Synthesis, Characterization and Studying Liquid Crystalline Properties of Some Azo - Schiff base Compounds Derivatives

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Received: 1 October 2017 **Accepted: 28 December 2017**

Abstract

Four azo-Schiff base liquid crystalline compounds with different polar groups named (A_1S, A_2S, A_3S, A_4S) have been synthesized and their structures were characterized by using (FTIR) spectrometry technique the peaks in the infrared spectrum matched the literature in diagnosing the functional groups while their liquid crystalline phase transition and temperature range was confirmed by differential scanning calometery (DSC) which indicate the presence of liquid crystalline phases, The textures of the synthesized liquid crystalline compounds were performed using polarized optical microscope which show a nematic phases in the (A_1S) and (A_3S) compounds .

Key word: Azo, Schiff base, Liquid crystal

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تحضير و تشخيص و دراسة الخصائص البلورية السائلة لبعض مشتقات مركبات الأزو و قواعد شف

نور صباح العبيدي

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الخلاصة

تم تحضير أربع مشتقات من مركبات آيزو – قواعد شف (A_1S, A_2S, A_3S, A_4S) البلورية السائلة ذات مجاميع قطبية مختلفة وتم تشخيصها باستخدام تقنية طيف الأشعة تحت الحمراء و وجدت القمم في طيف الأشعة تحت الحمراء تتطابق مع الأدبيات في تشخيص المجاميع الفعالة، في حين تم التأكد من ظهور الأطوار البلورية السائلة عند درجات الحرارة المختلفة عن طريق القياس التفاضلي كالوميتري و التي تشير إلى وجود إنتقالات بلورية سائلة، تم التأكد من ظهور الحالة البلورية السائلة باستخدام المجهر الضوئي المستقطب حيث أظهرت المركبات (A_1S) و (A_3S) الطور النيماتي.

الكلمات المفتاحية : الأزو ، قواعد شف ، البلورات السائلة.

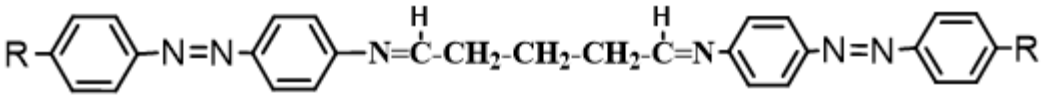
Introduction

Liquid crystals are an intermediate state (Mesophase**) [1]**, were discovered in the 1888, by Australian botanist Friedrich Reinitzer recorded the phase-transition temperatures of cholesteryl benzoate, which turns a milky white at 145.5^{o}C and transparent at 178.5 ^{o}C and he considered the possibility that a phase intermediate between that of the isotropic liquid and crystalline solid could exist **[2]**, the azobenzene, Schiff bases compounds are very interesting materials because of rich liquid-crystalline polymorphism such type of molecules with azo moiety are well known in literature **[3, 4]**, Azo compounds have been almost importance in many miscellaneous application areas such as in the textile, paper, coloring agents for foods and cosmetics industries its reversible optical storage, nonlinear optical (NLO) devices and liquid crystalline displays (LCDs) **[5]**, recently a homologous series of mesogenic azo compounds containing three rings in the main core and substituted with aromatic or hydroxyl groups on the central benzene nucleus was reported **[6, 7],** the optic axis of azobenzene groups becomes aligned perpendicular to the electric field vector of polarized light. Inert mesogens undergo alignment together with the azobenzene groups for cooperative motion **[8]** Liquid

crystals (LC) have been most extensively used as display materials. Successful applications of the LC display for calculators, sentences display, word processors, and full-color TV display **[9]**.

Experimental

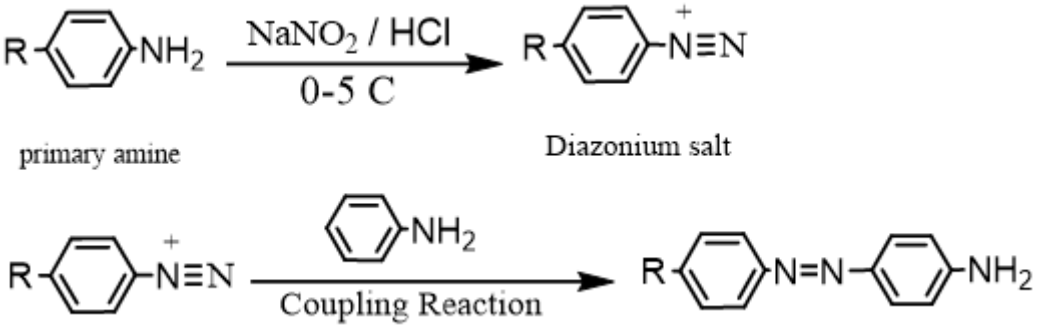
Synthesis of azo Schiff base liquid crystalline compounds, Scheme (1) show the general structure of the studied compounds.



R: COOH, $COCH_3$, Br and NO_2

Scheme 1: The general structure of the synthesized azo Schiff base compounds

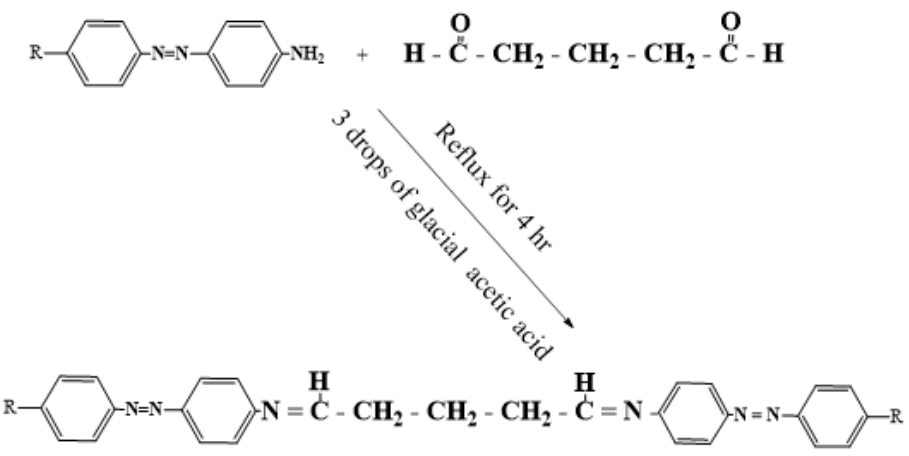
In the first step was synthesis a diazonium salts by four different primary amines, (0.002 mole) of (Na_2CO_3) in (12 ml) of distilled water ,and then addition of (0.005 mole) from the primary amine such as (*P*-amino benzoic acid) and heating until it dissolve completely, then after filtration and cooling using ice bath (0- 5ºC) we add (0.005 mole) of ($NaNO_2$) and stirring ,then by adding (1.25 ml) of HCl drop wise the good yields at (83%-91%), of aniline (0.0057 mole) and glacial acetic acid (0.5 ml) was added to the diazonium salt prepared in the first step as a drops with continuous stirring and cooling for 15 min ,then we get a precipitate which differ in colour for different primary amines ,then by adding (7.5 ml)from 10% NaOH and checking by using pH paper until the solution become a basic, then we add NaCl and filtering the produced solution which kept for 24 hours, the precipitate was then collected which represents the target amino azo benzene as given in Scheme (2).



R: COOH, $COCH_3$, Br, NO_2

Scheme 2: Synthesis root for the diazonium salts

The second step consist of the condensation reaction for amino azo benzene that is synthesized in the first step with the glutaraldehyde, In (250 ml) round bottom, put (0.01 mole) of glutaraldehyde dissolved in (10 ml) from absolute ethanol, then by adding (0.02 mole) from the amino azo benzene dye dissolved in (10 ml) absolute ethanol with three drops of glacial acetic acid and reflux the mixture with stirring for 4hr, the process of the reaction was followed by a thin layer chromatography technique and to ensure the purity of the produc the precipitate was collected, then after filtration and drying the product was recrystallized two times from ethanol to get the azo Schiff base compounds as shown in Scheme (3).



R: COOH, $COCH_3$, Br, NO_2

Scheme 3: Synthesis root for azo Schiff base compounds

Results and Discussion

Characterization by FT-IR spectroscopy

All the synthesized azo dyes and azo Schiff base compounds were characterized by using Berkin Elmer FT-IR, The spectrum of (A_1S) showed an absorption band at (3407 cm^{-1}) attributed to phenolic (O–H), the strong intensity band occurring at (1679 cm^{-1}) assignable to ν(C=N) of the azomethine, while (N=N) appeared at (1493 cm^{-1}), absorption bands for (C–H, aromatic), (C–H, aliphatic) and (C=C, aromatic) were recorded at (3063cm^{-1}, 2946-2866cm^{-1} and 1592cm^{-1}) respectively **[10]**, the IR spectrum for one azo dye sample (A_1)and one azo Schiff base compound (A_1S) was given in figure(1) and figure (2) respectively.

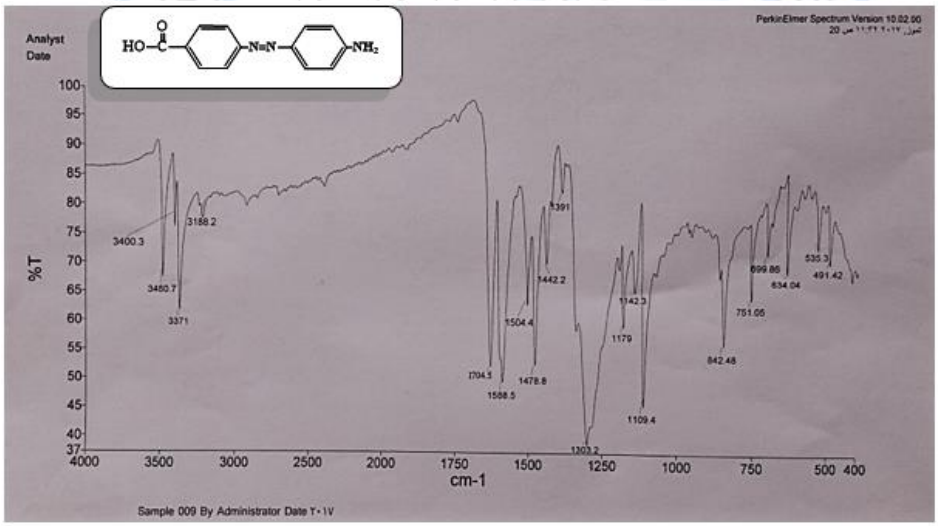


Figure 1: IR spectrum for azo dye sample A_1

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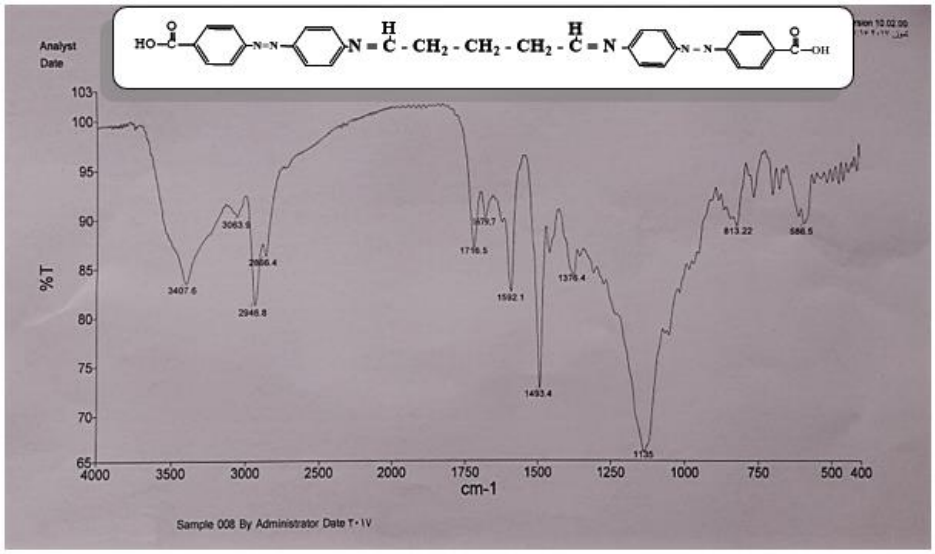

Figure 2: IR spectrum for azo Schiff base sample A1S

Table 1: important functional groups in Azo dyes samples

Compound	N-H st.	C-H st. aromatic	C=C aromatic	-N=N-	Other specific bands	
A_1	3400 3371	3188	1588	1504 1478	O-H C=O	3480 1704
A_2	3445 3403	3120	1528	1509	C-H aliphatic	2958
A_3	3440 3385	3095	1572	1511	C-Br	654
A_4	3444 3408	3083	1543	1504	----------	

Table 2: Important functional groups in Azo-Schiff base samples

Compound	C-H st. aromatic	C-H st. aliphatic	C=N st.	C=C aromatic	-N=N-	Other specific bands	
A_1S	3063	2946 2866	1679	1592	1493	O-H C=O	3407 1716
A_2S	3080	2944 2854	1657	1574	1504	----------	
A_3S	3074	2951 2863	1642	1578	1498	C-Br	664
A_4S	3066	2948 2861	1649	1559	1508	----------	

Differential scanning calorimetery DSC

The phase transition temperature of the synthesized Azo-Schiff base compounds were confirmed using (DSC) technique which indicate liquid crystalline transition from solid to nematic liquid crystal and then to isotropic liquid in the (A_1S) and (A_3S) compounds as given in fig.(3), fig.(4), respectively.

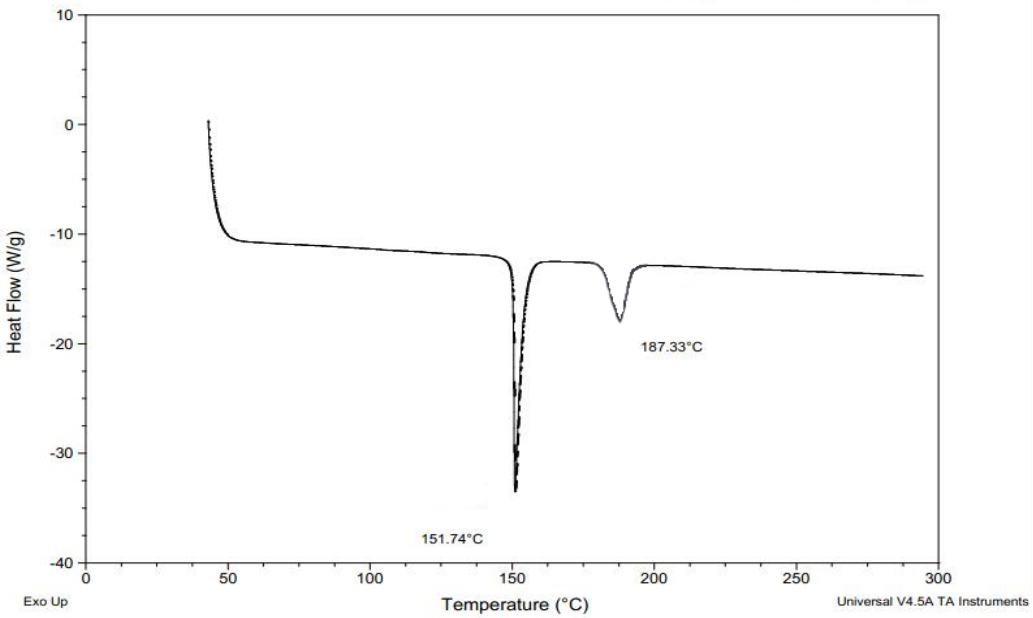

Figure 3: DSC for liquid crystalline compound A_1S

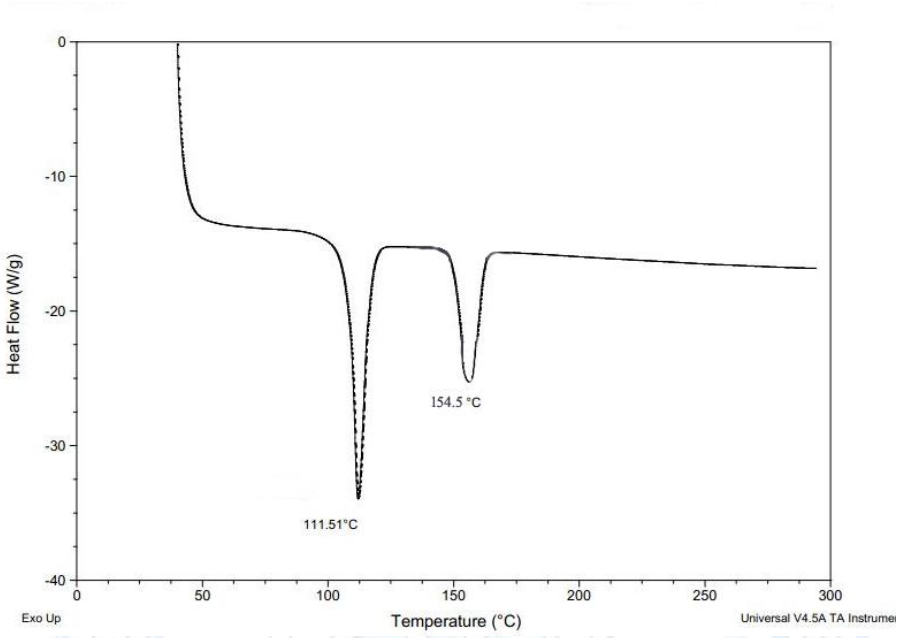

Figure 4: DSC for liquid crystalline compound A_3S

Polarized optical microscope

The textures of the samples in this research were investigated through hot stage Polarizing microscope model (LEICA DM 2500 P) with Digital Camera, in the laboratory service in the Ibn al-Haytham College of Education in which the temperature was measured by a digital thermometer with a thermocouple just in contact with the glass of the cell, the make clear nematic phase of the prepared compounds (A_1S , A_3S) may be interpreted on the basis that increase in temperature during the heating causing increases the particle 's energy and thus lead to overcome the attractive forces between molecules , which allows it to arrange themselves depending on the interactions and the new forces causing to be the order of molecules is as parallel within the same level, between classes and thus encourage the emergence of nematic phase **[11],** figures (5), (6), (7) and (8) show the textures of the prepared compounds samples respectively ,

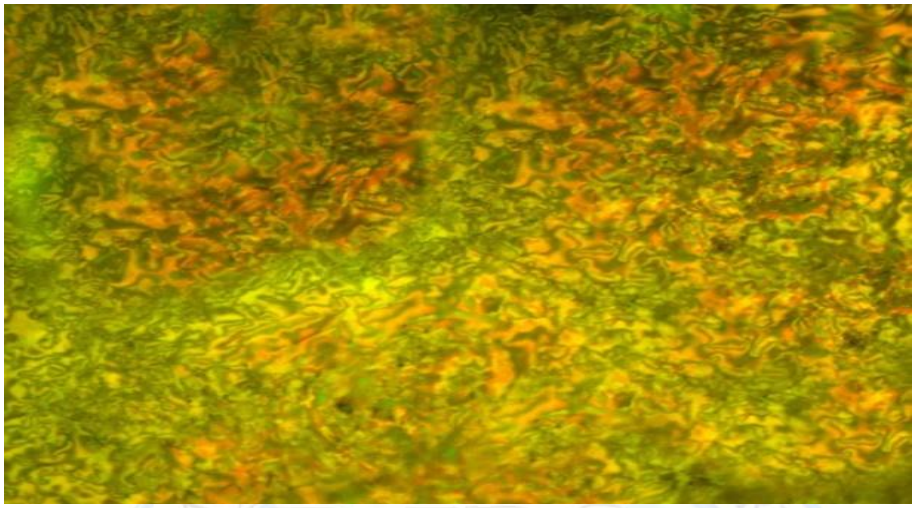

Figure 5: Nematic texture sample image of (A_1S) compound

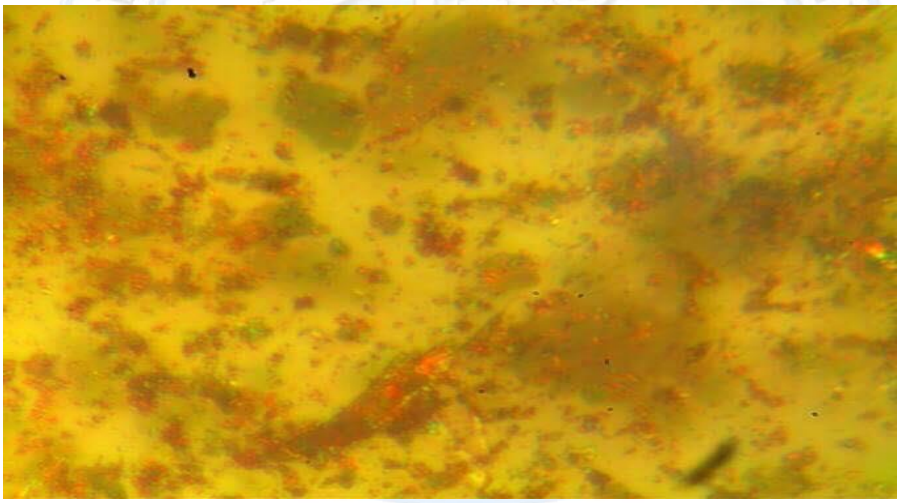

Figure 6: Non-liquid crystal sample image of (A_2S) compound

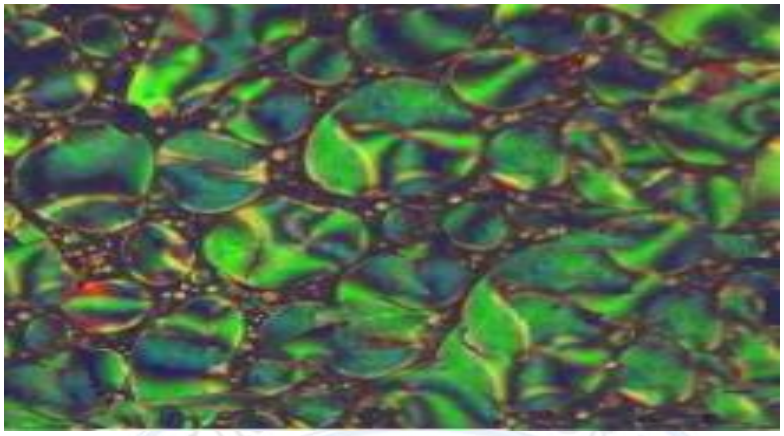

Figure 7: Nematic texture sample image of (A_3S) compound

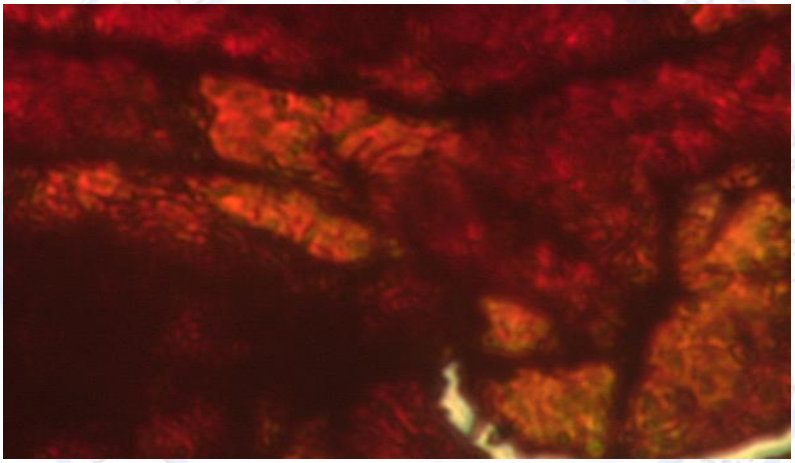

Figure 8: Non-liquid crystal sample image of (A_4S) compound

Conclusion

The synthesized azo – Schiff base compounds with four Compensations group show a clear liquid crystalline phases and some of them show a polymorphism behavior with an excellent color due to the presence of an azo group that is responsible for the absorption of light, the synthesized azo Schiff base compounds mostly show the more stable trans confirmation feature and this will make them exhibit the required linearity for mesophase formation, the appearance of liquid crystalline phases was strongly affected by the different polar groups such as (COOH, Br, NO_2, $CO\text{-}CH_3$) that is present which consequently enhance dipole-dipole interaction or dispersion forces that is responsible for mesophase formation .

References

1. G.Pcarawford,"Liquid Crystal";Colby-sawyer College New London, **(2005)** , Ch . 1 , P,1-2.
2. P. J. Collings and M. Hird. Introduction to Liquid Crystals. Taylor & Francis, London, (1997).
3. C-a.Yang, H. Xie, S. Chen, H. Zhang, Synthesis and phase structures of combined main-chain/side-chain liquid crystalline polymers with different-number azobenzene moiety in the side-chain based on mesogenjacketed liquid crystalline polymers. Liq Cryst. (2013), Vol.40 , P.11.
4. JS. Dave, PR. Patel, Influence of molecular structure on liquid crystalline properties and phase transitions in these structures, part II. Mol Cryst Liq Cryst. (1966), Vol.2 , P.115–123.
5. D. Bauman, A Plociennik. and K. Inglot, Molecular Interactions in Monolayers of Azo Dye/Liquid Crystal Mixtures at Interfaces, Acta Physica Polonica A,(2009) Vol. 116.
6. R.A. Vora, A.K. Prajapati, Azomesogens with 1,2,4 – trisubstituted benzene moiety. Bull. Mater. Sci. (2002),Vol. 25, P 355-358.
7. A.K. Prajapati, H.M. Pandya, N.L. Bonde, Naphthyl azomezogens with lateral chloro groups. J. Chem. Sci. (2004), 116, 227-233.
8. Ruslim and Ichimura, Macromolecules, (1999) Vol. 32, P 4254
9. T. Ikeda, H. Shin, K. Durga, K. Seiji, T. Shigeo, Macromolecules, (1990) P 23, 36.
10. R. M Silverstein, G. C. Bassler and T. C. Morril , "Spectrometric identification of Organic Compound " 4th Ed; , JhonWilyey and Sons . New York , (1981).
11. D.Demus, J.Goodby, G.w.Gray, H.W.Spiess, and V.Vill, "Handbook of Liquid Crystals", Wiley VCH , (1998).