SYNTHESIS, CHARACTERIZATION AND STUDY OF FLUORESCENT-HIGH PERFORMANCE POLYESTERS

Jignasa V. Modh and Saurabh. K. Patel*

Department of Chemistry, Veer Narmad South Gujarat University,
Surat-395007(Gujarat) India.
*E-mail: saurabh.silvina@gmail.com

ABSTRACT

Fluorescent-High performance polyesters have been synthesized by the polycondensation method at high temperature using cetrimide as initiator. Ten Polyesters were synthesized having different aliphatic-aromatic diols in the chain having s-triazine ring as the main moiety. Modification and introduction of the bulky pendent group in monomer structure increase the thermal stability of the polymers. The synthesized polymers have shown gray to black color. The solubility properties of synthesized polyesters were carried out in polar and non-polar solvents. The inherent and reduced viscosities were checked by Ubbelohde solution Viscometer and intrinsic viscosity was measured using Huggins and Kraemer's equations. Thermogravimetric analysis of all the polyesters has been carried out. The unique property of fluorescence of these polyesters makes them valuable candidates as high-performance materials.
Keywords: Polycondensation, Thermogravimetric Analysis, High Performance, Fluorescence, Viscosity.

INTRODUCTION

In recent years, many researchers have been affected by the synthesis and characterization of fluorescent - high-performance polymers.[1] High thermal stability of polymers due to the s-triazine moiety, it is notable that the s-triazine ring is heat resistant.[2,3] Polymers having S-Triazine ring become a subject of interest because of good thermal stability, enhanced toughness and low moisture absorption and commercially available high-performance engineering plastic materials.[4] The Triazine based material reveals outstanding high-temperature performance, which could be assigned to the N- heterocyclic structures[5]. Polymers containing the triazine ring as part of the polymer chain are usually insoluble and infusible. However, the thermal stability of the triazine ring makes it an attractive monomer for use in high-temperature polymers. High-performance polymers have been utilized in applications that demand services at elevated temperatures while maintaining their structural integrity and an outstanding combination of chemical, physical and mechanical properties.

Since the 1980s, fluorescent polymers utilized in commercial development further attracted tremendous scientific and industrial interest due to their potential in achieving the goal of light-emitting device technology that is economically viable for solid-state lighting and displays, which offer significant gains in power efficiency, color quality, and lifetime at a lower cost and less environmental impact than traditional incandescent and fluorescent lighting.[6-14]

Fluorescent polymeric materials have been achieved a great intentness owing to wide range application such as clean energy technologies[15], explosive sensing, pH/ temperature sensor, biological imaging[16] life science, material science, ultrasensitive molecular diagnosis and novel light-emitting Nano devices[17], and biological detection schemes, smart polymer machines, fluorescent chemosensor, fluorescent molecular thermometers, fluorescent imaging, drug delivery carriers, and so on.[18,19] Fluorescent polymers can be developed with different methods, generally, there are two admittances for the preparation of fluorescent polymers. One of them polymerization of a monomer having a fluorescent chromophore such as fluorescent compounds as initiator, fluorescent compounds as chain transfer agents, chemical bonding between fluorescent groups and polymers[20-24], the second is the chemical variation of polymers by fluorescent

molecules or fluorescent oligomers The second one is chemical alteration of commercially available polymers having reactive groups by using fluorescent dyes or organic molecules.[25, 26]

The present investigation aimed to synthesize new kinds of fluorescent polyesters bearing an outstanding combination of high-performance properties evolving owing to the attachment of s-triazine ring with coumarin ring.

EXPERIMENTAL

Material and Methods

Freshly prepared double distilled water was used for the preparation of solutions. Chemicals such as Sodium hydroxide pallets, Sodium bicarbonate, Thionyl chloride, Cetramide were used as received. The solvents carbon tetrachloride, chloroform, methanol, ethanol, acetone, benzene, n-butanol, ethyl acetate, amyl acetate, isoamyl acetate, dimethylformamide (DMF), dimethyl sulfoxide (DMSO) were received from Merck. Cyanuric chloride was purified recrystallization from pure benzene (m. p1460C).   Bisphenol-A (Atul Ltd.) was repeatedly crystallized from 50% aqueous acetic acid and finally purified by recrystallization from benzene (m.p.150ºC). Bisphenol-S and Bisphenol-F (Atul Ltd.) were recrystallized from benzene (m.p.187ºC). Neopentyl glycol, 1,4 Dihydroxy Naphthalene, 1,6 Haxene diol, 1,4 Butanediol, Resorcinol, Mono ethylene glycol, Diethylene glycol were received and purified by recrystallization from rectified spirit.

Synthesis of 2-(7-Hydroxy 4-methyl coumarino)-4, 6-dichloro-s-triazine [CT] [27]

A solution of cyanuric chloride (18.44g, 0.1M) in a 60ml acetone was added with stirring to a cooled solution (0-5ºC) of sodium bicarbonate (10.6g) in 100ml of distilled water, in a three-necked flask (250ml) equipped with a mechanical stirrer. This resulted in the formation of a slurry of cyanuric chloride. A solution of 7-hydroxy 4-methyl coumarin (17.60, 0.1M) in 10ml of acetone was added to the cold slurry of cyanuric chloride. The mixture was stirred for 2 hours at 0-5°C. The Off-white colored product was filtered, and recrystallized from ethanol and dried in vacuum desiccators. The yield was 78%. M. P. 120°C.

Synthesis of 2-(7-Hydroxy-4-methyl coumarino)-4,6-bis- (N-Phenyl anthranilic acid) s-triazine [CNT][27]
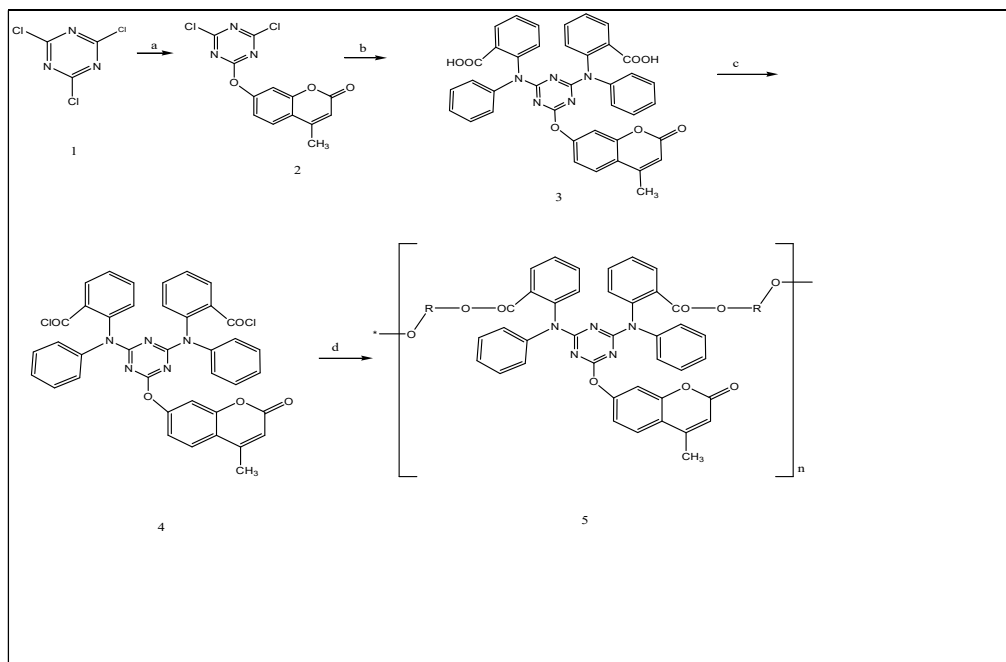
A solution of 2-(7-hydroxy 4-methyl coumarino)-4, 6-dichloro-s-triazine (32.40g, 0.1M) in 40ml of acetone was mixed with a solution of NaOH (16g, 0.4M) and N- phenyl anthranilic acid (42.64g, 0.2M) in 80ml double distilled water. The reaction was stirred for 2 hr at room temperature and 2 hr at 80°C. The separated solid was collected and washed with hot water. The product was dried in vacuum at 100°C. The yield was 80%. The product was recrystallized from acetone. M. P.189 °C.

Synthesis of 2-(7-Hydroxy-4-methyl coumarino)-4, 6-bis- (N-phenyl anthranyl chloride) s-triazine [CNTC] [28]

Thionyl chloride (11.9ml, 0.1mol) was added into 2-(7-hydroxy-4-methyl coumarino)-4,6-bis- (N-Phenyl anthranilic acid) s-triazine [CNT] (6.77g, 0.1M) in a dry round bottom flask. The reaction mixture was refluxed at 78ºC for 2 hr. At the end of the reaction, excess thionyl chloride was distilled and the dry product was collected. The yield was about 82%. The product was recrystallized from dimethylformamide. M. P. 267°C.

Synthesis of Polyesters[29, 30]

2-(7-hydroxy-4-methyl coumarino)-4,6-bis- (N-Phenyl anthranyl chloride) s-triazine [CNTC] (0.01M) in the minimum quantity of DMF (approx. 10ml) was stirred in a round bottom flask, then initiator cetrimide (0.25g) was added and heated up to 150ºC. After adding diol (0.02 M) the reaction temperature was raised to 160-180ºC and heated for 7 hrs. The reaction mixture was cooled and poured with constant stirring in 250ml of ice-cooled water. Solid was filtered, washed with hot water and dried. Different types of polyesters were synthesized from 2-(7-hydroxy-4-methyl coumarino)-4,6-bis- (N-Phenyl anthranilic chloride) s-triazine [CNTC] and various diols using a similar method. NC-1 to NC-10 polyesters have been synthesized by using Bisphenol-A, Bisphenol-S, Bisphenol-F, Neo-pentylglycol, 1,4dihydroxy Naphthalene, 1,6 Haxene diol, 1,4 Butanediol, Resorcinol, Mono ethylene glycol, diethylene glycol, respectively.

Scheme-1: Reagents: (a) 7-Hydroxy 4-methyl Coumarin in Acetone, 0-5 ºC, 2 hr; (b) CT in 40ml of Acetone was mixed with a Solution of NaOH and N- Phenyl Anthranilic Acid in 80ml Double Distilled Water. (c) Add Thionyl Chloride in CNT and reflux it 2 hr at 78ºC (d) HO-R-OH in DMF, Cetrimide, 8 hr at 160-180 ºC.

RESULTS AND DISCUSSION

Properties of Polyesters

Polyesters, which have been prepared from N-phenyl anthranilic acid, coumarin and different types of diols have unique colors. Most of the polyesters are gray to black (Table-1).

Table-1

Polyester	Diol	Colour
NC-1	Bisphenol-A	Black
NC-2	Bisphenol-S	Black
NC-3	Bisphenol-F	Black
NC-4	Neopentyl glycol	Dark grey
NC-5	1,4 Dihydroxyl naphthalene	Grey
NC-6	1,6 Haxene diol	Dark grey
NC-7	1,4 Butanediol	Black
NC-8	Resorcinol	Dark grey
NC-9	Mono ethylene glycol	Grey
NC-10	Di ethylene glycol	Grey

Solubility

Relative solubility of various polyesters synthesized from coumarin and N-phenyl anthranilic acid has been carried out in different solvents. It is shown that the solubility of the polyesters in different solvents reveals that polyesters are insoluble in aliphatic chlorinated solvents like chloroform, carbon tetrachloride. Polyesters are also insoluble in halogenated and Non- halogenated solvents such as chlorobenzene, benzene. Polyesters are partly soluble in acetone, methanol, ethanol, THF, n-butanol, isopropyl alcohol and ether while polyesters are soluble in dimethylformamide, dimethyl sulfoxide and ethyl acetate. The symbol ++ indicates that the solubility of polyesters to respective solvent, whereas ± ± indicates partly soluble and symbol -- indicates that polyester is insoluble in the respective solvent (Table-2).

Table-2: Relative Solubility of Polyesters

Solvent	NC-1	NC-2	NC-3	NC-4	NC-5	NC-6	NC-7	NC-8	NC-9	NC-10
DMF	++	++	++	++	++	++	++	++	++	++
DMSO	++	++	++	++	++	++	++	++	++	++
Chloroform	--	--	--	--	--	--	--	--	--	--
CCl$_4$	--	--	--	--	--	--	--	--	--	--
Acetone	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
Benzene	--	--	--	--	--	--	--	--	--	--
Chlorobenzene	--	--	--	--	--	--	--	--	--	--
Methanol	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
Ethanol	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
THF	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
n-Butanol	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
IPA	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
Ether	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±	± ±
Ethyl acetate	++	++	++	++	++	++	++	++	++	++

Viscosity

Intrinsic, reduced and inherent viscosity for all the polyesters at various concentrations were determined at $25 \pm 0.1°C$. The relative (ηrel) and specific (ηsp) viscosities, reduced and inherent viscosities were calculated from experimental data. Typical Huggins and Kraemer plots were used to obtain intrinsic viscosity for polyesters. Intrinsic, reduced and inherent viscosities along with Huggin's and Kraemer's constants for 1% solution are shown in Table-3.

Table-3: Viscosity Values and Huggins's (K') and Kraemer's Constants (K'').

Polyester	[η]	η_{sp} / C	ln η_{rel} / C	K'	K''
NC-1	0.800	0.982	0.684	0.284	0.171
NC-2	0.722	0.852	0.616	0.254	0.200
NC-3	0.653	0.772	0.572	0.279	0.190
NC-4	0.651	0.760	0.565	0.257	0.203
NC-5	0.480	0.558	0.443	0.339	0.160
NC-6	0.493	0.571	0.451	0.320	0.172
NC-7	0.431	0.490	0.398	0.318	0.178
NC-8	0.462	0.511	0.412	0.230	0.234
NC-9	0.382	0.430	0.357	0.331	0.172
NC-10	0.432	0.492	0.400	0.322	0.172

The observations of intrinsic viscosities of Polyesters [NC] reveal that NC-1 which contains Bisphenol–A as diol has the highest solution viscosity, whereas NC-9 has the lowest intrinsic viscosity which contains aliphatic Mono Ethylene Glycol. The range of inherent viscosity is 0.357 - 0.684 g/dl. The intrinsic viscosity of the polyesters obtained from coumarin and N-phenyl anthranilic acid follows the sequence given below:

NC-9 < NC-7 < NC-10 < NC-8 < NC-5 < NC-6 < NC-4 < NC-3 < NC-2 < NC-1

Typical *Huggins's* and *Kraemer's* plots were used to obtain intrinsic viscosity for each of polyesters [NC]. Intrinsic, reduced and inherent viscosities along with *Huggin's* and *Kraemer's* constants for 1% solution are shown in Figs.-1, 2 and 3.

IR spectra

IR spectra of polyester NC-4 (Fig.-4)revealed C-N stretching vibration at 1269 cm^{-1}, > C= O stretching vibration at 1665 cm^{-1}, Ar-O-Ar sym. at 1179cm^{-1} and Ar-O-Ar asymmetric at 1136. Out of plane vibration of s-triazine ring at 824.49 cm^{-1}, in-plane vibration of s- triazine at 1485 cm^{-1}, C=O stretching vibration of – COOR group at 1772 cm^{-1}, C-H stretching vibration of CH$_3$ at 2923 cm^{-1}.
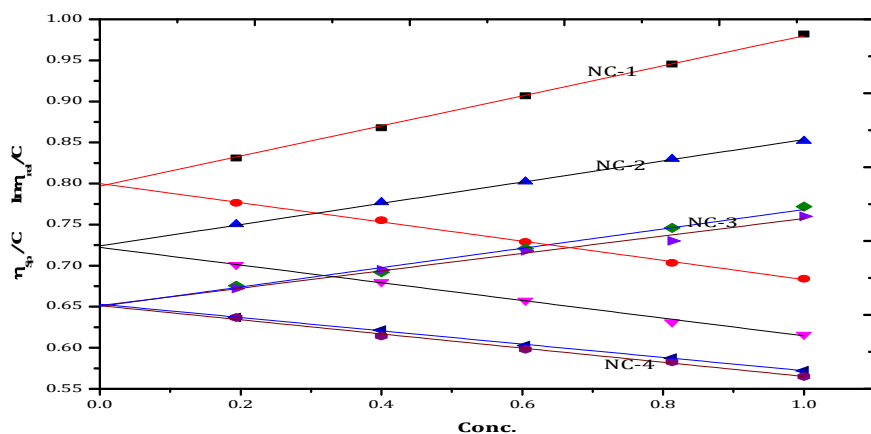
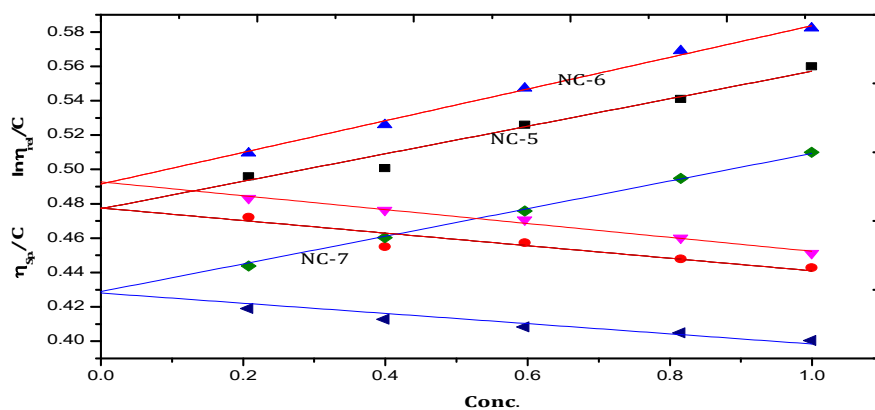Fig.-1: Typical Huggins's and Kraemer's Plots for NC-1, NC-2, NC-3, NC-2

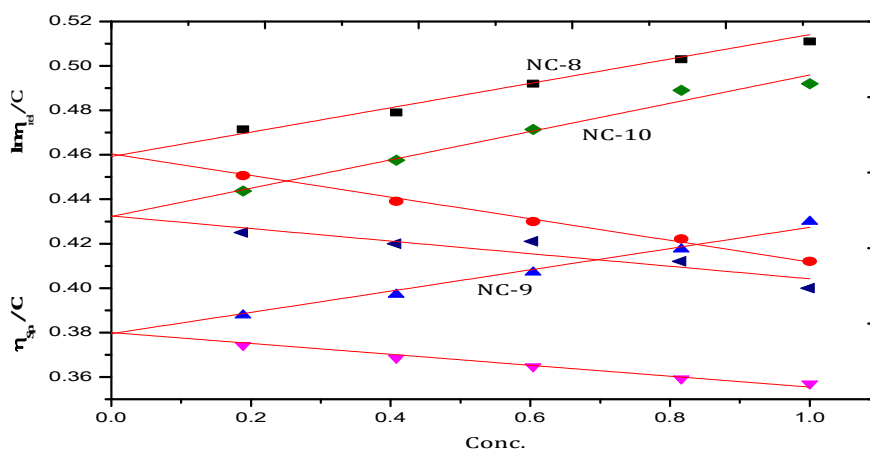Fig.-2: Typical Huggins's and Kraemer's Plots for NC-5, NC-6, NC-7

Fig.-3: Typical Huggins's and Kraemer's Plots for NC-8, NC-9, NC-10

IR spectra of polyester NC-10 (Fig.-5)revealed C-N stretching vibration at 1274cm^{-1}, > C= O stretching vibration at 1665 cm^{-1}, Ar-O-Ar sym. at 1158 and Ar-O-Ar asymmetric at 1135 cm^{-1}. Out of plane vibration of s-triazine ring at 839 cm^{-1}, in-plane vibration of s- triazine at 1488 cm^{-1}, C=O stretching vibration of – COOR group at 1770 cm^{-1}, C-H stretching vibration of CH$_3$ at 2922cm^{-1}. IR spectra of all polyesters are described in Table-4.
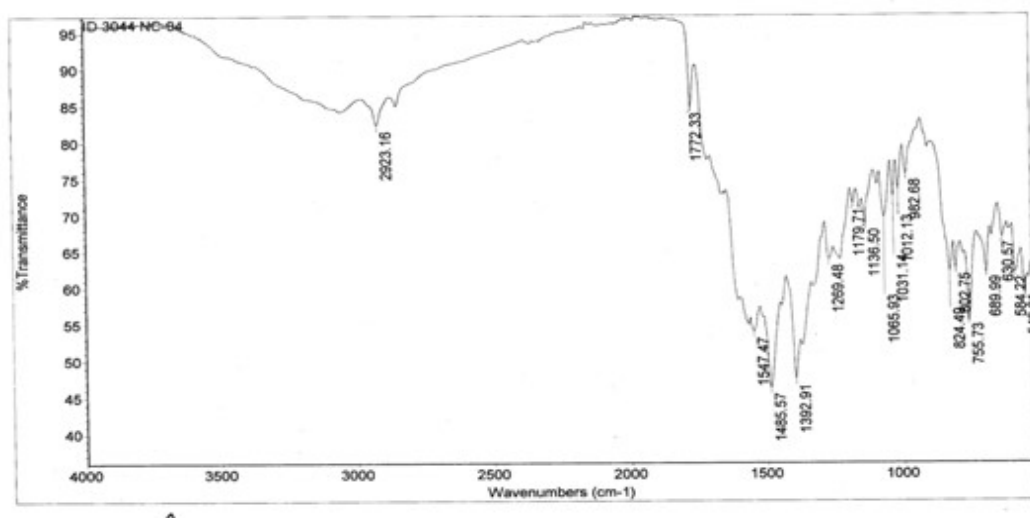
Fig.-4: IR Spectra of NC-4

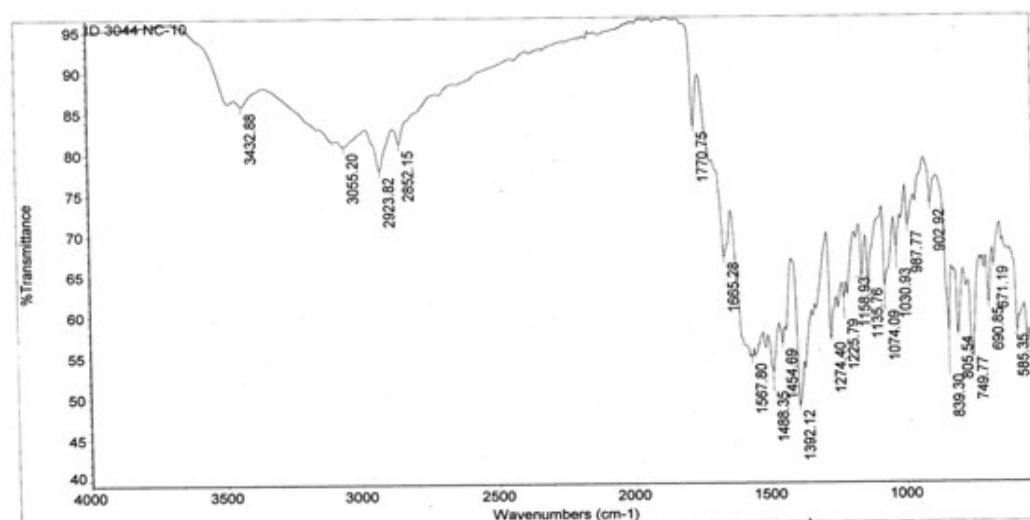Fig.-5: IR Spectra of NC-10

Table-4: IR Absorption Frequencies of NC Polyesters

Polyester (cm^{-1})	>C-N Stretching	>C=O Coumarine	Ar-O-Ar		s-triazine		>C=O -COOR
			(sym)	(asym)	Out Plane	In Plane	
NC-1	1225	1664	1175	1134	824	1486	1769
NC-2	1282	1676	1174	1140	833	1482	1770
NC-3	1226	1672	1160	1142	822	1484	1772
NC-5	1232	1670	1171	1144	823	1484	1770
NC-6	1229	1670	1165	1137	824	1484	1772
NC-7	1226	1665	1158	1135	824	1482	1768
NC-8	1225	1666	1159	1136	840	1491	1772
NC-9	1225	1665	1158	1135	839	1488	1771

^{1}H NMR Spectra

^{1}H NMR spectra of polyester NC-1(Fig.-6), the multiple signals of aromatic protons appear at 6.62-8.94 δ, the singlet at 1.54δ proves the presence of CH$_3$- group of Bisphenol-A and the singlet at1.24 δ indicates the presence of -CH$_3$- a group of coumarin, the singlet at 3.37 proves the presence of –CH$_2$– group.

1463

FLUORESCENT-HIGH PERFORMANCE POLYESTERS   Jignasa V. Modh and Saurabh. K. Patel

^{1}H NMR spectra of polyester NC-4 (Fig.-7), the multiple signals of aromatic protons appear at 6.12-7.78 δ, the singlet at 3.38 δ proves the ester linkage with Neo-Pentyl glycol and the singlet at 1.21δ indicates the presence of-CH_3- a group of coumarin, the singlet at 3.38 proves the presence of –CH_2 – group. ^{1}H NMR spectra of all polyesters are described in Table-5.
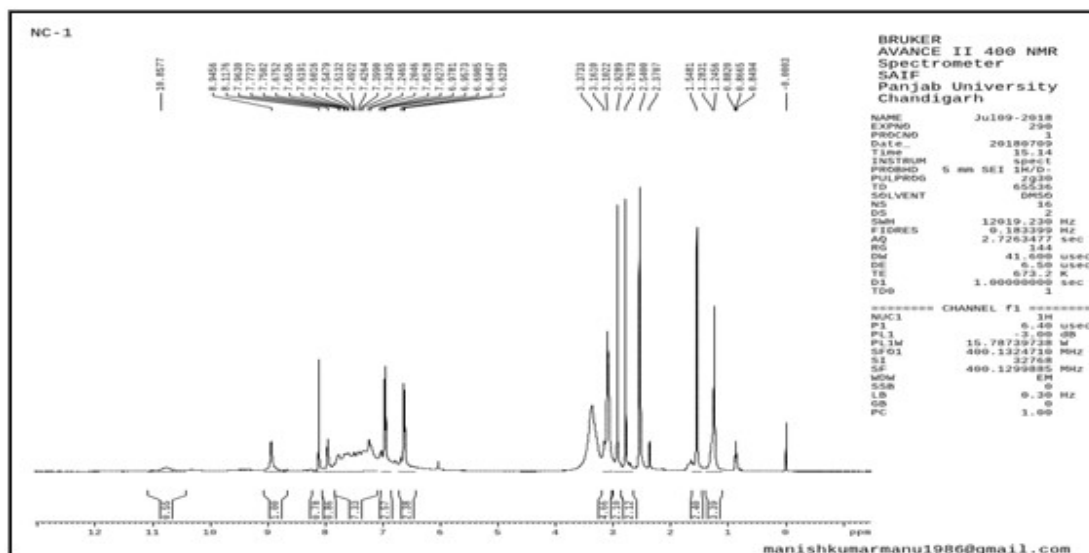
Fig.-6: ^{1}H NMR Spectra of Polyester NC-1
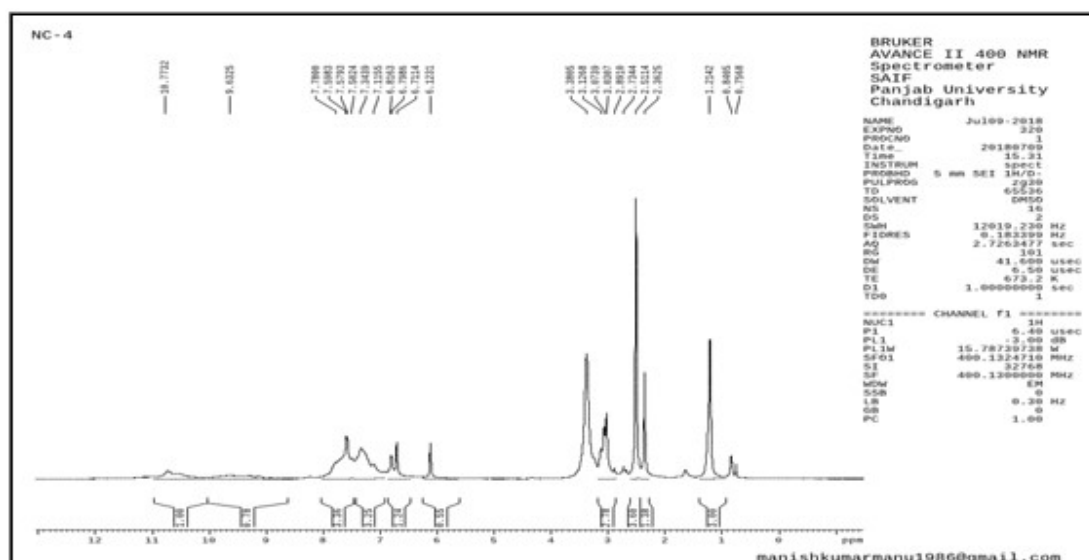
Fig.-7: ^{1}H NMR Spectra of Polyester NC-4

Table-5: ^{1}H NMR Chemical Shift of Polyesters [NC]

Polyester	Chemical Shift (δ ppm)		
	Ar-H Protons (m)	>CH_3- Group (s) Coumarin	–CH_2 – Group (s)
NC- 2	6.89-7.71	1.23	3.41
NC-3	6.15-7.65	1.20	3.38
NC-4	6.12-7.78	1.21	3.38
NC-5	6.11-7.15	1.20	3.39
NC-6	6.10-7.57	1.18	3.42

1464

NC-7	6.13-7.72	1.23	3.41
NC-8	6.14-7.75	1.21	3.40
NC-9	6.11-7.78	1.20	3.38
NC-10	6.87-7.71	1.21	3.40

Thermogravimetric Analysis

The TGA data were used to establish the initial degradation temperature, degradation rate, residual weight at the end of degradation, and degradation kinetic parameters. The weight loss of polyesters during thermal degradation is a function of degradation rate and degradation time. At a higher heating rate, although the degradation rate was higher, the time to reach a given temperature became shorter and the residual weight at a given temperature during thermal degradation may be higher. The remaining solid residue after complete pyrolysis was char and ash. TGA was used to determine the thermal degradation characteristics and kinetic parameters. An attempt is made to assess the thermal stability of some of the polyesters qualitatively based on visual obtained thermograms. T_0 and T_{10} are some of the main criteria of the thermal stability of the polyesters. The higher the T_0 and T_{10}, the higher will be the heat stability of polyesters. TGA curve obtains at a scan rate of 10°C/min for polyesters.

The thermal properties of the NC-1 were examined by TGA at a heating rate of 100ºC/min under a nitrogen atmosphere. The 10% weight loss temperature of the aromatic polyester in nitrogen was recorded at 277 ºC. The 50% weight loss temperature of the aromatic polyester in nitrogen was recorded at 567ºC.

The thermal properties of the NC-5 were examined by TGA at a heating rate of 100ºC/min under a nitrogen atmosphere. The 10% weight loss temperature of the aromatic polyester in nitrogen was recorded at 266 ºC. The 50% weight loss temperature of the aromatic polyester in nitrogen was recorded at 576 ºC.

TGA thermograms of NC-1 and NC-5 polyesters are shown in Figs.-8 and 9 respectively which exhibited high thermal stability.
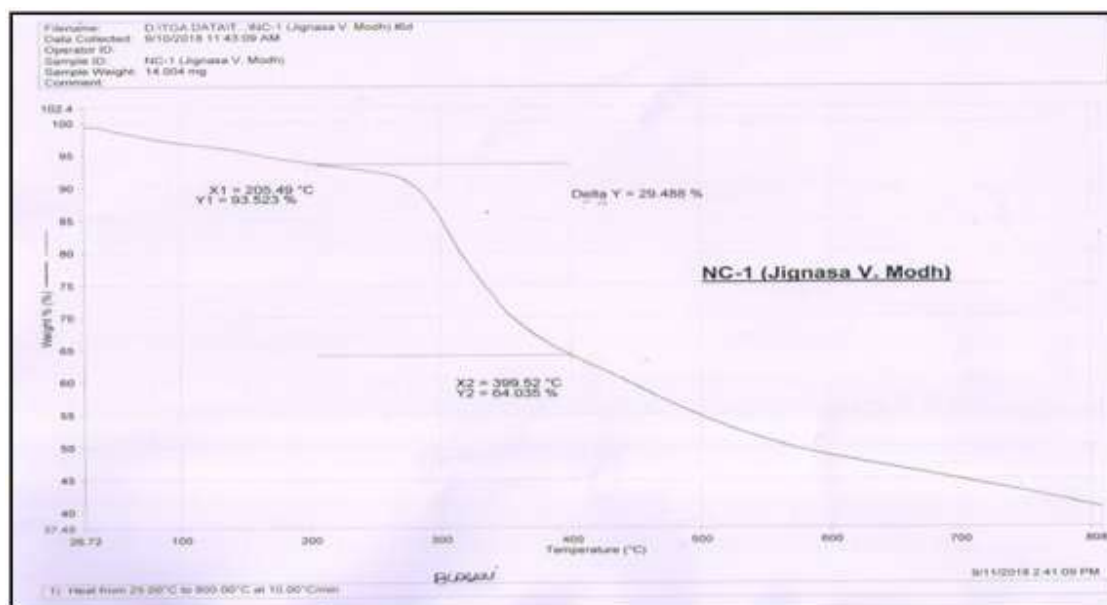

Fig.-8: TGA Thermograms of NC-1

Thermal characteristics of NC-1 and NC-5 are described in Tables- 6,7,8,9 and 10.

Table-6: Thermal Characteristics of Polyesters NC-1 and NC-5.

Polymer	T_0 (ºC)	T_{10} (ºC)	T_{max}		T_s ºC
			Step-1	Step-2	
NC-1	157.04	277.04	317.04	507.04	417.04
NC-5	146.49	266.49	316.49	516.49	416.49
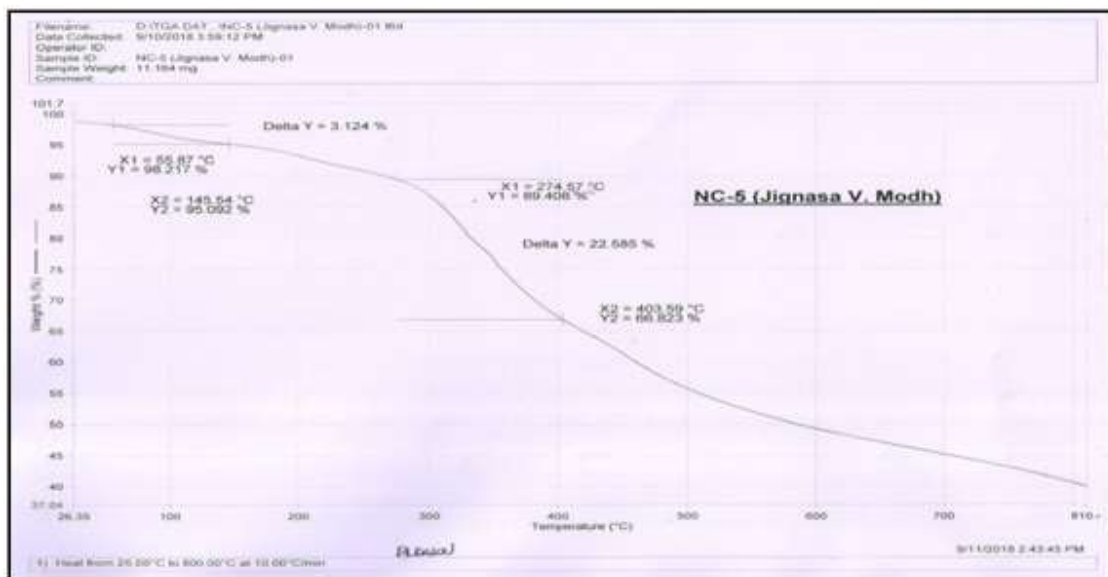
Fig.-9: TGA Thermograms of NC-5

Table-7: Broido Method of Polyesters NC-1.

T °C	%Wt	Y= Wt-W∞ / W0-W∞	1/Y	lnln [1/Y]	T ºK	1000/ T (K⁻¹)
290	86.07	0.7745	1.2911	-1.3645	563	1.7761
300	82.88	0.7195	1.3898	-1.1112	573	1.7452
310	79.46	0.6615	1.5117	-0.8837	583	1.7152
320	76.71	0.6148	1.6265	-0.7206	593	1.6863
330	74.15	0.5713	1.7503	-0.5801	603	1.6583
340	71.40	0.5246	1.9062	-0.4383	613	1.6312
350	69.43	0.4912	2.0358	-0.3412	623	1.6051

Table-8: Horowitz- Metzger Method of Polyester NC-1.

T °C	%Wt	1-α	1/ 1-α	lnln [1/1-α]	θ °K
290	86.07	0.7745	1.2911	-1.3645	-30
300	82.88	0.7195	1.3898	-1.1112	-20
310	79.46	0.6615	1.5117	-0.8837	-10
320	76.71	0.6148	1.6265	-0.7206	0
330	74.15	0.5713	1.7503	-0.5801	10
340	71.40	0.5246	1.9062	-0.4383	20
350	69.43	0.4912	2.0358	-0.3412	30

Table-9: Broido Method of Polyesters NC-5.

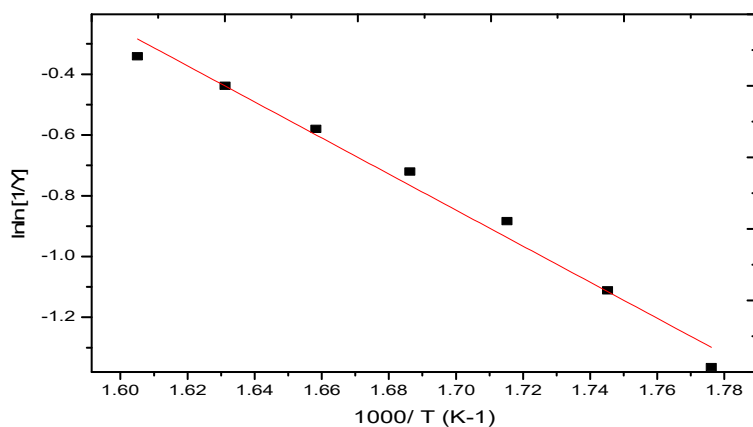| T ºC	%Wt	Y= Wt-W∞ / W0-W∞	1/Y	lnln [1/Y]	T ºK	1000/ T (K⁻¹)
280	88.47	0.8240	1.2135	-1.6424	553	1.8083
290	87.33	0.8046	1.2428	-1.5261	563	1.7761
300	85.74	0.7775	1.2861	-1.3798	573	1.7452
310	83.72	0.7430	1.3458	-1.2140	583	1.7152
320	81.44	0.7041	1.4202	-1.0475	593	1.6863
330	79.17	0.6654	1.5028	-0.8981	603	1.6583
340	77.35	0.6342	1.5767	-0.7867	613	1.6312

Fig.-10: Broido Plot for NC-1

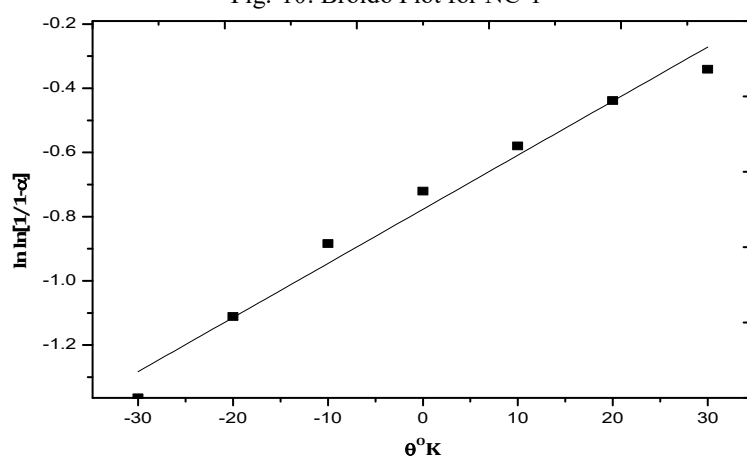
Fig.-11: Horowitz- Metzger Plot for NC-1.

Table-10: Horowitz- Metzger Method of Polyester NC-5.

T ºC	%Wt	1-α	1/ 1-α	lnln [1/1-α]	θ ºK
280	88.47	0.8240	1.2135	-1.6424	-30
290	87.33	0.8046	1.2428	-1.5261	-20
300	85.74	0.7775	1.2861	-1.3798	-10
310	83.72	0.7430	1.3458	-1.2140	0
320	81.44	0.7041	1.4202	-1.0475	10
330	79.17	0.6654	1.5028	-0.8981	20
340	77.35	0.6342	1.5767	-0.7867	30

Fig.-12: Broido Plot for NC-5

1467

Jignasa V. Modh and Saurabh. K. Patel
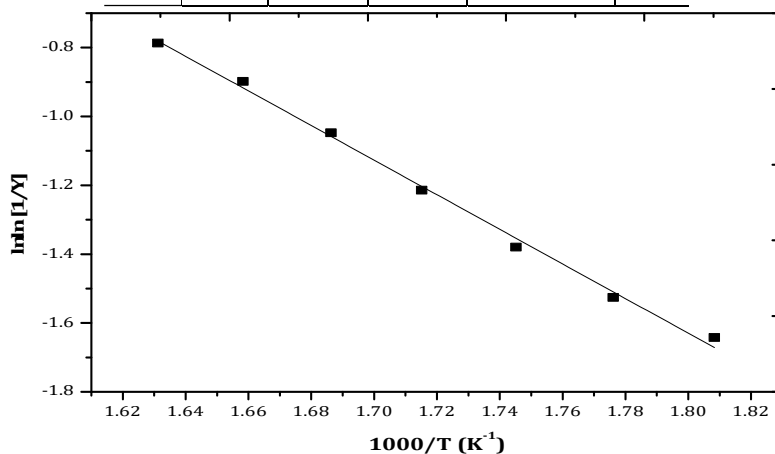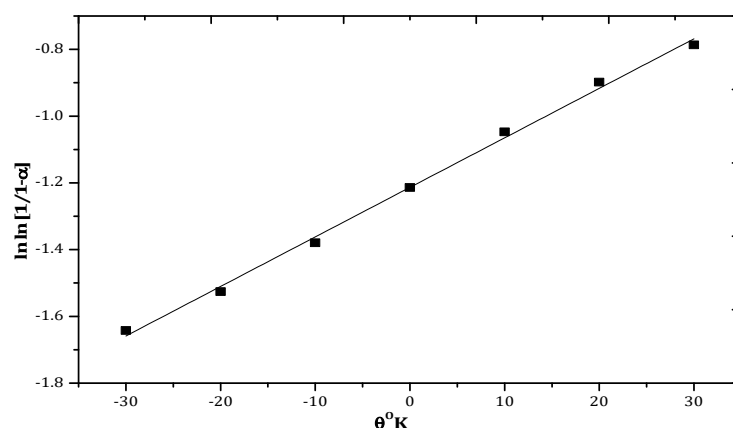
Fig.-13: Horowitz- Metzger Plot for NC-5

Linear deterioration analysis of the experimental data gives the straight lines. The values of apparent activation energy corresponding to degradation steps involved are evaluated from the data and are presented in Table. An examination of the energy of activation E in Table-11 reveals that both the methods yield analogous value for E.

Table-11: Activation Energy From Broido and Horowitz and Metzger Method.

Polymer Code	Broido	Horowitz- Metzger	
	Ea (K.Cal/mol)	Ts	Ea (K.Cal/mol)
NC-1	11.78	613	11.94
NC-5	9.97	608	10.28

Broido method is expected to provide comparatively consistent estimates of E than Horowitz-Metzger's method as no other temperature characteristics are involved. Activation energy Ea value for NC-1 and NC-5 are 11.78 and 11.96, respectively, which are calculated by Broido method. Activation energy Ea value for NC-1 and NC-5 are 9.97 and 10.28, respectively, which are calculated by Horowitz & Metzger method.

Fluorescence Spectra

The fluorescence spectrum of the polyesters NC-1 which is synthesized from 7 –Hydroxy 4- Methyl Coumarin, N-phenyl anthranilic acid and Bisphenol – A as an aromatic diol and the polyester NC-6 which is synthesized from 7 –Hydroxy 4- Methyl Coumarin, N-phenyl anthranilic acid and 1,6 Haxene Diol as an aliphatic diol are shown in Figs.-14 and 15.
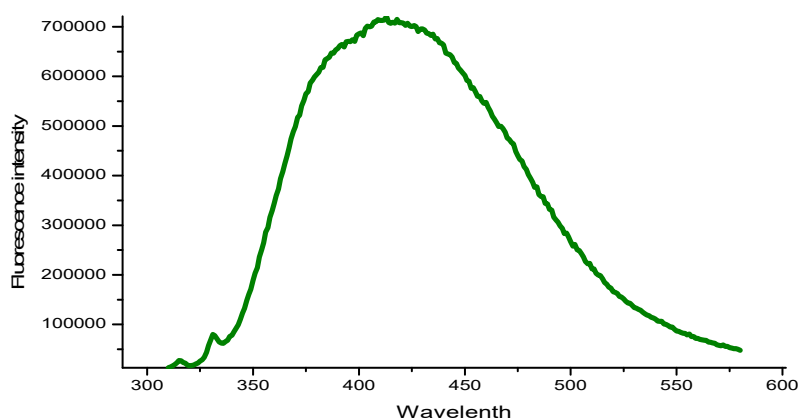

Fig.-14: Fluorescence Spectrum of NC-1.

Polyester NC-1 and NC-6 were dissolved in DMSO-D_6 and then excited at 310 nm. Emission spectra were recorded between 250 and 800 nm. Upon excitation at 250 nm, the fluorescence spectrum of NC-1 and NC-

6 indicates a broaden emission range between 290- 600 nm. The emission peak of NC-1 at 425 nm and an emission peak of NC-6 at 400 nm. The fluorescence intensity of NC-6 is higher than NC-1. The diminishing of fluorescence intensity does not follow the first-order kinetics model. One can suggest that at least two processes are responsible for the decrease of fluorescence: (1) concentration of fluorescent decreases due to photo cyclization reaction, and (2) fluorescence photo quenching operates in this system via the intermolecular mechanism of energy transfer in photo stationary state.
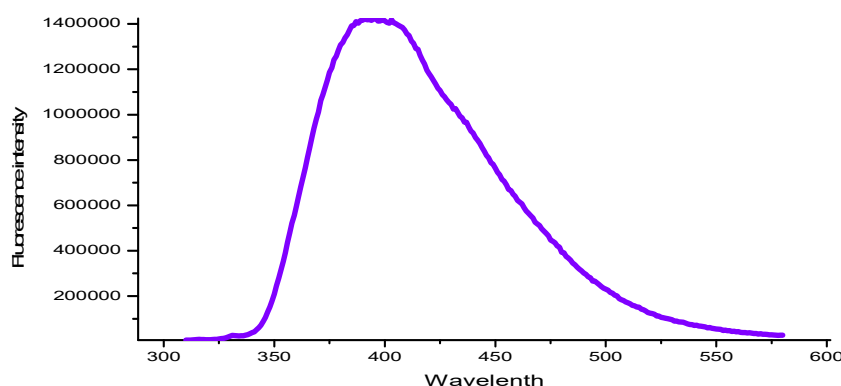

Fig.-15: Fluorescence Spectrum of NC-6.

CONCLUSION

Newer polyester having an s-triazine ring with N-phenyl anthranilic acid and 7- hydroxy 4 methyl coumarin linkage in the main chain was successfully synthesized by high-temperature polycondensation. The resulting polyesters show outstanding colors and good thermal stability. All the polyesters have poor solubility in halogenated and non-polar solvents, but soluble in dimethylformamide, dimethyl sulfoxide, tetrahydrofuran and ethyl acetate. All the synthesized polyesters show excellent fluorescence which can be used in fluorescent probe, advanced bioimaging, ultrasensitive molecular diagnosis, novel light-emitting nanodevices, chemosensors, biological imaging and drug delivery.

ACKNOWLEDGMENT

REFERENCES

1. K. Wang, W. Huang, P. Xia, C. Gao, D. Yan, *Reactive & Functional Polymers,* **52**, 143(2002), **DOI:**10.1016/S1381-5148(02)00088-3
2. J. Lin, Y. Yuki, H. Kunisada, S. Kondo, *Applied Polymer Science*, **40**, 2113(1990), **DOI:** 10.1002/app.1990.070401124
3. K. Saida, M. Sakai, T. Narahara, Japan Patent (Jpn Kokai Tokkoya Koho), **52**, 136(1977)
4. C.P.R. Nair, K.N. Ninan, *Polymers & Polymer Composites*, **12(1)**, 55(2004**), DOI:** 10.1177/096739110401200105
5. H. Sheng, F. Zhao, X. Yu, K. Naito, X. Qu, Q. Zhang, *High Performance Polymer,* 1(2015), **DOI:** 10.1177/0954008315591192
6. P. May, *Polymer electronics. Phys. World*, **8**, 52(1995)
7. H. Nakada, T. Tohma, *Inorganic and Organic Electroluminescence*; (Wissenschaft-und- Technik: Berlin), Germany, 385(1996)
8. A.O. Patil, A.J. Heeger, F. Wudl, *Chemical Reviews*, **88(1)**, 183(1988), **DOI:** 10.1021/cr00083a009

9. J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L.Burns, A.B. Holmes, *Nature*, **347**, 539(1990)
10. D. Bradley, *Current Opinion in Solid State & Material Science*, **1**, 789(1996)
11. A.C. Show, H.J. Tzu, H.L. Hsin, *Journal of the Chinese Chemical Society*, **57**, 439(2010)
12. K.C. Fox, *New Science*, **141**, 3(1994)
13. D.R. Baigent, N.C. Greenham, J. Grüner, R.N. Marks, R.H. Friend, S.C. Moratti, A.B. Holmes, *Synthetic Metals*, **67**, 3(1994)
14. P. Yam, *Scientific American*, **273**, 74(1995)
15. M. Tasior, Y.M. Poronik, O. Vakuliuk, B. Sadowski, M. Karczewski, D.T. Gryko, *The Journal of Organic Chemistry*, **79(18)**, 8723(2014), **DOI:** 10.1021/jo501565r
16. C. Yu, Y. Wu, F. Zeng, X. Li, J. Shi, S. Wu, *Biomacromolecules,* **14(12)**, 4507(2013), **DOI:** 10.1021/bm401548u
17. M.A. Halim, *Nanomaterials*, **3**, 22(2013), **DOI:** 10.3390/nano3010022
18. J. Donovalová, M. Cigáň, H. Stankovičová, J. Gašpar , M. Danko, A. Gáplovský, P. Hrdlovič, *Molecules*, **17**, 3259(2012), **DOI:** 10.3390/molecules17033259
19. L.H. Zhang, T. Jian, L.B. Wan, *Chemistry-An Asian Journal*, **7,** 1583(2012), **DOI:** 10.1002/asia.201200070
20. W.Y. Li, J.G. Xu, X.W. He, *Analytical Letters*, **33(15)**, 3183(2000), **DOI:** 10.1080/00032719.2000.10399494
21. I. Soutar, L. Swanson, F.G. Thorpe, C. Zhu, *Macromolecules,* **29(3)**, 918(1996), **DOI:** 10.1021/ma9508717
22. J.R. Lakowicz, Plenum Press, New York, (1999).
23. J.S. Yang, T.M. Swager, *American Chemical Society,* **120(21)**, 5321(1998), **DOI:** 10.1021/ja9742996
24. M.A. Winnik, S.M. Bystryak, Z. Liu, *Macromolecules*, **31(20)**, 6855(1998), **DOI:** 10.1021/ma980672y
25. D. V. Vasava, S. K. Patel, *International Letters of Chemistry, Physics and Astronomy,* **70**, 48 (2016)
26. K. Wang, W. Huang , P. Xia , C. Gao , D. Yan, *Reactive & Functional Polymers,* **52(3),** 143(2002), **DOI:** 10.1016/S1381- 5148(02)00088-3
27. A. Solankee, R. Patel, K. Patel, *Der Pharma Chemica*, **3 (6)**, 317(2011)
28. S.G. Sanadhya, S. L. Oswal and K.C. Parmar, *Journal of Chemical and Pharmaceutical Research*, **6(4)**, 705**(**2014)
29. Y.T. Chern and C.M. Huang, *Polymer,* **39(11),** 2325(1998), **DOI:**10.1016/S0032-3861(97)00519-3
30. P. Ambrosanioa, R. Centorea, S. Concilioa, B. Panunzib, A. Sirigua, N. Tirelli, *Polymer*, **40**, 4923(1999), **DOI:** 10.1016/S0032-3861(98)00720-4

[RJC-5683/2020]