Final report

On

The work done under

The UGC Scheme of Major Research Project

(UGC's letter F. No. F.No. 39-811/2010(SR) dated:11-01-2011)

(Duration: from 01.02.2011 to 31.01.2014)

Entitled

"Liquid Crystal Forming Polymers: Synthesis, characterizations and their evaluation for potential applications"

Submitted

To

University Grants Commission

New Delhi, India

By

Prof. (Dr.) R. C. TANDEL

(Principal investigator)

Department of Applied Chemistry
Faculty of Technology and Engineering, Kalabhavan
The M.S. University of Baroda, Vadodara
Gujarat

March, 2014

FACULTY OF TECHNOLOGY & ENGGINEERING
The Maharaja Sayajirao University of Baroda
UGC Major Research Project, Applied Chemistry Department
RECEIPT AND EXPENDITURE STATEMENT FOR THE YEAR 2013-2014

16/6/2014

Sanction Letter	:	**F. No.39-811/2010(SR) 11.01.2011**
Total cost of the Project	:	**Rs. 8,63,800.00**
Date of Implementation of the Project	:	**01.02.2011**
Date of completion of the Project	:	**31.01.2014**
Title of the Project	:	**"Liquid Crystal Forming Polymers : synthesis, characterizations and applications"**

Sr. No.	Sanctioned Heads	Fund Allocated (Rs.)	Total Grant Received up to 2013 (Rs.)	Expenditure 2011-2012 (Rs.)	Expenditure 2012-2013 (Rs.)	Expenditure 2013-2014 (Rs.)	Total expenditure Up to March 2014 (Rs.)	Balance as per Received Grants on 31st march 2013 (Rs.)
A.	**Non- Recurring**							
1.	Books & Journals	30,000.00	30,000.00	--	12,932.00	----	12,932.00	17,068.00
2.	Equipments	2,00,000.00	2,00,000.00	--	1,99,890.00	---	1,99,890.00	110.00
B.	**Recurring**							
1.	Project Fellow	2,88,000.00	1,44,000.00	53,419.00	88,000.00	65,333.00	2,06,752.00	-62,752.00
2.	Chemicals/Glassware	2,00,000.00	1,00,000.00	25,984.00	1,52,304.00	---	1,78,288.00	-78,288.00
3.	Hiring Services	20,000.00	10,000.00	-	-	--	--	10,000.00
4.	Contingency	50,000.00	25,000.00	9,942.00	12,247.00	--	22,189.00	2,811.00
5.	Travel/Field work	20,000.00	10,000.00	3,964.00	11,352.00	---	15,316.00	-5,316.00
6.	Overhead charges	55,800.00	55,800.00	--	48,753.00	---	48,753.00	7,047.00
	TOTAL	**8,63,800.00**	**5,74,800.00**	**93,309.00**	**5,25,478.00**	**65,333.00**	**6,84,120.00**	**- 1,09,320.00**

Total Grant Sanctioned	:	**Rs. 8,63,800.00**
Total Grant Received up to 31st March, 2013	:	**Rs. 5,74,800.00**
Expenditure up to 31st March, 2014	:	**Rs. 6,84,120.00**
Total Balance on 31st march, 2014	:	**Rs. - 1,09,320.00**

(Dr. R.C.Tandel)

Principal Investigator

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

TALATI & TALATI
BARODA
Chartered Accountants

Registrar
M. S. University of Baroda

HEAD
Department of Applied **Chemistry**

DEAN
Faculty of Tech. & Engg.

Chief Accounts Officer (O.S.D.)
The M.S. University of Baroda
Vadodara.

Dean
Faculty of Tech & Engg
M. S. University of Baroda
Baroda

talati & talati
Chartered Accountants

Audit Report

We have examined the Receipt and Payment Account of "Liquid Crystal forming Polymers: Synthesis, characterization and their evaluation for potential applications of Department of Baroda." Of UGC Major Research Project, Applied Chemistry Department, Faculty of Science, M.S.University of Baroda, for the Period 1st April, 2013 to 31st March, 2014, which are in agreement with the Books of Accounts maintained by the Principal Investigator.

We have obtained all information & explanations, which to the best of our knowledge and belief were necessary for the purpose of Audit.

In our opinion and as per the information and explanations given to us, the said accounts give true and fair view.

In case of Receipt and Payment Account of the period ending on 31st March, 2014.

The presented particulars are annexed hereto.

For talati & talati
Chartered Accountants

(CA. Nishith Desai)
Partner
14.10.2014
Vadodara.

TALATI & TALATI
BARODA
Chartered Accountants

Title Project "Liquid crystal forming Polymers: Synthesis, characterization and their evaluation for potential applications."

Receipt and Payment Account for the period 01/04/2013 to 31/03/2014

Receipt	**Amount (Rs.)**	**Payment**	**Amount (Rs.)**
Grant received in the financial year 2012-13	**NIL.**	**Excess of expenditure over grant in Financial year 2012-13**	**43,987**
		Project Fellow	65,333
Excess of Expenditure over income	**1,09,320**	**Sub Total (Expenses)**	**1,09,320**
TOTAL	**1,09,320**	**TOTAL**	**1,09,320**

We further certify that...

As per our audit Rs. 1,09,320/- is deficit grant as on 31st March, 2014. The accounts have been checked with vouchers and records produced before us and it are certified that the grant has been utilized for the purpose for which it is sanctioned as shown in the statement of Expenditure.

Utilization Certificate is attached herewith.
As per our Report of even date annexed herewith.

For talati & talati
Chartered Accountants

(CA. Nishith Desai)
PARTNER

14.10.2014
Vadodara.

Principal Investigator

UGC Major Research Project
Department of Chemistry
M.S. University of Baroda.

(Dr. R.C. Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Annexure-V

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG NEW DELHI–110002

STATEMENT OF EXPENDITURE IN RESPECT OF MAJOR RESEARCH PROJECT

1. Name of Principal Investigator : Prof. (Dr.) R.C. TANDEL

2. Dept. of University/College : Department of Applied Chemistry, Faculty of Tech. and Engg. The M.S.University of Baroda, Vadodara

3. UGC approval No. and Date : F.No. 39-811/2010(SR) dated:11-01-2011

4. Title of the Research Project: **"Liquid Crystal Forming Polymers: Synthesis, Characterizations and their Evaluation for Potential Applications"**

5. Effective date of starting the project : **01-02-2011**

6. a. Period of Expenditure : **From 1-02-2011 to 31-01-2014**

b. Details of Expenditure:

Sr. No.	**Items**	**Amount Approved (Rs.)**	**Total Expenditure incurred (Rs.)**
1.	Books & Journal	30,000.00	12,932.00
2.	Equipments	2,00,000.00	1,99,890.00
3.	Honorarium (project fellow)	2,88,000.00	2,06,752.00
4.	Contingency	50,000.00	22,189.00
5.	Travel/fieldwork	20,000.00	15,316.00 (As per Annexure:VI)
6.	Chemicals & Glassware	2,00,000.00	1,78,288.00
7.	Hiring Services	20,000.00	------
8.	Overhead	50,800.00	48,753.00

*Re-appropriated to the Contingency from the budget head "Travel/Field Work".

c. Staff Date of Appointment : 11.07.2011

1.	Honorarium to PI (Retired Teachers) @Rs. 18,000/-p.m.	------	------	-----	------
2.	**Non-GATE/Non-NET** Rs.4,000/- p.m. for initial 2 years and Rs. 16,000/- p.m. for the third year.	11.07.2011	31.01.2014	2,88,000.00	2,06,752.00

1. It is certified that the appointment(s) have been made in accordance with the terms and conditions laid down by the Commission.
2. It as a result of checks or audit objective, some irregularly is noticed, later date, and action will be taken to refund, adjust or regularize the objected amounts.
3. Payment @ revised rates shall be made with arrears on the availability of additional funds.

It is certified that the grant of <u>Rs. **5,74,800.00**</u> **<u>(Rupees Five Lakh seventy Four Thousand Eight Hundred only)</u>** received from the University Grant Commission under the scheme of support for Major Research Project entitled **"Liquid Crystal Forming Polymers : synthesis, characterizations and applications"** vide UGC letter No. F**<u>. 39-811/2010(SR) dated 11-01-2011,</u>** out of which **<u>Rs 6,84,120.00</u> (Rupees six lakh eighty four thousand one hundred twenty only)** has been fully utilized for the purpose of which it was sanctioned and in accordance with the terms and conditions as laid down by the University Grants Commission.

Principal Investigator

(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head

Applied Chemistry Dept.

Registrar
M. S. University of Baroda.

Registrar

The M.S. Univ. of Baroda

3/12/14

Chief Accounts Officer (O.S.D.)
The M.S. University of Baroda
Vadodara.

TALATI & TALATI
BARODA

Annexure- VI

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002.

STATEMENT OF EXPENDITURE INCURRED ON FIELD WORK

Name of the Principal Investigator

Name of the Place visited	Duration of the Visit		Mode of Journey	Expenditure Incurred (Rs.)
	From	To		
Indore	Vadodara	Indore	Rail	3964=00
Delhi (UGC)	Vadodara	Delhi	Air	11352=00
			TOTAL (Rs.)	15316=00

Certified that the above expenditure is in accordance with the UGC norms for Major Research Projects.

Signature of Principal Investigator

(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head,
Applied Chem. Department

Registrar
M. S. University of Baroda.
The M. S. Univ. of Baroda

UGC Major Research Project
"Synthesis... Polymers ...Applications"
Chemistry Department
Faculty of Science
M.S. University of Baroda.

Annexure –VIII

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002

Final Annual Report of the work done on the Major Research Project

1. Project report No: **Final Report**

2. UGC Reference No: **F.39-811/2010(SR) dated:11-01-2011**

3. Period of report: From 1/02/2011 to 31/01/2014

4. Title of the research project: **" Liquid Crystal Forming Polymers : synthesis, characterizations and applications"**

5. (a) Name of the Principal Investigator : Dr. R.C.Tandel

(b) Dept. and University/College where work has progressed: Department of Applied Chemistry, The M.S.University of Baroda Dist. Vadodara, Gujarat state, India

6. Effective date of starting of the project: 1-02-2011

7. Grant approved and expenditure incurred during the period of the report:

a. Total amount approved: Rs. 8, 63,800.00 (1st installment received Rs. 5,74,800 /-)

b. Total expenditure : Rs. 6, 84,120.00

c. Report of the work done: please refer attached Sheet:I

i. Brief objective of the project: please refer attached Sheet : II)

ii. Work done so far and results achieved and publications, if any (Paper Attached)
"Synthesis and study of main chain chalcone polymers exhibiting nematic phases",
Tandel R C., Gohil Jayvirsinh and Patel Nilesh K.,
Research Journal of Recent Sciences, Vol.1 , 122-127, 2012

iii. Has the progress been according to original plan of work and towards achieving the objective? Yes

iv. Please indicate the difficulties, if any, experienced in implementing the project: A little bit delay in characterization of derivatives.

v. If project has not been completed, please indicate the approximate time by which it is likely to be completed: completed

vi. If the project has been completed, please enclose a summary of the findings of the study. Two bound copies of the final report of work done may also be sent to the Commission: Kindly refer attached **Sheet : I.**

vii. Any other information which would help in evaluation of work done on the project. At the completion of the project, the first report should indicate the output, such as (a) Manpower trained (b) Ph. D. awarded (c) Publication of results (d) other impact, if any: Mr. Jayvirsinh D.Gohil, a Project fellow.

Principal Investigator
(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head
Applied Chemistry Dept.

Registrar
The M.S. Univ. of Baroda

Registrar
M. S. University of Baroda

Annexure – IX

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002
UGC F . No.-39-811/ 2010(SR) 11.01.2011

YEAR OF COMMENCEMENT 01 | 02 | 2011

TITLE OF THE PROJECT : **"Liquid Crystal Forming Polymers : synthesis, characterizations and their evaluation for potential applications"**

<table>
<tr><td>1.</td><td>Name Of the Principal Investigator</td><td colspan="4">Dr R.C.Tandel</td></tr>
<tr><td>2.</td><td>Name of the University/College</td><td colspan="4">M.S. University of Baroda</td></tr>
<tr><td>3.</td><td>Name of the Project Fellow appointed</td><td colspan="4">Mr.Jayvirsinh D.Gohil</td></tr>
<tr><td rowspan="2">4.</td><td rowspan="2">Academic qualification</td><td>Sr.no.</td><td>Qualification</td><td>Year</td><td>%age</td></tr>
<tr><td>1.</td><td>M.Sc.</td><td>2010</td><td>63.54</td></tr>
<tr><td>5.</td><td>Date of joining</td><td colspan="4">11.07.2011</td></tr>
<tr><td>6.</td><td>Date of Birth of Project Fellow</td><td colspan="4">30.06.1985</td></tr>
<tr><td>7.</td><td>Amount of HRA, if drawn</td><td colspan="4">--------</td></tr>
<tr><td>8.</td><td>Number of Candidate applied for the post</td><td colspan="4">09</td></tr>
</table>

CERTIFICATE: **This is to certify that all the rules and regulation of UGC Major Research Project outlined in the guidelines have been followed. Any lapses on the part of the University will liable to terminate of said UGC project.**

Principal Investigator

(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head

Applied Chemistry Dept.

Registrar
M. S. University of Baroda.
The M. S. Univ. of Baroda

Annexure – X

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFAR MARG
NEW DELHI – 110 002
UGC F. No.-39-811/ 2010(SR) 11.01.2011

This is certify that Mr. Jayvirsinh Dilipsinh Gohil is eligible to draw a House Rent Allowance @ 2800/-(20% of revised fellowship,14000/-) as per Centre Government Rules.

Principal Investigator
(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head
Applied Chemistry Dept.

Registrar
Registrar
M. S. University of Baroda
The M.S. Univ. of Baroda

☎ 23238351, 23232701, 23237721, 23234116
23235733, 23232317, 23236735, 23239437

UGC Website : www.ugc.ac.in

विश्वविद्यालय अनुदान आयोग
बहादुरशाह जफर मार्ग
नई दिल्ली-110 002
UNIVERSITY GRANTS COMMISSION
BAHADURSHAH ZAFAR MARG
NEW DELHI-110 002

F.2-2/2011(SAP-II)

December, 2011

The Registrar
All Universities

Sub: - Enhancement of fellowship amount in respect of the Research Fellows/Project Fellows working under the schemes of Major Research Projects and Special Assistance Programme of UGC.

Sir,

I am directed to inform you that the UGC has revised the fellowship amount in respect of the above fellows w.e.f. 1.4.2010 as per details given below.

Project Fellows in SAP / MRP	**Existing Rate (Rs.)**	**Revised Rate (Rs.)**	**House Rent Allowance (HRA)**
Non-Gate/ Non NET Candidates	Rs.8,000/- p.m.	(i)Rs.14,000/-p.m. for initial 2 years (ii)Rs.16,000/-p.m. from the third year onwards.	As per Central govt. norms
Gate/GPAT/NET Candidates	Rs.8,000/- p.m.	(i)Rs.16,000/-p.m. for initial 2 years (ii)Rs.18,000/-p.m. from the third year onwards.	As per Central govt. norms

This may please be brought to the notice of all the departments of the University. The department/university may send the claim for the arrears accordingly.

Yours faithfully

(V.P. Arora)
Under Secretary

Copy to :- FA, DS(FD), SO(FD-III)
DS(MRP), UGC
SO(SR/MRP) SO(HR/MRP)

(V.P. Arora)
Under Secretary

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

UGC Major Research Project
"Synthesis .. Polymers ...Applications"
Chemistry Department
Faculty of Science
M.S. University of Baroda.

Dr. R. C. Tandel
Professor

Department of Applied Chemistry
Centre of Advanced Studies in Chemistry & DST-FIST sponsored Department
Faculty of Technology and Engineering, Kalabhavan, Vadodara 390 002
India Tel: +91-265-2410512
Email: tandelcy@yahoo.com

The Maharaja Sayajirao University of Baroda

Statement showing the details of sanctioned fellowship and arrears of the revised fellowship & HRA to be paid for revised fellowship w.e.f. 1-4-2010

1.Name of the Project : **"Liquid Crystal Forming Polymers : Synthesis, characterizations and their evaluation for potential Applications"** of **Dr. R. C. Tandel**, Department of Applied Chemistry (01-02-2011 to 31-01-2014)

2. Sanction Letter No. Date : **F.No.39-811/2010 (SR), dated 11-01-2011**

3. Starting Date : 01-02-2011

4. Name of the Project Fellow : **Jayvirsinh Dilipsinh Gohil**

5. Date of Appointment : **11-07-2011**

(1) Ist year – 11-07-2011 to 10-07-2012

(2) IInd year – 11-05-2012 to 10-05-2013

(3) IIIrd year – 11-05-2013 to 05-09-2013

Sr. No.	Month/ Year	Already Sanctioned (Rs.)	Revised Fellowship	Difference/ Arrears (To be paid)	Arrears of Payable HRA (To be Paid)	Total Diff./Arrears (Fellowship + HRA) (To be paid)
1.	July, 2011(**1st year**) (21 days)	5,419.00	9,484.00	4,064.00	1,897.00	5,961.00
2.	August, 2011	8,000.00	14,000.00	6,000.00	2,800.00	8,800.00
3.	September, 2011	8,000.00	14,000.00	6,000.00	2,800.00	8,800.00
4.	October, 2011	8,000.00	14,000.00	6,000.00	2,800.00	8,800.00
5.	Nov, 2011	8,000.00	14,000.00	6,000.00	2,800.00	8,800.00
6.	December, 2011	8,000.00	14,000.00	6,000.00	2,800.00	8,800.00

1.	**Grant (As per Revised Fellowship) with HRA**	**Fellowship:** **Payable HRA:**	3,65,505.00 73,101.00
		Total:	**4,38,606.00**
2.	**Grant (As per Sanctioned Fellowship)**	**Fellowship:** **Payable HRA:**	2,06,752.00 00.00
		Total:	**2,06,752.00**
3.	**Arrears Claimed (To be released)**	**Fellowship:** **Payable HRA:**	1,58,751.00 73,101.00
		Total:	**2,31,852.00**

Principal Investigator

(Dr. R C Tandel)

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Head

Applied Chemistry Dept.

HEAD
[illegible]

Registrar
M. S. University of Baroda

Registrar

The M.S. Univ. of Baroda

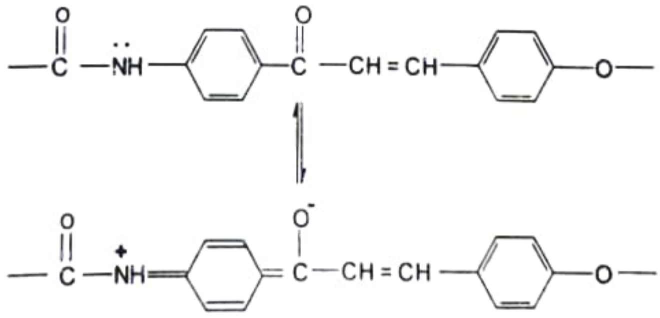
UGC Major Research Project
"Synthesis... Polymers ...Applications"
Chemistry Department
[illegible]

SHEET : I (Final Report)

Report of work done:

The literature survey was carried out to collect information regarding main chain and side-chain polymers having potential for applications. Based on the literature survey the project work was designed. Main chain chalcone polymers were synthesized by condensing acid chlorides of dicarboxylic acids having different flexible spacers with respective amino-hydroxy chalcone and dihydroxy chalcone. A common observation is that the increase in flexibility lowers the transition temperatures and increases stability of nematic phases. A good texture is observed after keeping a polymer sample for sometime on the hot stage of the polarizing microscope. The absence of smectic phase in all the polymers is quit surprising even with ten spacers and one of the amide linkage do not exhibit smectic mesophase. DSC results indicate typical behaviour.

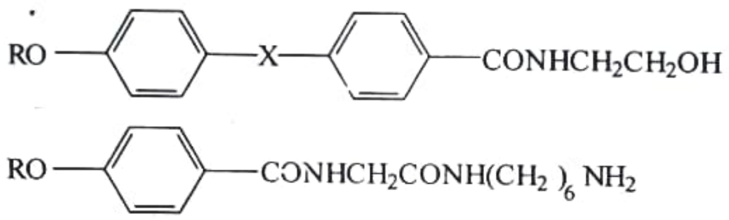
Polyester and polyesteramide having chalcone linkage with increased flexibility by increasing number of methylene spacers to six and ten i.e. $(\text{-CH}_2\text{-})_6$ and $(\text{-CH}_2\text{-})_{10}$ in aromatic diacid moiety, increase the intensity of fluorescence and show higher thermal stability than monomers. The molecule of polyesteramide having chalcone linkage have an electron withdrawing carbonyl group decreasing the possibility of hydrogen bonding by decreasing basicity of *-CONH –* linkage. Due to this reason the enhanced fluorescence properties observed in polyesteramides. Polyesteramides having additional electron withdrawing group (>C=O) attached to benzene nucleus. Cannonic structure in the polyesteramides would also transfer of electron due to the conjugated structure from one end of the molecule to another. [Published paper: "Synthesis and study of main chain chalcone polymers exhibiting nematic phases", Tandel R C., Gohil Jayvirsinh and Patel Nilesh K., Research Journal of Recent Sciences, Vol.1 , 122-127, 2012 , copy attached with final report]



The literature survey was carried out to collect information regarding side-chain polymers having potential for applications. Based on the literature survey the research work was designed in the following sequence.

1) Synthesis of pendant groups
2) Synthesis of monomers with new pendant groups
3) Polymers with pendant groups

Four pendant groups were synthesized involving multistage synthesis steps with following general structure:



where R=C_4H_9 and C_8H_{17}, X=COO and CONH linkages

The pendant groups have different terminal groups. Though they have mesogenic core, except one intermediate none of the intermediates exhibit mesomorphic behavior. This is due to the presence of one or more –CONH- linkages in the chain. At present monomers are being synthesized by using these "pendant group compounds".

Side chain polymers with flexible spacers exhibit mesomorphism. The concept of 'flexible spacer' was originally proposed by Finkelmann et.al. (1). However, it has been pointed out that without 'flexible spacers' side chain polymers can exibit mesomorphism. Even polymer exhibiting mesomorphism with main chain having a broad segment as side chain have been reported. Ringsdorf et al. (2) demonstrated that cross-linking was not necessary in order to maintain cholesteric properties in a polymer. Through use of the concept of flexible spacer groups to decouple the mesogenic units from the restrictions of the main polymer chain, they found a 1:1 methacrylate co-polymer consisting of cholesteryl esters with spacer groups of different length that exhibited cholesteric properties.

Shibaev et al., (3) studied thermotropic Liquid Crystal (LC) polymers having an amide linkage. Gallot et al., (4) reported polyacrylamide segment containing LC polymers. This shows interest in Liquid Crystalline polymers with amide linkage is increasing. Number of polyacrylates and polymethacrylates having side chain with ester linkages and mesogenic pendant groups are reported (5).

The non-mesogenic segment of polymers from P_1 to P_2 is amido-acids. Similar compounds with an ester linkage exhibit liquid crystalline properties. Earlier studies have shown that amide linkage enhanced mesomorphic behaviour of a system (6). In the present study 4-(4'-n-Alkoxy benzoyl)-amino benzoic acids have been synthesized.

R= $-C_4H_9$ and $-C_8H_{17}$

The data indicates that none of the monomers exhibit mesomorphism (7). Acid chloride of respective amido-acid condensed with one mole of 2-amino ethanol also show non-liquid crystalline properties (C4-OH and C8-OH, M.P. 121 and 114 °C respectively). It seems that the amide linkage might be inducing intermolecular hydrogen bonding which would be non-conducive to mesomorphism. Monomers having ester linkage with similar structures give melting points at 143 and 136 °C, respectively. Polymers having ester-amido linkages exhibit birefringence and good fluorescence properties. In the present study it has been found that both polymers exhibit birefringence on cooling the melt with the shear- force. It seems, the melt results in homeotropic arrangement hence classical structure of nematic or smectic phase is not observed.

Solubility :

Solubility of polymers was checked in some common organic solvents at room temperature as well as on heating. Both polymers were completely insoluble in CCl_4, $CHCl_3$, toluene, ethyl acetate, solvent ether at room temperature as well as on heating. It shows good solubility in DMF, DMSO and N- methyl -2-pyrrolidone at room temperature but completely soluble on heating.

Viscosity:

Intrinsic viscosity of polymer samples was calculated by using one point method. The viscosity data indicates that η_{int} value of polymer P-2 is higher compared to P-1 indicates that flexible methylene spacer in polymer MAP-2 is responsible for little higher viscosity of polymer. Intrinsic viscocity of polymer samples P-1 and P-2 was calculated by using one point method as well as it was determined graphically to verify linearity of the viscosity results.

Viscosity data of Polyacrylates :

Solvent:N-Methyl-2-Pyrrolidone ; Temperature :25.0 °C ; Concentration : 0.5 %

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
MAP-1	1.0201	0.0201	0.0805	0.0796	0.0801
MAP-2	1.0436	0.0436	0.0872	0.0853	0.0860

TGA :

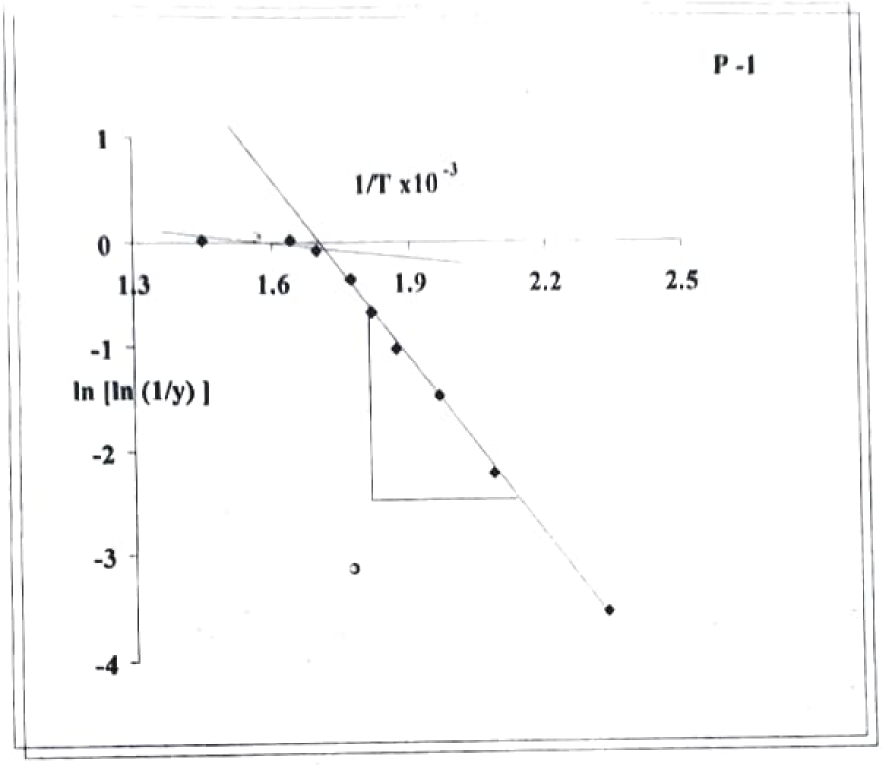
Thermogram of polyacrylates (P-1 and P-2) undergoes two step decomposition. The polymer P-1 loses 10% of its weight at 385 °C. In the range of 391- 410 °C the sample loses 40% of its weight with a maximum rate at 475°C. Above 485 °C, the second step of degradation commences which involves a further weight loss of 12% up to 550 °C with a maximum rate of 520 °C.

The polymer P-2 loses 10% of its weight at 345 °C. In the temperature range 315-410 °C, the polymer sample loses 33% of its weight. The maximum rate of weight loss occurs at 375 °C. Beyond 450 °C the second decomposition step commences with a loss of 11% of its weight, having low rate of weight loss compared to the first step. The maximum rate of weight loss occurs at 565 °C. Using Broido method, the values of activation energy (Ea), for the first step of thermal decomposition are calculated as 36.95, 31.41 and 20.79, that indicate MAP-1 is highly stable.

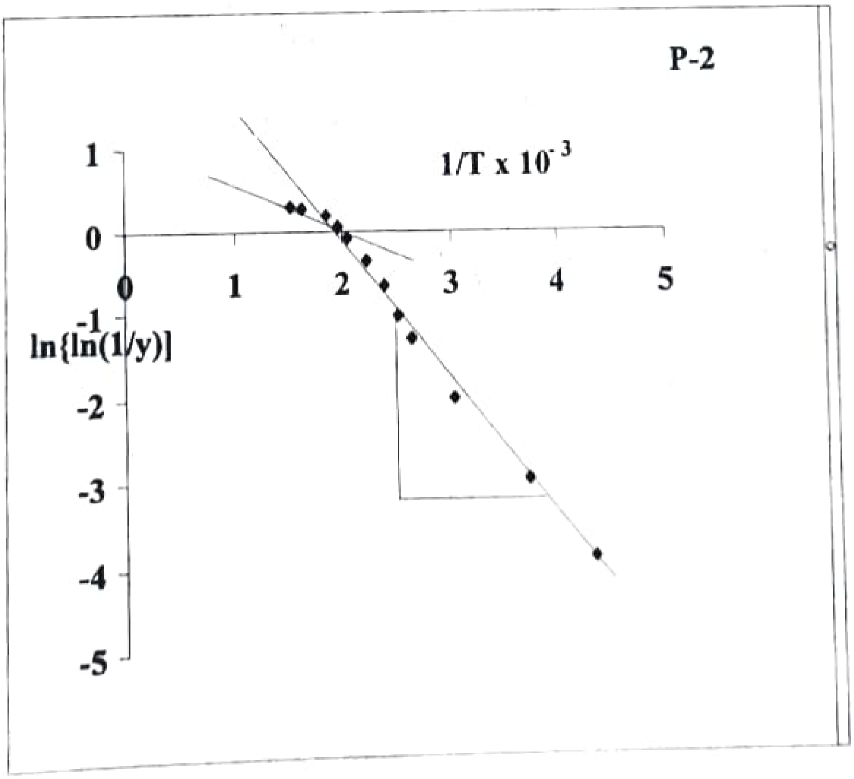
Activation energy (K.cal.mole^{-1}) calculated according to Broido method

Obs. No.	Polymer	Energy of Activation (Ea) (K.cal.mole^{-1})
1.	P-1	37.55
2.	P-2	32.53

Thermal stability of the polyacrylates studied is established on the basis of T_{max} for the first step of decomposition.



Typical Broido plots of ln[ln(1/y)] versus 1/T for step I and step II



Typical Broido plots of ln[ln(1/y)] versus 1/T for step I and step II

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Optical polarized microphotograph of Nematic liquid crystalline phase (Thread like texture) of EP-4 on cooling at 154 ^{0}C (Paper Published)

SHEET: II

Objectives of the project :

Objective of the project is to design, synthesize and evaluate fluorescent mesogenic polymers. It is envisaged that mesogenic polymers due to their highly ordered structure will give quite stable polymer and will also enhance the fluorescence properties.

It is known that polymers having the order of liquid crystalline structure will exhibit all round desired physical properties for better application of polymers. Hence they are also called "self reinforced polymers". If they are designed with fluorescent molecules, we will have a highly ordered fluorescent polymer and if the fluorescence is exhibited in the day light, one can obtain polymers, which can be compared with light emitting diodes.

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Synthesis and Study of Main Chain Chalcone Polymers Exhibiting Nematic Phases

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Abstract

The mesogenic main chain polymers of general structure-I were synthesized and their different properties are studied. All the polymers exhibit nematic phases. Classical nematic textures are observed in these polymers. None of the dihydroxy, amino-hydroxy or dicarboxy compounds shows liquid crystalline properties. The role of flexible methylene spacers, degree of polymerization and central linkage on exhibition of all the polymers is discussed. All the polymers are characterized by standard methods.

Keywords: Liquid crystalline polymers, nematic phase, chalcone linkage, crystalline I –crystalline II etc.

Introduction

The rarity of mesogenic compounds having chalcone linkage and potential of polymers with this linkage for application prompted [1] to study the polymers with chalcone linkage. The first mesogenic homologous series with chalcone linkage have been reported [2] and studied polyesters and polyester-amides by varying flexible methylene spacers from $-(CH_2)_2-$ to $-(CH_2)_4-$ in carboxy phenoxy diacid moiety[3,4]. They also varied the flexibility by using rigid and flexible dicarboxylic acids as co-monomer. The chemistry and physics of high-performance fiber spinning based on main-chain liquid crystal polymer (MCLCP) solutions and melts was discussed, which is the largest industrial application of liquid crystal technology[5]. Recently Schiff-base chalcone linkage thermotropic mesogens have synthesized and study the effect of substituent on liquid crystalline properties[6,7]. The side chain liquid crystalline photoactive polymers with chalcone pandent chalcone moiety were synthesized and characterized[8,9]. However polymers exhibited relatively higher transition temperatures.

The flexibility of the dicarboxylic acid moiety in the system increased by introducing 'oxyethylene spacers' in the place of methylene spacers[10,11]. Solid to mesomorphic and mesomorphic to isotropic transition temperatures were drastically reduced but florescent behavior was not affected. One striking feature of "oxyethylene spacer" polymers was that smectic mesophase was eliminated. This prompted us to investigate polymeric ester and ester-amide having chalcone linkage with increased flexibility by increasing number of methylene spacers to 6 and 10 i.e. $-(CH_2)_6$ and $-(CH_2)_{10}-$. With this in view polyester-amides and polyesters containing chalcone linkage were synthesized by the route given in Figure 1.

It was proposed in the present study to concentrate on flexibility of carboxyl phenoxy diacid moiety by increasing flexibility with high number of methylene spacers to evaluate the effect of increased flexibility on mesogenic properties of polymers with this in view polymers were synthesized by route given in figure 1.

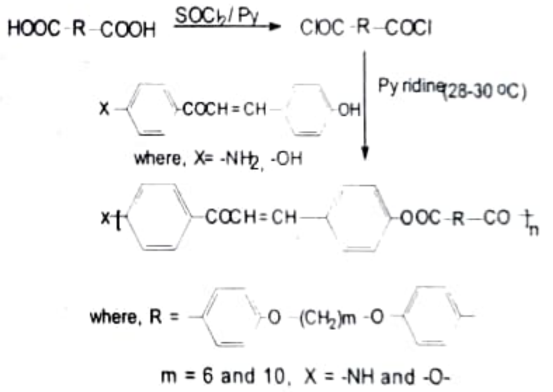

Figure-1
Synthetic route to Polychalcones

Measurements : The synthetic route adopted for the synthesis of polychalcones is shown in Figure:1. Elemental analysis were performed with a Perkin-Elmer 2400, C,H,N analyzer. The IR of polymers was recorded on Perkin-Elmer with KBr pellet. The optical textures of the polymers samples were studied with a Leitz Laborlux 12 Pol (Germany) polarizing microscope fitted with a Kofler heating stage. Ubbelohde Viscometer was used for the measurement of viscosity of polymers in dimethyl formamide as a solvent.

Dr. R. C. Tandel
Principal Investigator
UGC Major Research Project

Material and Methods

Preparation of Different Diacids ω-bis (4-carboxy phenoxy) oligo ethers: Following different diacids were used for the synthesis of polymeric chalcones:1,6-bis(4'-carboxy phenoxy) hexane (DA-I),1,10-bis(4'-carboxy phenoxy) decane (DA-II) The diacids DA-I and DA-II) were synthesized by the same method reported in the literature [12, 13] for synthesis of 1,2-bis (4'-carboxy phenoxy)ethane. p-Hydroxy benzoic acid (0.2 mole) was dissolved in 100 ml 22.4% potassium hydroxide solution (0.4 mole) and 30 ml of alcohol in round bottom flask. Approximate dibromide (0.11 mole) was added to the flask and whole mass was refluxed for 8-10 hours. Reaction mixture was allowed to cool, then acidified with cold 1:1 hydrochloric acid. Solid mass obtained was filtered and washed with water and dilute alcohol. Diacids obtained were recrystallized several times from DMF solvent till constant melting points were obtained. DA-I : 290 °C, Reported 290-292 °C [12,13], DA-II : 273 °C, Reported 273-274 °C [12,13]

Synthesis of Diacid Chlorides of Diacids DA-I and DA-II [14]: Diacid chlorides were prepared by reacting the corresponding diacids with excess of thionyl chloride and heating on a water-bath till the evolution of hydrogen chloride gas ceased. Excess of thionyl chloride was distilled off under reduced pressure using vacuum pump and the diacid chlorides left behind as a residue was used in next reaction without further purification.

Synthesis of different Chalcone: Synthesis of 4,4'-dihydroxy chalcone: **4,4'-dihydroxy benzylidene acetophenone** (HC): 4,4'-dihydroxy chalcone was synthesized according to the hot condensation process[17] 13.6 gms (0.1 mole) 4-hydroxy acetophenone and 13.2 gms (0.1 mole) 4-hydroxy benzaldehyde were dissolved in minimum amount of ethanol, 55 ml of 50% potassium hydroxide was added to the above solution. The flask was heated at 50 °C for twenty hours. The solution was acidified by cold 6 N HCl solution (congored), Yellow crystalline solid separated, which was filtered and washed with water. It was recrystallized from ethanol melting point 204 °C .

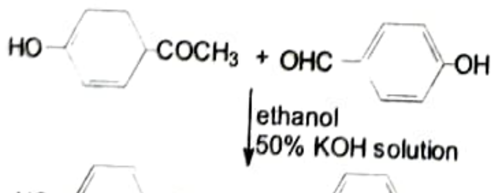

Figure 2
Synthesis of 4,4'-dihydroxy chalcone

Synthesis of 4-amino-4'-hydroxy chalcone: 4-amino-4'-hydroxy benzylidene acetophenone (AHC): 4 -Amino-4'-hydroxy chalcone was prepared by extending the procedure[18] for the para substituted derivative. 13.5 gms (0.1 mole) 4-Amino acetophenone, 12.2 gms (0.1 mole) 4-hydroxy benzaldehyde and a few drops of piperidine in absolute ethanol (40 ml) were taken in round bottom flask and were refluxed for twelve hours. The reaction mass was concentrated up to its half the volume and then reaction mass was poured to ice-water mixture with stirring, solid separated, which was filtered, dried and crystallized from ethanol, M.P. 217 °C

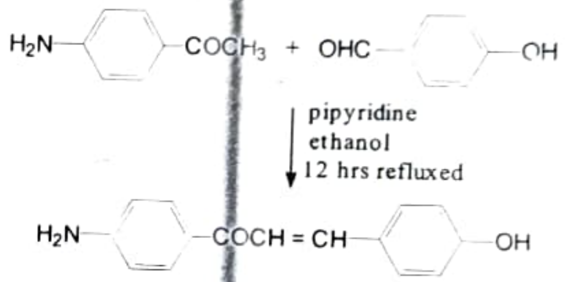

Figure-3
Synthesis of 4-amino-4'-hydroxy chalcone

Polycondensation of different diacid chloride with different chalcones: The diacid chloride of DA-I and DA-II were condensed with respective chalcones by solution polycondensation reaction, pyridine was used as a solvent. The appropriate diacid chloride (0.005 mole) was dissolved in 10 ml dry pyridine and cooled to 0°C in an ice-bath. The solution of respective chalcone (0.005 mole) in 5 ml dry pyridine was added to the diacid chloride with constant stirring. The reaction mixture was guarded against moisture absorption. The temperature of mixture was allowed to rise to room temperature (28-30°C) and stirred for two more hours. It was finally poured into ice-hydrochloric acid mixture and solid separated was filtered, washed with water followed by alcohol to remove unreacted starting materials. Polymers were purified by solvent-non solvent method. DMF was used as a solvent and methanol was used as a non-solvent. The transition temperatures and viscosity data are recorded in table 1 and 2, respectively.

In the IR spectrum of EP-1 and EP-2, the characteristic keto-ester linkage was observed at 1720 and 1740 cm^{-1}, keto of -CH = CHCO – at 1660 and 1655 cm^{-1}, -CH=CH-Ar at 1560 and 1555 cm^{-1} and ν_{C-H} bending of alkane at 1460 and 1455 cm^{-1}, respectively and IR spectrum of EP-3 and EP-4 the characteristic keto-ester linkage was observed at 1740 and 1720 cm^{-1}, -NH- bending at 1690 and 1690 cm^{-1}, -CONH-R at 1510 and 1500 cm^{-1}, keto of amide at 1600 and 1590 cm^{-1}, -CH=CH-Ar at 1570 and 1575 cm^{-1}, respectively. ν_{C-H} bending of aromatic ring obtained at 760, 750 cm^{-1} etc.

Table-1
Transition temperatures of polychalcones

Code no.	**X =**	**m =**	**Transition Temperatures °C**	
			Nematic	**Isotropic**
EP-1	-O-	6	140.0	190.0
EP-2	-O-	10	150.0	280.0
EP-3	-NH-	6	124.0	190.0
EP-4	-HN-	10	141.0	169.0

Results and Discussion

Reference to table 1 indicates that polymers EP-1 to EP-4 exhibit only nematic mesophases. The comparison of mesogenic properties of different polymers is a difficult task as the mesogenic properties of polymers depend not only on the chemical constitution but also on the molecular weight and polydispersity of the system.

In the present study the structure of all the polymers vary uniformly hence intrinsic viscosity values [η_{int}] are taken to compare the properties of polymers. Due to the solubility parameters of the polymers molecular weight determination could not be done by other method. Number of researchers has studied the effect of increased flexibility of methylene spacers on different polymeric systems[19-22]. A common observation is that the increase in flexibility lowers transition temperatures and induces smectic phases in certain cases[23-25].

Reference to table 1 indicates that increase in flexibility in each system affects solid mesomorphic as well as mesomorphic-isotropic transition temperatures. Compared to EP-1, EP-2 polymers, EP-3 and EP-4 polymers exhibit lower solid-nematic and nematic-isotropic transitions. Normally an amide linkage enhances mesogenic thermal stability. It seems the unsymmetrical linkages (ester and amide) in the repeat unit may be responsible in lowering of solid-nematic and nematic-isotropic transitions of EP-3 and EP-4 polymers. Reference to table:1 further shows that when amide linkage (EP-3 and EP-4), the transition temperatures are severally affected. These results indicate that amide linkage bring down solid-nematic as well as nematic-isotropic transition temperatures.

The polymers exhibit very fine texture similar to nematic phase in small molecules. This is an interesting aspect, normally a good texture is observed after keeping a polymer sample for sometime on the hot stage of the microscope (figure-a and b).

The absence of smectic phase in all the polymers is quite surprising. Even with ten spacers and one of the amide linkage EP-3 and EP-4 do not exhibit smectic mesophase. This may be due to the increased flexibility of the systems.

Polymer EP-1, EP-2 and EP-3 were studied by using Mettler DSC-4000. Polymer EP-1 does not exhibit endothermic peak for nematic-isotropic transition temperature. Only one endothermic peak is obtained for crystalline-nematic transition temperatures. However on cooling the melt an exothermic peak is observed for isotropic-nematic transition temperatures. Polymer EP-2 exhibits one additional endothermic peak between the two recorded transitions Solid-Nematic and Nematic-Isotropic.

It is difficult to account this endothermic peak. However on cooling the melt exothermic peak are not observed for any of the transitions. In the case of polymer EP-3 an endothermic peak for Solid-Nematic transition temperatures is observed. An additional peak between the two transition temperatures is obtained in this polymer also. The DSC results are in conformity with certain unusual mesogenic series[26,27]

Reference to table-1 shows that the polymers EP-1 to EP-4 exhibit nematic mesophase only. The comparison of mesogenic properties of different polymers is a difficult task as the mesogenic properties of polymers depend not only on the chemical constitution but also on the molecular weight and polydispersity of the system. In the present study the structures of all the four polymers vary uniformly hence intrinsic viscosity values [η] are taken to compare the properties of polymers.

The nematic.-isotropic. Transition temperatures do not differ much in the case of EP-1 and EP-3 even though -0- is replaced by -NH- in EP-3. However, the transition temperature of EP-2 is much higher compared to all the other three polymers which is difficult to explain. A little difference can be explained on viscosity results, but here difference is large enough.

Molecular weight and polydispersity data can through some light which could be obtained for EP-1 (molecular weight 2028) and EP-4 (molecular weight 1960) only. An interesting aspect worth noting is that polymer EP-3, even after cooling exhibits nematic texture. This trend is not observed in other similar polymers. The intrinsic viscosity obtained by using one point method[21], indicates that this procedure can be used. The procedure followed by condensation polymerisation gives consistent data. Intrinsic viscosity does not defer markedly from EP-1 to EP-4.

DSC Results (table 4) indicate typical behavior. Except polymer EP-1 none of the polymers exhibit endothermic for nematic-isotropic transition temperatures. In the case of polymer EP-3 an extra peak not matching with microscopic results is observed at 67°C. Reexamination of the slide of polymer EP-3 indicated that there is no phase change at this temperature. This indicates that the endothermic peak at 67°C in the case of EP-3 may be due to Crystalline I - crystalline II transition. Enthalpy change in polyesters EP-2 to EP-4 from solid-nematic differs and is higher for EP-4. However in the case of EP-3 the ΔH value (J/g) is much less due to second crystalline modification. The major enthalpy change in crystalline-I to crystalline-II phase change in EP-3 suggests that it might be a highly ordered phase. Only X-ray study can through some light on this aspect.

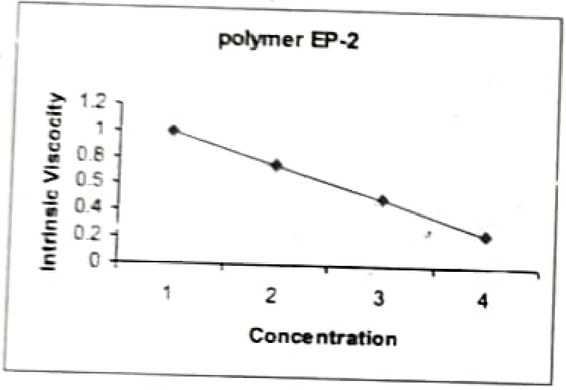

Figure-4
Intrinsic viscosity against different concentration

Figure-4
Optical polarized microphotograph of Nematic liquid crystalline phase (Thread like texture) of EP-2 on heating at 245°C

Figure: 5
Optical polarized microphotograph of Nematic liquid crystalline phase (Thread like texture) of EP-4 on cooling at 154°C

Table-2
Viscosity data of the Polychalcones Solvent: Dimethyl Formamide
Concentration: 0.5% **Temperature: 34.4 °C**

Code	η_{rel}	η_{sp}	η_{red}	η_{inh}	η_{int}
EP-1	1.0665	0.0665	0.1330	0.1288	0.1298
EP-2	1.0705	0.0705	0.1410	0.1363	0.1374
EP-3	1.0679	0.0679	0.1358	0.1314	0.1325
EP-4	1.0724	0.0724	0.1449	0.1397	0.1411

Calculated by One Point method (15)

Table- 3
Viscosity data of Polymers Solvent: N-Methyl-2-Pyrrolidone, Temperature: 34.4°C

Polymer	Concentration (%)	η_{rel}	η_{sp}	$\eta_{intrinsic}$ (dl/gm)	
				One pt. method	Graphical
EP-2	1.0	1.1500	0.1500	0.1423	0.1340
	0.75	1.1107	0.1107	0.1419	
	0.50	1.0705	0.0705	0.1374	
	0.25	1.0345	0.0345	0.1363	

Table-4
Calorimetric data of Polychalcones and Polycarbonates Heating rate = 10 °C

Sr.No.	Polymer	Wt. mg.	Phases	Peak Temp.°C (Microscopic Reading)	ΔH J/g	ΔS J/g.°K	Total ΔS J/g.°K
1	EP-1	17	K-Nematic	144.8 (140.0)	2.44	0.00584	
			Nematic-Iso.	190.3 (190.0)	0.39	0.00084	0.0067
2	EP-2	17	K-Nematic	141.1(150.0)	4.51	0.0109	
			Nematic-Iso.	- (256.0)	-	-	0.0109
3	EP-3	17	Extrapeak	67.0	5.38	0.0158	
			K-Nematic	121.1(124.0)	0.79	0.0020	0.0178
			Nematic-Iso.	- (190.0)	-	-	
4	EP-4	10	K-Nematic	143.1 (141.0)	9.09	0.0219	
			Nematic-Iso.	- (169.0)	-	-	0.0219

( ) Values indicate microscopic data, K indicates crystalline. Iso. = isotropic

Table-5
GPC Data of the Polymers

Polymer	Mn	Mw	Mw/Mn	Molecular weight
EP-1	633	2100	318	2028
EP-4	955	2453	2.569	1960

Conclusion

Polyesters and polyesteramides having chalcone linkage with increased flexibility by increasing number of methylene spacers show higher thermal stability than monomers. All the polymers exhibit nematic mesophases. Except polymer EP-1 none of the polymers exhibit endothermic for Nematic-Isotropic transition temperatures.

Acknowledgement

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