

Structure and Properties of Functionalized Polyfluorenone Containing Hetero Aromatic Side Chains

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Abstract The optical properties of substituted fluorenones with diverse structures have been analyzed using molecular orbital calculations in order to understand the structure-property relations. Based on theoretical predictions, synthesis of some model compounds has been attempted. The experimentally obtained optical properties are in close agreement with the theoretically obtained results.

Keywords: Conjugated polymer; UV-Visible spectroscopy; Band gap; Structure and properties; Molecular orbital calculations.

INTRODUCTION

The design and synthesis of the p-conjugated oligomers and polymers with novel optical and electronic properties are playing a vital role in the area of advanced materials research^[1]. These studies have lead to a better understanding of the structure-property relationship, which in turn has enabled the design of materials with tailored properties. The combination of semi-conducting properties and high luminescence efficiency of conjugated oligomers and polymers has opened the way to the development of polymer light emitting diodes, light emitting electrochemical cells and solid-state lasers^[2]. Among the p-conjugated materials numerous polyfluorenones with diverse structures have been probed and the structure-property relationship of these polymers have been exploited in recent years particularly due to their (i) structural versatility (color tuning by substitution at 9-position), (ii) solubility upon fictionalization and (iii) environmental stability^[3]. The low luminescence efficiency of polyfluorenones in solid-state limits their use as the emissive layer in LEDs. In order to achieve better efficiency, multilayer technology is being adopted, wherein materials containing p-electron deficient heterocyclic moieties have been utilized as electron transporting hole blocking layer (ETHB)^[4]. But these additional layers may cause in heterogeneity in the device due to phase separation/crystallization, affecting the efficiency. Hence the design of ETHB incorporated single layer devices is gaining importance.

The present investigation (i) explores the possibility of incorporating ETHB groups into 9-position of fluorenone unit to achieve greater efficiency in LEDs and (ii) studies its structural influence on optical properties. Benzotriazole group is proven to have electron transporting properties^[5] and benzothiazole is widely used in various studies^[6, 7]. Another strategy is to synthesize ETHB incorporated materials as they offer great possibilities in varying the direction and magnitude of the mesomorphism and potential optoelectronic properties. Fundamental understanding of the electronic and optical characteristics of conjugated materials is of interest, since small variations in chemical structure can play a vital role in modifying the characteristics. Hence,

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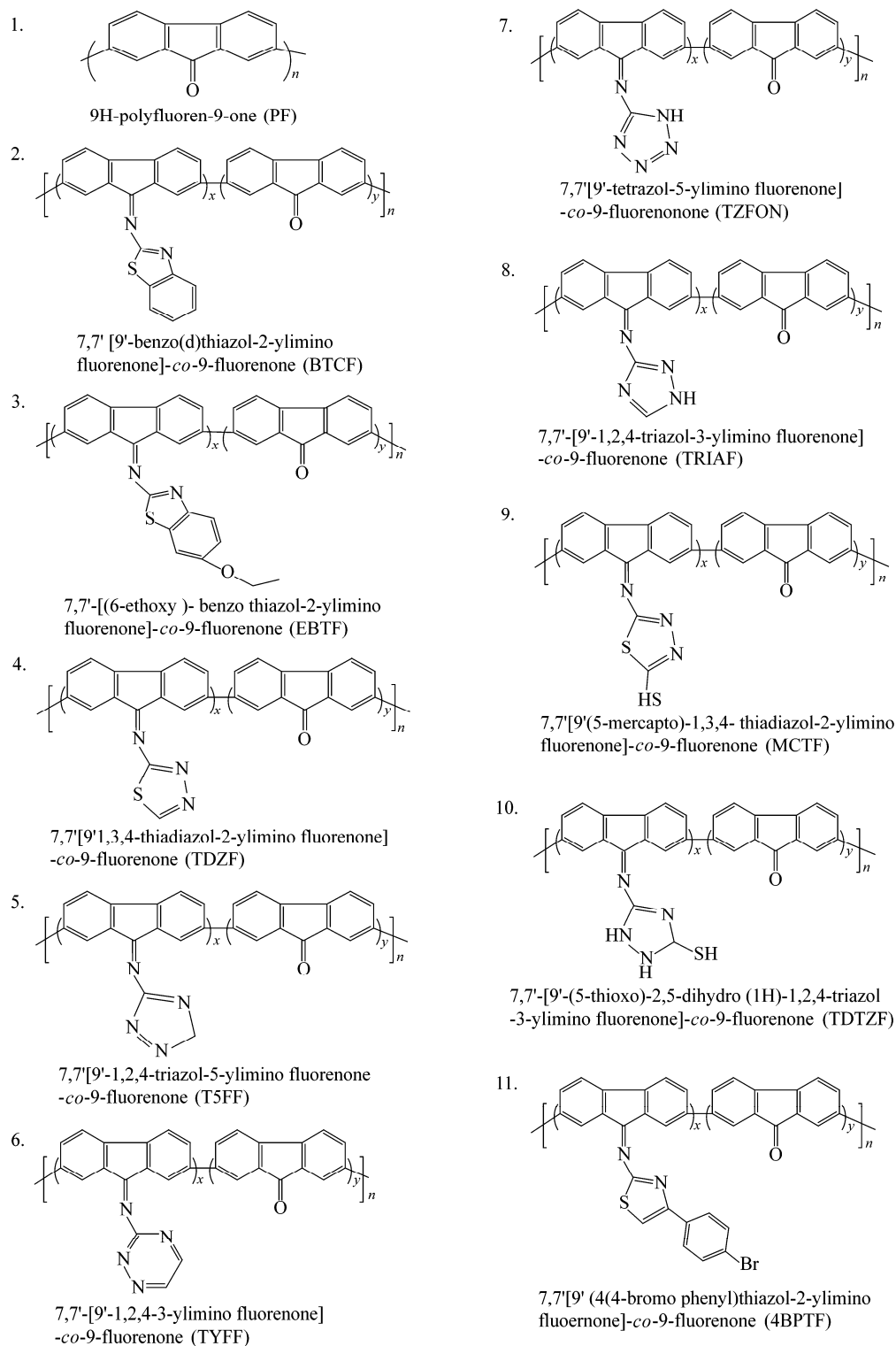


Fig. 1 Polyfluorenones coupled with different hetero aromatic amines

there has been a considerable amount of quantum chemical calculations performed on polyfluorenone and its derivatives. Brocks^[8] studied the electronic and geometrical structures of polyfluorenone and its derivatives using density functional methodology. Cornil *et al.*^[9] theoretically studied the relation between the geometric and optical properties of oligofluorenone in both neutral and oxidized states and the results were extrapolated to predict the properties of polymers^[10–12]. In these studies, the electronic structure and the band gaps of polymers have been considered^[13].

Computing HOMO-LUMO (highest occupied molecular orbital-lowest unoccupied molecular orbital) energies with different substituents is a simple step to predict the substituent effect on polymer band gaps and can be exploited in designing new materials. In the present study, molecular orbital calculations have been performed on some of the ETHB incorporated materials (Fig. 1).

Molecular orbital calculations were also performed on fluorenone (F) oligomers for comparison. In order to substantiate the theoretically predicted properties of the above compounds, the synthesis of some of the model compounds were carried out.

THEORETICAL METHODOLOGY

The Cerius2 package from Accelrys has been used for generating the initial geometries and Gaussian 98 program^[14] has been used for semi-empirical AM1, density functional theory (DFT) (B3LYP/3-21G*) calculations. Molecular-orbital calculations prove to be extremely useful when dealing with p-conjugated oligomers and polymers. In the present study semi-empirical and density functional molecular-orbital calculations are performed on polyfluorenones containing five-membered/six-membered rings bearing sulphur and nitrogen at different positions. The optimized geometries are obtained using AM1 calculations and single-point calculations are performed at the DFT B3LYP/6-31G* level to predict the band gap. The HOMO-LUMO gap in the DFT calculations and the excitation energy with significant oscillator strength are taken as the band gap of the polymer^[12]. The calculated band gaps are plotted against inverse number of monomer units (1/N) and extrapolated to infinite number of units to get the value for the polymer.

EXPERIMENTAL

Chemical Polymerization

Monomers were added to a stirred solution of FeCl₃ (ferric chloride) in chloroform under nitrogen atmosphere^[15, 16]. The mixture was stirred for 70 h at room temperature. The reaction mixture was quenched by adding it to water. The precipitated solid material was separated by filtration and washed with water. The crude product obtained was dissolved in chloroform and reprecipitated with water. The refined polymer was washed with water and dried at room temperature under vacuum overnight. The obtained polymers were soluble in conventional solvents (acetonitrile, chloroform, toluene and tetrahydrofuran) and were able to be processed to films by a solution-casting method.

The Schiff Base Formation of Polyfluorenone and Hetero Aromatic Amines

One of the most interesting features of PF is the possibility of precise tuning of its spectroscopic properties by grafting of appropriate chromospheres *via* the carbonyl group present in the fluorene-9-one segment. To a well-stirred solution of polyfluorenone (500 mg), with corresponding amine in dry toluene (70 mL) under nitrogen atmosphere at 0 °C, TiCl₄ was added drop wise (0.2 mL), over a period of 1 h. The dark brown reaction mixture was stirred at room temperature for 1 h which is followed by refluxing for 48 h. The reaction mixture was cooled at 10 °C, diluted with diethyl ether (150–200 mL) and was stirred until the color of the precipitate totally changed to light yellow^[17, 18]. The mixture was filtered through and the collected precipitate was washed with diethyl ether. Concentration of the combined filtrate and washings gave the fluorenimine.

Characterization

1 mg of polymer was dissolved in 10 mL acetonitrile to obtain approximate concentration of 1×10^{-2} g/dL. Later 20 μ L of the above solution was made up to 3 mL (*ca.* 6.6×10^{-5} g/dL). UV-Visible spectrum was recorded

using a Carry 50 Bio/UV-Visible spectrophotometer. The above solution was also used for photo luminescence studies using Carry eclipse fluorescence spectrophotometer. Infra red spectra of the polymers were recorded using KBr pellet technique with an ABB MB 3000 IR spectrometer.

The polymer solution up of approximately 1 mL concentration was coated on Pt working electrode. Tetrabutyl ammonium hexafluorophosphate (TBAHB) was taken as support electrolyte. Ag/AgCl electrode was taken as working electrode, and Pt wire electrode was taken as support electrode. The oxidation and reduction potentials were calculated with respect to ferrocene standard.

RESULTS AND DISCUSSION

The recent development in information technology, energy and other vital areas that demand appropriate materials is very high. The scope of the development of organic semiconductors used in general areas, such as display technology, non-conventional energy management *etc* is very promising. In the present investigation, design and properties are computed for number of functionalized polyfluorenones. Copolymers of functionalized polyfluorenone are synthesized and their optical characteristics are studied in detail.

Recently, it has been reported that time-dependant density-functional theory gives a satisfactory reproduction of the excitation energies^[11]. In addition, the DFT method has been used successfully to study band gaps in conjugated polymers, where the HOMO-LUMO difference provides a good estimate of the excitation energy. Recently Levy and Nagy^[19] developed a DFT version of Koopmans' theorem, showing that the energy gap can be estimated from the eigen values of Kohn-Sham equations. Since oligomers may serve as model compounds for the respective polymers, the investigation of well-defined model oligomers has therefore become useful to gain insight in the structural and electronic peculiarities of the corresponding polymers. Hence, in the present study, theoretical calculations on monomer, dimer and trimer were performed, which provide more insights on how the property varies with the increase of chain length. The band gap is now well correlated to the conjugated chain length, and hence, real structure-property relationships become more viable. In the present study, semi empirical Austin model 1 (AM1) is used for the geometry optimization. Molecular orbital calculations were performed using density-functional theory with three-parameter functional and the 6-31G* basis sets to estimate HOMO, LUMO energies and the derived parameters such as band gap.

The most common approximation for predicting band-gaps of conjugated polymers realize on extrapolating the band-gaps to the full polymer from scaling of the band-gap of a series of oligomeric molecules having increasing length. The obtained HOMO, LUMO, band-gap (BG) and dipole moment (DP) and heat of formation (HF) for monomer, dimer and trimer of different imines of polyfluorenone are presented in Table Ia.

The HOMO values decrease with increasing number of monomer units whereas the LUMO values increase with the number of monomer units. The band-gap also decreases with increasing number of monomer units, while the dipole moment and heat of formation show an increasing trend. Oligomeric approach is being used to extrapolate the properties of polymers. This has been done by plotting the properties with the reciprocal number of monomer units. The graph is extrapolated to zero to get the properties of the polymer. The obtained results of different electronic properties are presented in Table Ib.

Comparison of results obtained for (EPFBT) and (PFBT) shows that addition of ethoxy groups changes the band-gap due to the inductive effect. The change is much pronounced when compared to the variation in band-gap of (PFTZ) and (PFTA). Comparison of the results obtained for (PFTA) and (PFTZA) indicates their variation in electronic properties by changing the ring size and position of nitrogen groups. Even though the dipole moment does not show a characteristic variation, the HOMO and LUMO values show characteristic change.

Table Ia. Results obtained from different polyfluorenone systems at computational studies

S.No.	Compound		HOMO	LUMO	BG (eV)	DP (μ)	HF (kJ/mol)
1	PF	1	6.7734	-2.1671	4.6063	3.4999	-575.4342
		2	6.8311	-2.3695	4.4616	6.5558	-1149.6683
		3	6.8393	-2.4620	4.3773	9.3408	-1723.9016
2	PFBT	1	6.0349	-2.6161	3.4188	2.7472	-1277.0634
		2	5.9674	-3.3004	2.6670	6.8161	-2551.8235
		3	5.6158	-3.2139	2.4019	10.9910	-3828.1424
3	EPFBT	1	6.2874	-2.4140	3.8724	1.6570	-1430.9221
		2	6.2099	-2.4648	3.7451	2.8507	-2860.6494
		3	6.1461	-2.6881	1.4580	11.0098	-4234.7405
4	PFTZ	1	6.6980	-2.6539	4.0441	2.9524	-1139.4350
		2	6.6904	-3.0509	3.0509	10.4199	-2277.6455
		3	6.1911	-2.8746	3.3165	16.1247	-3415.4680
5	PFTA	1	7.0042	-2.1611	4.8431	2.5070	-796.6130
		2	5.8945	-2.3366	3.5579	5.4411	-1592.0322
		3	6.2450	-2.4253	3.8197	8.4446	-2387.4524
6	PFTZA	1	6.2428	-2.3913	3.8515	3.4059	-834.6906
		2	5.9369	-2.5214	3.4155	5.9915	-1668.1857
		3	5.9541	-2.6169	3.3372	9.1093	-2501.6808
7	PFTON	1	7.3000	-2.7390	4.5610	6.5740	-812.6224
		2	6.5574	-2.9154	3.6420	11.7556	-1624.0530
		3	6.8369	-2.9842	3.8527	16.5708	-2435.4833
8	PFTRA	1	7.0042	-2.1611	4.8431	2.5100	-796.6130
		2	5.9010	-2.3192	3.5818	4.9374	-1592.0327
		3	6.2276	-2.4133	3.8143	7.4002	-2387.4521
9	PFTDZT	1	5.8126	-2.6215	3.1911	1.8672	-1537.6164
		2	5.6694	-2.6580	3.0114	2.8363	-3074.0373
		3	5.5236	-2.6849	2.8387	3.5785	-4610.4582
10	PFDHT	1	6.0676	-2.1932	3.8844	2.2626	-1194.7970
		2	5.8846	-2.3439	3.5408	4.7683	-2388.4005
		3	5.9353	-2.4101	3.5252	7.5134	-3582.0041
11	BPPFT	1	6.9372	-2.2419	4.6953	1.0899	-3925.3991
		2	5.8716	-2.8030	3.0686	4.8163	-7849.8105
		3	5.4803	-3.2245	2.2558	1.8844	-11773.702

HOMO- Highest Occupied Molecular Orbital

LUMO- Lowest Unoccupied Molecular Orbital

BG-Band Gap

DP-Dipole moment

HF-Heat of formation

Table Ib. Results obtained from computational studies of polymers

S.NO.	Compound	HOMO	LUMO	BG (eV)	DP (μ)	HF (kJ/mol)
1	PF	6.8769	-2.5964	4.2804	11.4229	-2117.0602
2	PFBT	5.5589	-3.6536	1.9053	13.7808	-4700.9857
3	EPFBT	1.9440	-2.6539	1.2901	12.0874	-5211.5470
4	PFTZ	6.1675	-3.1249	2.6835	21.1715	-4194.7476
5	PFTA	5.5398	-2.5422	2.9975	10.4560	-3171.0001
6	PFTZA	5.7564	-2.7046	3.0520	10.8994	-3072.3466
7	PFTON	6.3666	-3.1009	3.2657	20.1047	-2991.0423
8	PFTRA	5.5257	-2.5191	3.0065	9.0634	-2932.0490
9	PFTDZT	5.4254	-2.7095	2.7159	4.2335	-7592.9223
10	PFDHT	5.8187	-2.5101	3.3086	9.2379	-4399.2259
11	BPPFT	4.7759	-3.6034	1.1725	4.1869	-14460.594

Comparison of (PFTZA) and (PFTOZ) shows that by increasing the number of nitrogen atoms, the HOMO and LUMO values show the characteristic increasing. The dipole moment interestingly shows a two fold increase. Addition of $-SH$ groups phenomenally changes the oxidative properties (HOMO) of (PFTZ). The band-gap also increases due to the influence of $-SH$ groups, the heat of formation approximately double due to the above effect (comparison of PFTDZT and PFTZ). The overall result obtained from computational studies clearly indicates the influence of electronegativity, the number, position and linking of the electronegative elements like sulphur and nitrogen on different properties. Copolymerization of fluorenone functionalized with hetero aromatic side chains and polyfluorenones was studied in order to increase the number of electron participating in opto-electronic mechanisms. Fluorenone is polymerized using $FeCl_3$ chemical polymerization method, the FTIR spectra of polyfluorenone and polyfluorenones with coupled hetero aromatic compounds are shown in Fig. 2.

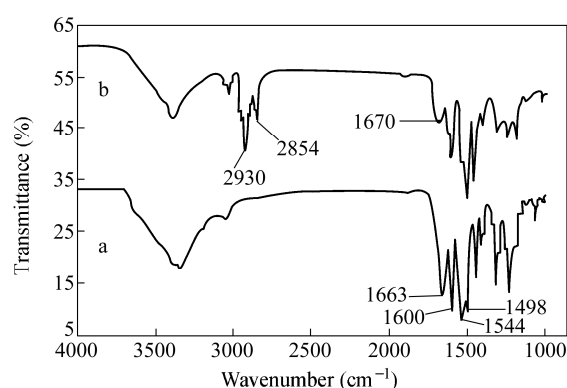


Fig. 2 FTIR spectra of (a) polyfluorenone and (b) polyfluorenone with hetero aromatic compounds

The peaks at 3061 cm^{-1} and 3013 cm^{-1} correspond to aromatic $C-H$ stretching while the cyclic ketone group shows its peak at 1740 cm^{-1} . The $C=C$ stretching is seen at 1611 cm^{-1} while the peak around 1600 cm^{-1} corresponds to aromatic $C-H$ stretching. $C-H$ deformation is obtained at 736 cm^{-1} . The IR patterns of all copolymers are similar.

The absorption spectra of the copolymers are taken in acetonitrile solution. The spectral absorption is considered for the band-gap of the copolymer. Addition of ethoxy groups increases the onset by 0.05 eV due to the electron releasing nature of ethoxy groups. Comparison of TDZF and T5FF shows due to the increase in electro-negativity of nitrogen the onset is red-shifted by 70 nm , similarly comparison of (TYFF) and (TZFON) shows that the onset is blue-shifted by 83 nm , due to the influence increase in the number of nitrogen.

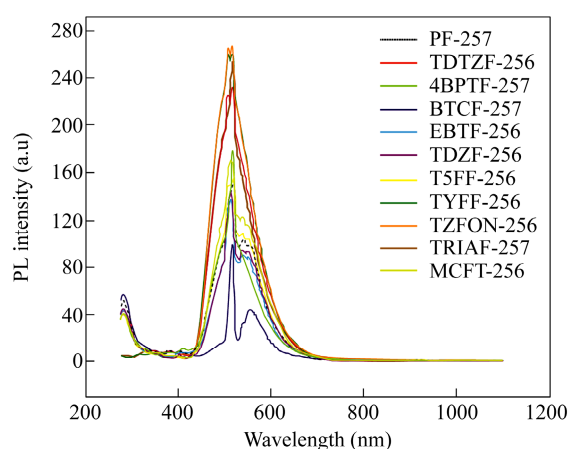
It is interesting to note that due to the presence of ethoxy groups (BTCF and EBTF), the excitation coefficient is three fold increased. Similarly there is a two fold increase in absorption coefficient when the number of nitrogen atoms in the ring is increased (T5FF and TZFON). The presence of $-SH$ groups also increases the absorption coefficient of the polymer solution (TDZF and MCTF).

Cyclic voltammetry of the copolymers is studied and the obtained cyclic voltatomograms for different polymers and the oxidation and reduction potentials are used to calculate the HOMO and LUMO values of copolymers by using $Ag-AgCl$ and ferrocine standard. The obtained results are given in Table II.

Photoluminescence (PL) spectra of the copolymer solutions are studied to understand the influence of hetero aromatic side chain structure on photoemission. The PL spectra of all the copolymers obtained for an excitation of 256 nm are compared in Fig. 3.

Table II. Electrochemical data obtained from cyclic voltammetry

S.NO.	Compound	Oxidation potential	Reduction potential	BG (eV)
1	PF	5.6660	4.1128	1.5532
2	BTCF	5.4704	3.8599	1.6105
3	EBTF	5.6449	3.8347	1.8102
4	TDZF	5.5324	3.7622	1.7702
5	T5FF	5.2285	3.6312	1.5973
6	TYFF	5.4141	3.6504	1.7637
7	TZFON	5.5639	3.7150	1.8486
8	TRIAF	5.5582	3.8414	1.7168
9	MCTF	5.4930	3.8477	1.6453
10	TDTZF	5.4990	3.4809	2.0181
11	4BPTF	5.1195	3.5275	1.5920

**Fig. 3** Photoemission wavelengths obtained for different copolymers

It is interesting to note that due to the influence of side-chains the maxima obtained around 550 nm are shifted. The emission intensity of samples is in the order of $7 > 9 > 10 > 8 > 6 > 5 > 1 > 4 > 3 > 11 > 2$ (S.No.).

The above results clearly indicate the influence of 5 member / 6 member rings, electro negativity of atoms, presence of inductive effect, and linkage. The results from the overall studies clearly show that the hetero-aromatic side-chain on the functional groups present in the copolymer affects the HOMO, LUMO and band-gap. The inductive effect of functional groups present in side-chain influences the above properties. The absorption maximum and the onset are also affected by the above parameters. The PL intensity and wavelength of emission for the copolymers can be finely tuned by appropriate substituting the hetero aromatic pentane groups and the functional group, and changing the electro negativity of elements present there.

CONCLUSIONS

The development in the area of organic metals shows support towards their potential utilization in opto-electronics. Conjugated polymers which can take the function of electron transporting and hole blocking (ETHB) layers and are used in current LED and solar cell technology are of current interest for getting appropriate materials towards single layer technology. The potential candidates for ETHB functions are the nitrogen and oxygen containing electron deficient hetero-cyclic moieties such as oxadiazole, triazole, triazine, pyridine, etc.

The HOMO, LUMO and band-gap, the inductive effect of functional group present in side-chain influence the above properties. The absorption maximum and the onset are also affected by the above parameters. PL spectra obtained for different copolymers such as that the PL intensity and wavelength of emission, cover the entire visible region. The wavelength of maximum emission is in the order of $7 > 9 > 10 > 8 > 6 > 5 > 1 > 4 > 3 > 11 > 2$ (S.No.).

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