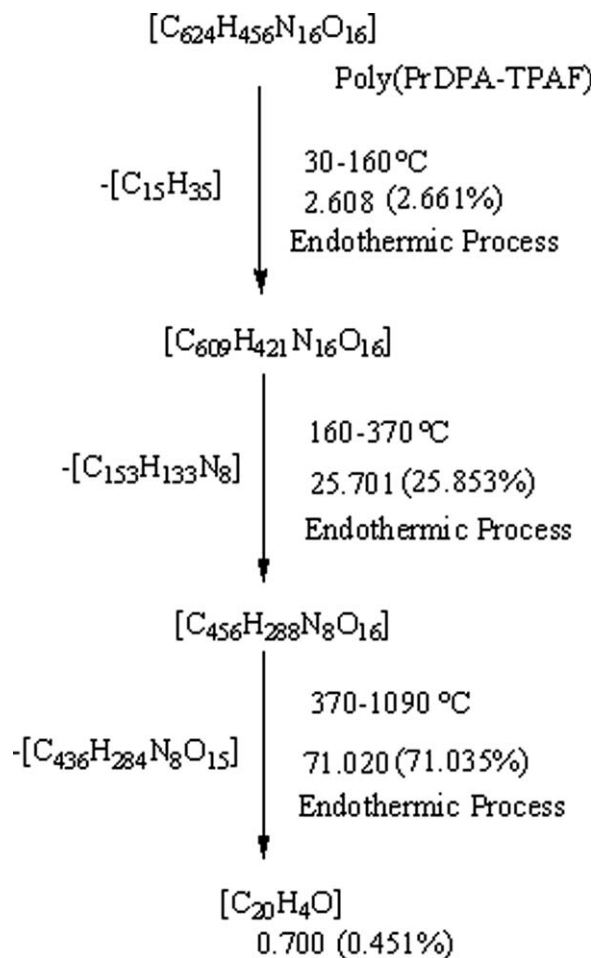


Figure 6 Proposed thermal decomposition pattern of Poly(PrDPA-TPAF).

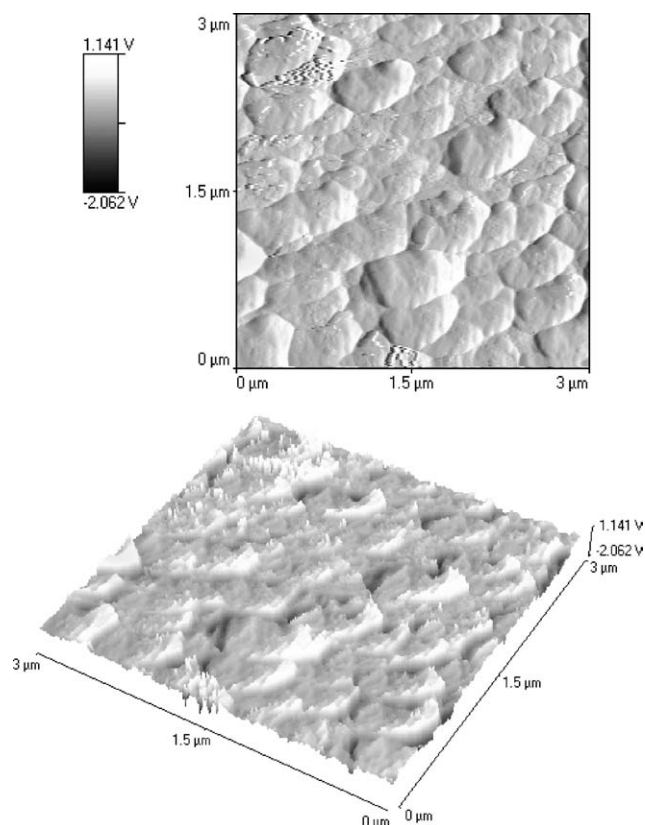
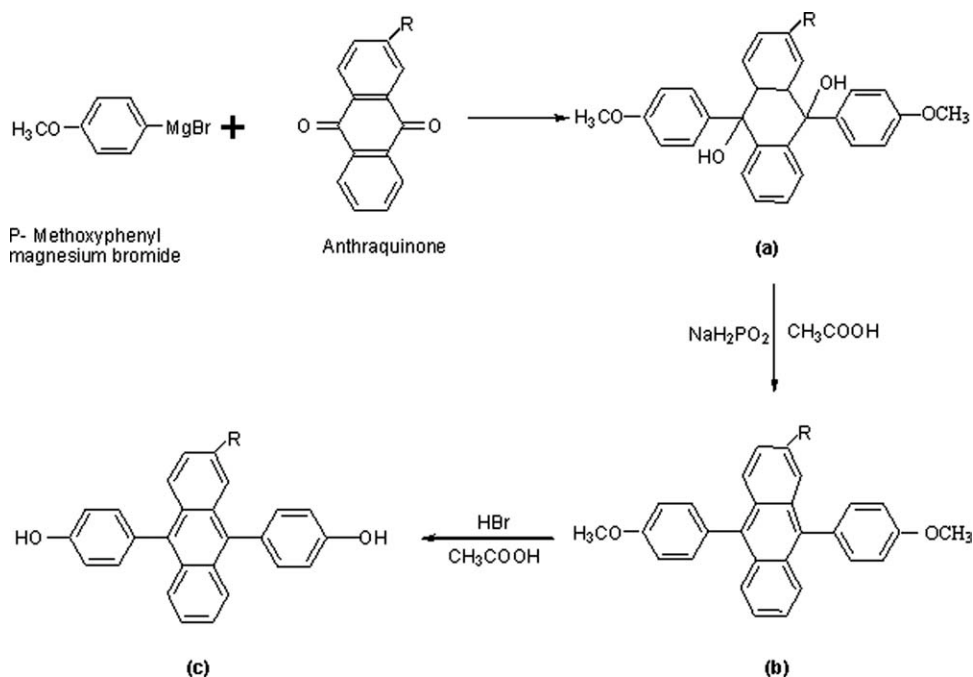


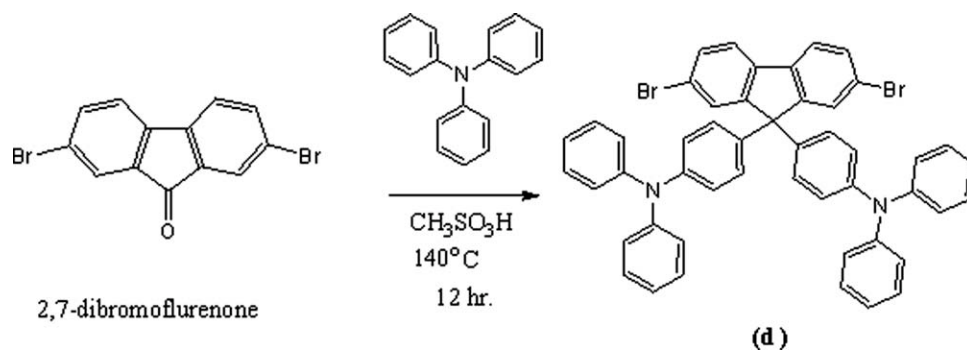
Figure 7 Representative AFM image of Poly(DPA-TPAF).

Atomic force microscopy

The atomic force micrographs revealed smooth and uniform morphology. The Figure 7 showed the micrograph of poly(DPA-TPAF) and corresponding



Scheme 1 General synthesis of 9,10-di(*p*-hydroxyphenyl)anthracene monomer.



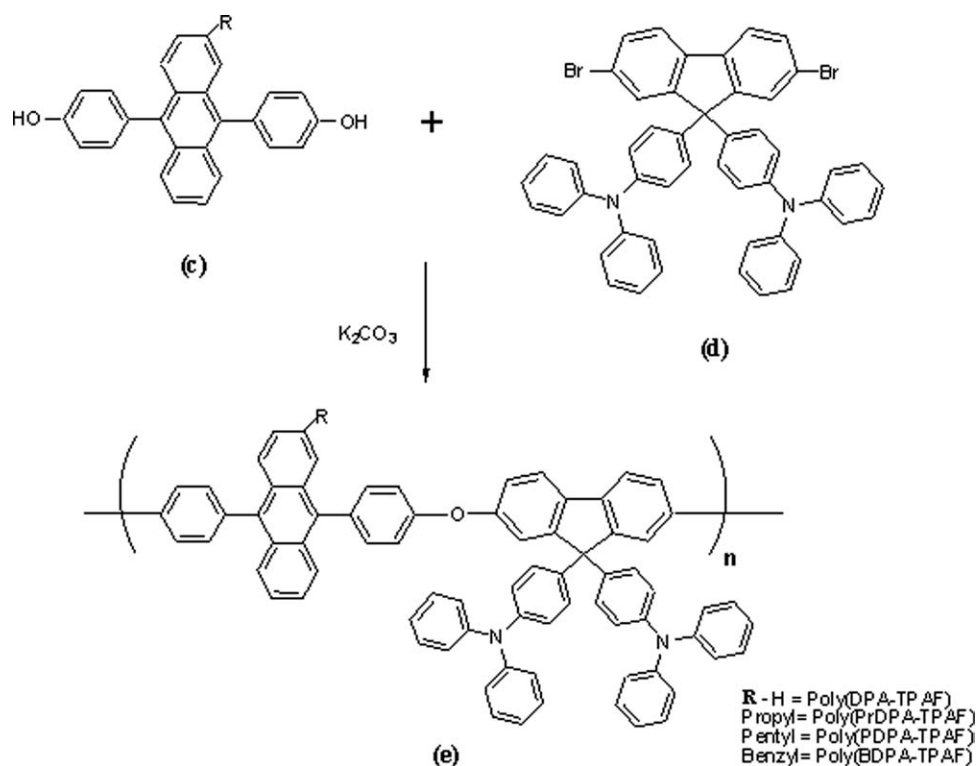
Scheme 2 Synthesis of 9,9-bis(4-triphenylamine)-2,7-dibromofluorene monomer.

three dimensional image. The films of the polymers display a rather homogenous substrate coating without surface defects such as pinholes and crystal formation. The microscopic or macroscopic phase separation was not observed in the images. The images obtained were compared with the other TPA-substituted polyfluorenes investigated earlier.²⁴ The literature survey shows that, similar smooth surface morphology was observed for some blue LEPS.²⁴

CONCLUSIONS

We synthesized conjugated fluorene-based copolymers bearing TPA and DPA units in the polymer backbone. By the incorporation of a TPA moiety

into the polymer system, the resulting copolymers obtained showed good thermal stability and emission property. The high quantum efficiency of these polymers may have resulted from intra molecular energy transfer from a TPA-substituted fluorene unit which might acts as electron transporting materials during radiative process. The electrochemical band gaps for these polymers were slightly higher than the optically determined ones this may be due to interface barrier for charge injection. In general, band gaps increases with the size of substituent attached on DPA moiety. The atomic force micrographs showed uniform surface morphology and microscopic or macroscopic phase separation was not observed in the images.



Scheme 3 General synthesis of polymer.

References

1. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* 1990, 347, 539.
2. Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew Chem Int Ed* 1998, 37, 402.
3. Shim, H. K.; Jin, J. I. *Adv Polym Sci* 2002, 158, 192.
4. Ko, S. W.; Jung, B. J.; Ahn, T.; Shim, H. K. *Macromolecules* 2002, 35, 6217.
5. Hwang, D. H.; Shim, H. K.; Lee, J. I.; Lee, K. S. *Chem Commun* 1994, 2468.
6. Kido, J.; Hongawa, K.; Nagai, K. *Macromol Symp* 1994, 84, 81.
7. Ahn, T.; Shim, H. K. *Macromol Chem Phys* 2001, 202, 3180.
8. Peng, Q.; Yan, L.; Chen, D.; Wang, F.; Wang, P.; Zou, D. *J Polym Sci Part A: Polym Chem* 2007, 45, 5296.
9. Zhao, Q.; Liu, S. J.; Huang, W. *Macromol Chem Phys* 2009, 210, 1580.
10. Keszthelyi, C. P.; Bard, A. J. *J Electrochem Soc* 1973, 120, 241.
11. Heller, C. A.; Henry, R. A.; McLaughlin, B. A.; Bliss, D. E. *J Chem Eng Data* 1974, 19, 214.
12. Collinson, M. M.; Wightman, R. M. *Anal Chem* 1993, 65, 2576.
13. Benzman, R.; Faulker, L. R. *J Am Chem Soc* 1972, 94, 6317.
14. Kim, Y. H.; Kwon, S. K.; Yoo, D. S.; Rubner, M. F.; Wrighton, M. S. *Chem Mater* 1997, 9, 2699.
15. Yang, Z.; Karasz, F. E.; Geise, H. J. *Macromolecules* 1993, 26, 6570.
16. Sokolik, I.; Yang, Z.; Karasz, F. E.; Morton, D. C. *J Appl Phys* 1993, 74, 3584.
17. Cimrov, V.; Remmers, M.; Neher, D.; Wegner, G. *Adv Mater* 1996, 8, 146.
18. Pei, Q. B.; Yang, Y. *Synth Mater* 1996, 80, 131.
19. Häber, J.; Müllen, K.; Salbeck, J.; Schenk, H.; Scherf, U.; Stehlin, R.; Stern, R. *Acta Polym* 1994, 4, 244.
20. Knight, A. W.; Greenway, G. M. *Analyst* 1994, 119, 879.
21. Jones, R. N. *Chem Rev* 1947, 41, 353.
22. Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. *Adv Mater* 2002, 14, 809.
23. Shu, C. F.; Dodda, R.; Wu, F. I.; Liu, M. S.; Jen, K. Y. *Macromolecule* 2003, 36, 6698.
24. Bolognesi, A.; Betti, P.; Botta, C.; Destri, S.; Giovannella, U.; Moreau, J.; Pasini, M.; Porzi, W. *Macromolecules* 2009, 42, 1107.
25. Precker, W. J. *Eur J Phys* 2007, 28, 493.
26. Kim, Y. H.; Soon, K. K. *J Appl Polym Sci* 2006, 100, 2151.
27. Kissinger, P.; William, R. *Techniques in Electroanalytical Chemistry*, 2nd ed.; Heinemann Laboratory, Dekker, New York, 1996.
28. Coetzee, J. F. *Recommended Method for Purification of Solvents and Tests for Impurities*; Pergamon Press: New York, 1982.
29. Lubert, K. H.; Wagner, M.; Olk, R. M. *Anal Chim Acta* 1996, 336, 77.
30. Pommerehe, J.; Vestweber, H.; Guss, W.; Mahrt, R. F.; Bassler, H.; Porsch, M.; Daub, J. *Adv Mater* 1995, 7, 551.
31. De Leeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth Met* 1997, 87, 53.
32. Pei, J.; Yu, W. L.; Huang, W.; Heeger, A. J. *Macromolecules* 2000, 33, 2462.
33. Chen, Z. K.; Huang, W.; Wang, L. H.; Kang, E. T.; Chen, B. J.; Lee, C. S.; Lee, S. T. *Macromolecules* 2000, 33, 9015.
34. Janietz, S.; Bradley, D. D. C.; Grell, M.; Giebele, C.; Inbasekaran, M.; Woo, E. P. *Appl Phys Lett* 1998, 73, 2453.
35. Santhanam, K. S. V.; Bard, A. J. *J Am Chem Soc* 1966, 88, 2669.
36. Vega, J. F.; Rastogi, S.; Peters, G. W. M.; Meijer, H. E. H. *J Rheol* 2004, 48, 663.