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Mesogenic materials incorporating 4H-1,2,4-triazol-3-thiol moiety: Synthesis, characterization and liquid crystals study

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Three series of monomers, polymers and thioester cyclic compounds containing 4H-1,2,4-triazol-3-thiol moiety were synthesized and examined for their liquid crystalline properties. All monomers, polymers and thioester compounds were characterized by elemental analysis and FTIR, ^{1}H-NMR and mass spectroscopy. The phase transition and mesomorphic properties were investigated by polarized optical microscope (POM) and differential scanning calorimetry (DSC). The monomer with terminal phenyl substituent display dimorphism nematic and smectic A (SmA) mesophases. The corresponding polymers derived from acrylic and phenyl acrylic acid monomers show nematic mesophase. The only thioester cyclic compound derived from terephtaloyl chloride show nematic mesophase. The liquid crystalline behavior has been discussed in terms of structural property relationships.

1. Introduction

During the past decades many series of liquid crystalline compounds containing heterocyclic groups have been synthesized due to their potentially wide range of applications, such as in the optical, electrical and biological medical fields [1–8]. The incorporation of heterocyclic moieties into the rigid core of thermotropic liquid crystals can result in large changes in their mesophases and physical properties. The rich polymorphism usually observed of such structures was attributed to their medium to strong lateral dipole, high polarizability and anisotropy, low symmetry and non-planar structure caused by heteroatoms, such as nitrogen, oxygen and sulfur atoms [9–11]. Usually five member heterocycles are involved and they form part of the core in rod-shaped, bent-shaped, or disc-shaped molecules [12–14].

The triazole ring, which has a five-membered ring of two carbon atoms and three nitrogen atoms, has two isomers, 1,2,3- and 1,2,4-triazole. The recognized electron-deficient nature and electron acceptors properties in 1,2,4-triazoles have lead them to be excellent candidates used in many potential applications as organic and bioactive materials [15,16]. The mesomorphic properties of 1,2,3-triazole isomer derivatives have extensively been carried out in last decade [17–27], while the formation of 1,2,4-triazole derivatives mesophases has rarely been reported.

Thaker and Patel [28,29] have reported the synthesis and mesomorphic properties of two homologous series containing 1,2,4-triazole ring at the terminus of the molecule viz. 4-[(4H-1,2,4-triazol-4-ylimino) methyl] phenyl 4-alkoxybenzoate and 3-hydroxy-4-[(4-1,2,4-triazol-4-ylimino)methyl] phenyl 4-alkoxybenzoate (where alkoxy group C_nH_{2n+1}; n = 1–8, 10, 12, 14 and 16). All the derivatives are mesomorphic in nature showing enantiotropic nematic phase and the higher member of both series shows smectic C (SmC) phase. A twelve new bent-shaped mesogens containing 4-amino-1,2,4-triazole as a central rigid core and terminal alkoxy substituent have recently been reported [30]. The homologues with short alkoxy terminal groups do not show any mesomorphic properties, whilst the analogue with the longest alkoxy terminal groups exhibit enantiotropic smectic A (SmA) and banana B1, B2, B6 and B7 phases with wide mesomorphic temperature ranges. We have previously reported the synthesis of two mesogenic homologous series of mesomorphic compounds containing 1,2,4-triazole and 1,3,4-thiadiazole in the molecule viz. 1,4-bis{3-[2-(4-alkoxybenzelideneamino)- 1,3,4-thiadiazole-5-ethylenethio] 1,2,4-triazole-5-yl} phenyl and 5-(4-meth-oxyphenyl)-3-[2-(4-n-xybenzelidenamino)-1,3,4- thiadiazole-5-methylenethio]-1,2,4-triazole. All compounds of the former series exhibited an enantiotropic nematic mesophase. The compounds of the later series exhibited enantiotropic nematic and monotropic smectic A

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(SmA) mesophases [31].

The present work deals with synthesis, characterization and the liquid crystalline behavior of monomers, polymers and compounds containing 4H-1,2,4-triazol-3-thiol unit. The liquid crystalline behavior and the structural property relationship were also investigated.

2. Experimental

2.1. Materials and characterization

All chemicals were supplied by Sigma-Aldrich Chemicals Co and used without further purification. The solvents were commercial grade quality and were dried and distilled before use. Infrared spectroscopy were carried out with a Shimadzu 600 S Fourier transform infrared spectrometer using KBr pellets.^{1}H-NMR spectra were recorded on a Brucker 500 MHz spectrometer. Tetramethylsilane was used as an internal standard and used DMSO and $CDCl_3$ as solvents. Mass spectrum was recorded on IEOL JMS-7 high resolution instrument using the electron impact (EI) method. Elemental analysis (C, H, N) were carried out using a Perkin-Elmer model 2400 instrument. Uncorrected melting points were measured by using Gallen Kamp melting point apparatus. The transition temperatures and phase transition enthalpies were determined using a DSC, STA PT-1000LINSIS at a heating rate of 5 °C/min. Temperature and heat flow calibrated with standard indium of purity < 99.99%. Mesomorphic textures were observed using a Leica microscope DM 2500 M equipped with Mettler 600 heating stage.

2.2. Synthesis

The synthetic route used for the synthesis of compounds and polymers are outlined in Schemes 1 and 2. Acryloyl chloride, 3-phenylacryloyl chloride and methacryloyl chloride were prepared according to the procedure described in the literature [32].

2.2.1. Synthesis of 1,2-phenylene-bis(N-carbothioamide-hydrazide) [I]

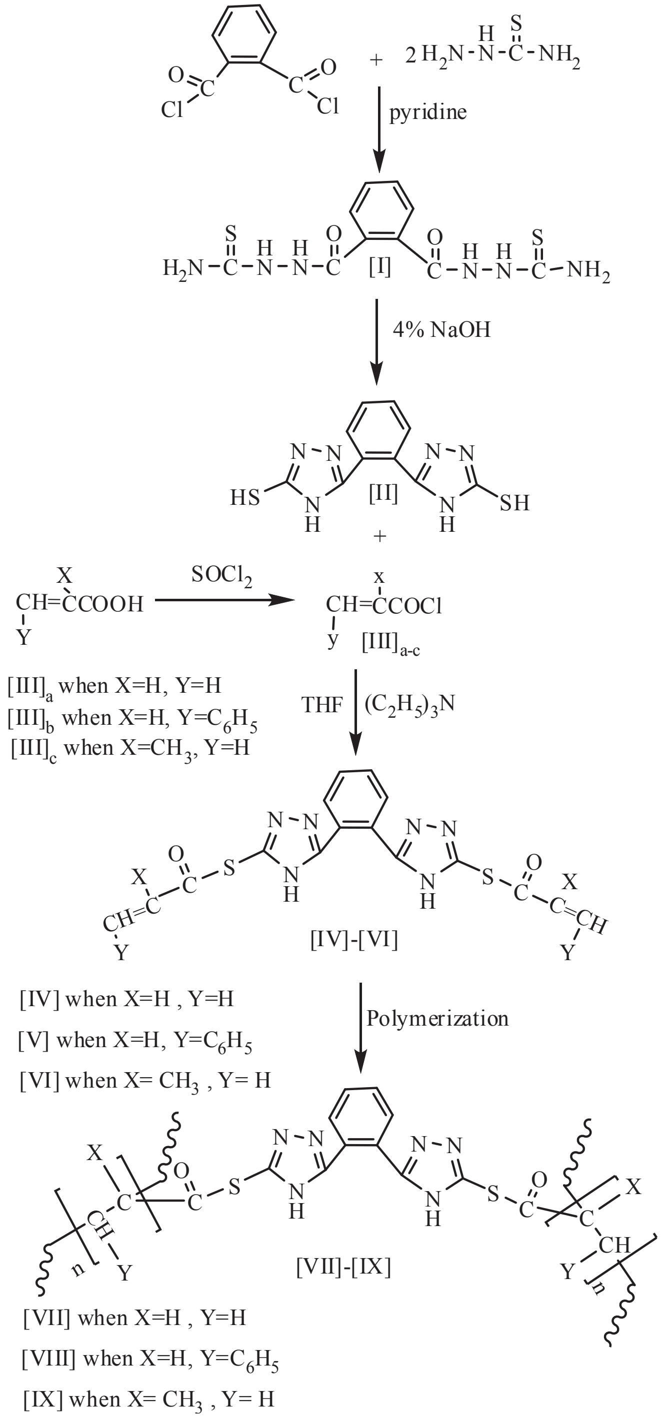
To a stirred solution of compound thiosemicarbazide (0.91 g, 10 mmol) in dry pyridine 15 mL at -5 °C, was added dropwise a solution of phthaloyl chloride (1.015 g, 5 mmol) in dry benzene 15 mL at −5°C. The stirring was continued for half an hour at -5 °C and then overnight at room temperature. The solvent was evaporated and added 30 mL water. The precipitate was filtered and recrystallized from ethanol.

Yield: 76%, m.p. 208–210°C; FTIR (KBr) (cm-1): 3396-3174 (υNH2, υNH), 1683 (υC = O), 1261 (υC = S); ^{1}H-NMR (500 MHz, DMSO, *d* ppm): 7.56–7.92 (m, 4H, Ar—H), 8.65 (s, 2H, NH2), 9.69 (s, 1H, NHC═S), 12.75 (s, 1H, NHC═O). MS (m/z+1) = 313(M+.), 236(M+. − C_6H_5), 248(M+. − C_5H_5). Anal. Calcd for $C_{10}H_{12}N_6O_2S_2$: C, 38.46; H, 3.85; N, 26.92; S, 20.51. Found: C, 37.97; H, 4.12; N, 26.50; S, 20.87.

2.2.2. Synthesis of 1,2-phenylene-bis(4H-1,2,4-triazol-3-thiol-5-yl) [II]

A solution of compound [I] (3.12 g, 10 mmol) and 20 mL 4% aqueous sodium hydroxide solution was refluxed for 6 h. After that, the mixture was filtered, and then the resulting filtrate was acidified with 10% HCl. The product was filtered and washed with water, then recrystallized from ethanol.

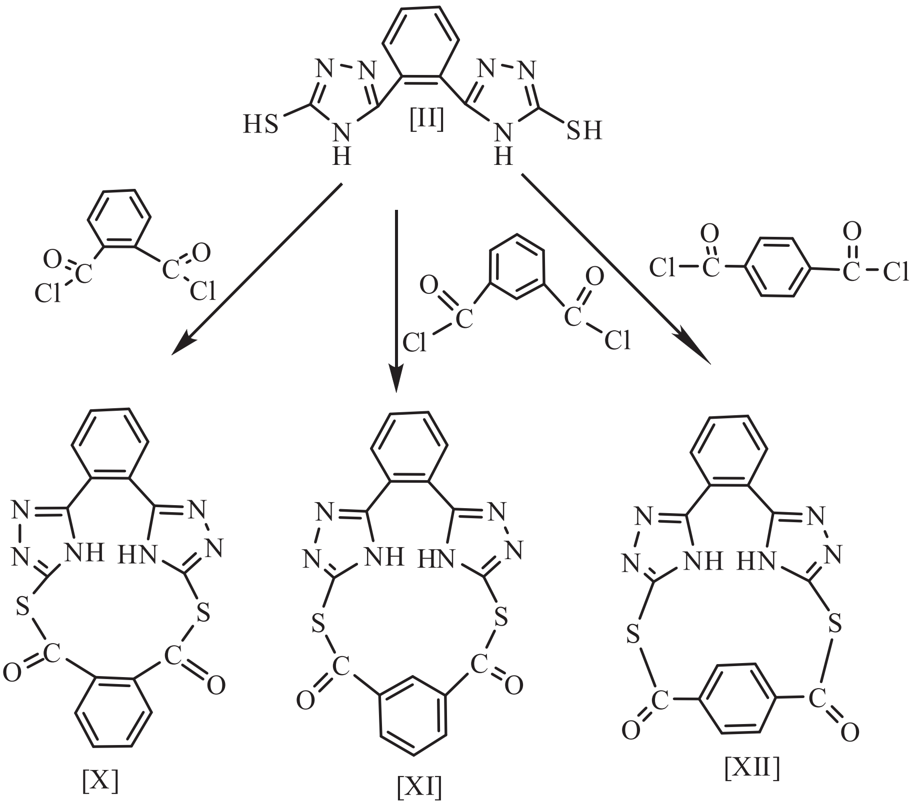
Yield 60%, m.p. 319–320°C. FTIR (KBr) (cm^{-1}): 3422 (υ_{NH}), 2651 (υ_{SH}), 1627 ($\upsilon_{C=N}$ of 1,2,4-triazole ring), 1220 ($\upsilon_{C=S}$). ^{1}H-NMR (500 MHz, DMSO, *d* ppm): 7.34–7.67 (m, 4H, Ar—H), 13.50 (s, 1H, for proton of NH traizole ring and NH group tautomeric forms with SH group); MS (m/z+1) = 277(M+.), 212(M+. − C_5H_5), 200(M+. − C_6H_5), 173(M+. − C_6H_5CNH). Anal. Calcd for $C_{10}H_8NS_2$: C, 43.48; H, 2.90; N, 30.43; S, 23.19. Found: C, 42.82; H, 3.11; N, 29.92; S, 22.87.



Scheme 1. The synthetic route of monomers [IV], [V] and [VI] and polymers [VII], [VIII] and [IX].

2.2.3. Synthesis of S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) diprop-2-enethioate [IV], S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) bis(3-phenylprop-2-enethioate) [V] and S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) bis(2-methylprop-2-enethioate) [VI]

To a stirred solution of compound (II) (10 mmol), triethylamine



Scheme 2. The synthetic route of thioester compounds [X], [XI] and [XII].

(2 mL) in dried of 10 mL THF, was added dropwise acryloyl chloride, 3-phenylacryloyl chloride or methacryloyl chloride (20 mmol) at 0°*C*. After addition has been completed the resulting suspension was stirred at the same temperature for 5 h. The triethylamine hydrochloride salt was precipitated. It was filtered and filtrate was poured with stirring into ice water (100 mL), then the mixture was extracted with of chloroform (50 mL). The organic phase was dried over anhydrous magnesium sulphate. The chloroform solution was evaporated to give the desired product.

2.2.3.1. S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) diprop-2-enethioate [IV]. Yield 62%, m.p. 96–98°*C*; FTIR (KBr) (cm^{-1}): 3417 (υ_{NH}), 3068 cm^{-1} ($\upsilon_{Ar\text{-}H}$), 1678 ($\upsilon_{SC=O}$), 1634 ($\upsilon_{CH2=CH\text{-}}$), 1624 ($\upsilon_{C=N}$ of 1,2,4-triazole ring). MS (m/z+1) = 385.

2.2.3.2. S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) bis(3-phenylprop-2-enethioate) [V]. Yield 69%, m.p. 106–108°*C*; FTIR (KBr) (cm^{-1}): 3410 (υ_{NH}), 3050 ($\upsilon_{Ar\text{-}H}$), 1682 ($\upsilon_{SC=O}$), 1637 ($\upsilon_{CH2=CH\text{-}}$), 1625 ($\upsilon_{C=N}$ of 1,2,4-triazole ring). MS (m/z+1) = 413. Anal. Calcd for $C_{18}H_{16}N_6O_2S_2$: C, 52.43; H, 3.88; N, 20.39; S, 15.53. Found: C, 51.31; H, 3.42; N, 20.93; S, 14.79.

2.2.3.3. S,S′-5,5′-(1,2-phenylene)bis(4H-1,2,4-triazole-5,3-diyl) bis(2-methylprop-2-enethioate) [VI]. Yield 60%, m.p. 112–114°*C*; FTIR (KBr) (cm^{-1}): 3415 (υ_{NH}), 3059 ($\upsilon_{Ar\text{-}H}$), 1695 ($\upsilon_{SC=O}$), 1633 ($\upsilon_{CH2=CH\text{-}}$), 1621 ($\upsilon_{C=N}$ of 1,2,4-triazole ring); ^{1}H-NMR (500 MHz, $CDCl_3$, *d* ppm): 1.41 (s, 3H, CH_3), 4.99 (d, J = 1.39 Hz, 1H, CH_2=C-), 5.69 (d, J = 1.41 Hz, 1H, CH_2=C-), 6.24–7.10 (m, 4H, Ar–H), 13.10 (s, 1H, for proton of NH traizole ring); MS (m/z+1) = 537.

2.2.4. Synthesis of thioester polymers [VII-IX]

Polymers were synthesized by free-radical polymerization technique from the corresponding monomers using benzoyl peroxide as an initiator in toluene at 80 °C for 48 h: Monomer IV, V or VI (5 mmol) and benzoyl peroxide (2 wt%) were dissolved in dry toluene and gentle steam of nitrogen purged into the solution. The solution was kept in an oil bath at 80 °C for 8 h. Then the solution was cooled and poured into excess of acetone to precipitate the polymer. The solution was filtered and the precipitate washed firstly with 15 mL of toluene and secondly with 15 mL of acetone, and was dried at 60 °C under vacuum for 48 h to afford the desired polymer.

2.2.4.1. Polymer [VII]. Yield 70%, m.p. 159–161°*C*; FTIR (KBr) (cm^{-1}): 3406 (υ_{NH}), 3064 ($\upsilon_{Ar\text{-}H}$), 1683 ($\upsilon_{SC=O}$), 1621 ($\upsilon_{C=N}$ of 1,2,4-triazole ring); ^{1}H-NMR (500 MHz, $CDCl_3$, *d* ppm): 1.22–1.55 (m, 2H, –CH_2–), 3.04–3.90 (m, 1H, –CH–), 7.56–9.33 (m, 4H, Ar–H), 11.63 (s, 1H, for protons of NH traizole ring).

2.2.4.2. Polymer [VIII]. Yield 65%, m.p. 192°*C*; FTIR (KBr) (cm^{-1}): 3420 (υ_{NH}), 3070 ($\upsilon_{Ar\text{-}H}$), 1672 ($\upsilon_{SC=O}$), 1627 ($\upsilon_{C=N}$ of 1,2,4-triazole ring).

2.2.4.3. Polymer [IX]. Yield 76%, m.p. > 300°*C*; FTIR (KBr) (cm^{-1}): 3408 (υ_{NH}), 3066 ($\upsilon_{Ar\text{-}H}$), 1698 ($\upsilon_{SC=O}$), 1624 ($\upsilon_{C=N}$ of 1,2,4-triazole ring).

2.2.5. Synthesis of 1,2-phenylene bis [1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [XI], 1,3-phenylene bis [1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [XII] and of 1,4-phenylene bis [1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [XIII]

These compounds were synthesized by using the same procedure given for the synthesis of compounds [IV], [V] and [VI], but used 10 mmol of phthaloyl chloride, isophthaloyl chloride or terephthaloyl chloride instead of 20 mmol of acryloyl chloride, 3-phenylacryloyl chloride and methacryloyl chloride.

2.2.5.1. 1,2-Phenylene bis [1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [X]. Yield 85%, m.p. 197–198°C; FTIR (KBr) (cm^{-1}): 3412 (υ_{NH}), 3086 ($\upsilon_{Ar\text{-}H}$), 1689 ($\upsilon_{SC=O}$), 1620 ($\upsilon_{C=N}$ of 1,2,4-triazole ring); ^{1}H-NMR (500 MHz, DMSO, *d* ppm): 7.55–8.06 (m, 8H, Ar–H), 13.02 (s, H, for proton of NH traizole ring); MS (m/z+1) = 417.

2.2.5.2. 1,3-Phenylene bis [1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [XI]. Yield 60%, m.p. 214–216°C. FTIR (KBr) (cm^{-1}): 3409 (υ_{NH}), 3100 ($\upsilon_{Ar\text{-}H}$), 1683 ($\upsilon_{SC=O}$), 1618 ($\upsilon_{C=N}$ of 1,2,4-triazole ring). MS (m/z+1) = 417.

2.2.5.3. 1,4-Phenylene bis[1,2-phenylene bis(4H-1,2,4-triazole-3-thioester-5yl)] [XII]. Yield 76%, m.p. 296–298°C. FTIR (KBr) (cm^{-1}): 3418 (υ_{NH}), 3009 ($\upsilon_{Ar\text{-}H}$), 1681 ($\upsilon_{SC=O}$), 1626 ($\upsilon_{C=N}$ of 1,2,4-triazole ring). MS (m/z+1) = 417. Anal. Calcd for $C_{18}H_{10}N_6O_2S_2$: C, 53.20; H, 2.46; N, 20.69; S, 15.76. Found: C, 52.15; H, 3.13; N, 21.80; S, 14.98.

3. Results and discussion

3.1. Synthesis and characterization

All compounds and their corresponding polymers were prepared by the synthetic route described in Schemes 1 and 2. All of the new synthesized compounds gave satisfactory analysis for the proposed structures, which were confirmed on the basis of their elemental analysis; FTIR and ^{1}H-NMR. The observed values of the elemental analyses of the synthesized compounds are in well agreement with theoretical values indicating structure of respective compounds.

The carbothioamide derivative [I] was prepared by reacting of phthaloyl chloride with 2 mol of thiosemicarbazide by neucleophilic addition reaction. The FTIR spectrum of compound [I] showed absorption stretching band at 1261 cm^{-1} that could be assigned to C=S group in addition to new bands for asymmetric and symmetric stretching vibration of NH_2 and NH groups appears between 3396 and 3174 cm^{-1}, also showed stretching band of $\upsilon_{C=O}$ (amide) group at 1683 cm^{-1}. The ^{1}H-NMR spectrum for compound [I], showed multiple signals in the region *d* = 7.56–7.92 ppm for four aromatic protons, singlet signal appeared at *d* = 8.65 ppm for two protons of NH_2 groups, signals at *d* = 9.69 and 12.75 ppm for two protons of NHC=S and NHC=O groups. The mass spectrum of compound [I] shows the peaks at m/z = 77 and 65 of characteristic fragmentation for the aromaticity of compound [I].

The cyclization of carbothioamiede derivative [I] in medium of aqueous sodium hydroxide then acidification with hydrochloric acid led to formation of principal key heterocyclic compound, 1,2,4-triazole-3-thiol derivative [II]. The FTIR spectrum for compound [II] showed disappearance bands of the $\upsilon_{C=O}$ (amide) groups, that observed in the starting materials and showed new absorption stretching band at 2651 cm^{-1} that attributed to the υ_{SH} and 1220 cm^{-1} for $\upsilon_{C=S}$ group. Also, showed stretching bands at the 3422 cm^{-1} and 1627 cm^{-1} for $\upsilon_{N\text{–}H}$ and $\upsilon_{C=N}$ (endocyclic) of 1,2,4-triazole ring [33], respectively, this is evidence for ring closure. The ^{1}H-NMR spectrum for compound [II], showed multiple signals in the region *d* = 7.34–7.67 ppm for four aromatic protons and signal at *d* = 13.50 ppm for proton of NH traizole ring and NH group tautomeric forms with SH group. The mass spectrum of compound [II] shows peak attributed to the presence of triazole ring (m/z = 104, 102, 57 and 40) also showed peaks at m/z = 77 and 65 for the aromaticity.

The thio ester monomers [IV], [V] and [VI] were produced from the reaction of compound 4H-1,2,4-triazol-5-thiol [II] with acryloyl chloride, 3-phenylacryloyl chloride and methacryloyl chloride in presence of triethylamine as acid acceptor. The FTIR spectra of these compounds showed disappearance bands of SH and C=S groups for compound [II] with appearance absorption stretching band of the thioester ($\upsilon_{SC=O}$) group at 1678 cm^{-1} [34]. The ^{1}H-NMR spectrum for compound [VI] (as a representative example), showed signal at *d* = 1.41 ppm for three protons of CH_3 group, signals appeared at *d* = 4.99 and 5.69 ppm for two protons of (CH_2=C-) group and signals in the region *d* = 6.24–7.10 ppm for four aromatic protons also signal at *d* = 13.10 ppm for the proton of NH traizole rings.

The resulting prop-2-enethioate monomers ([IV], [V] and [VI]) were converted to the corresponding polymers by free-radical polymerization technique using benzoyl peroxide as an initiator in dry toluene as a solvent. The characteristic absorption bands in the range at (1634–1637 cm^{-1}) in FTIR spectra [35,36] corresponding to (–CH=CH–) groups of monomers were completely disappeared as a result of the opening of the double bond on these groups, this is confirmed that the polymerization reaction took place. The ^{1}H-NMR spectrum for polymer [VII] (as a representative example), showed signals at *d* = 1.22–1.55 ppm for protons of (–CH_2–) groups, signals appeared at *d* = 3.04–3.90 ppm for proton of (–CH–) groups and signals in the region *d* = 7.56–9.33 ppm for aromatic protons and signal at *d* = 11.63 ppm for proton of NH traizole rings.

Also, synthesized another thio ester compounds [X], [XI] and [XII] by reaction of compound 4H-1,2,4-triazol-5-thiol [II] with diacid chlorides (phthaloyl, isophthaloyl or terephthaloyl chloride). The FTIR spectra of these compounds also showed disappearance bands of SH and C=S for compound [II] with appearance absorption stretching band of the thio ester ($\upsilon_{SC=O}$) group. The ^{1}H-NMR spectrum for compound [X], (as a representative example) show many signals in the region *d* = 7.55–8.06 ppm for the eight aromatic protons and a singlet signal at *d* = 13.02 ppm for two protons of NH traizole rings. The data of elemental analysis, FTIR, and ^{1}HNMR spectrum along with mass spectrum analyses data confirmed the structural formula of the synthesized monomers, polymers and thioester compounds.

3.2. Mesomorphic properties

The liquid crystalline properties of all compounds and polymers were investigated by POM and DSC. Generally, the thermal behavior obtained by DSC is consistent with the data observed by POM, where it was possible to identify the mesomorphic character of the mesophases. Phase identification was based on the optical textures, using the classification systems reported by Sackmann and Demus [37] and Gray and Goodby [38]. The phase transitions temperatures and thermodynamic data are summarized in Table 1.

In order to study and analysis the mesomorphic behavior of the synthesized compounds, the target compounds and polymers were grouped into three sets, series A, B and C; for monomers containing bifunctional prop-2-enethioate group ([IV], [V] and [VI]) (series A). The corresponding polymers of monomers of series A ([VII], [VIII] and [IX]) (series B), and the last three thio ester compounds ([X], [XI] and [XII]) (series C).

In series A only compound [V] showed liquid crystalline properties (Table 1), while the compounds [IV] and [VI] did not show any liquid crystalline behavior but changes from the solid crystalline state to the isotropic liquid phase. The DSC thermogram of compound [V] (Fig. 1) shows three transitions on first heating. Under the POM Compound [V] exhibit enantiotropic dimorphism liquid crystalline behavior. On slow cooling from the isotropic

Table 1
Transition temperatures (°C) and transition enthalpies ΔH(kJ/mol) of monomers ([IV], [V] and [VI]), polymers ([VII], [VIII] and [IX]) and thio ester compounds ([X], [XI] and [XII]) determined by DSC (10°C/min) during first heating.

Compound No.	Transition temperatures (°C)(ΔH, kJ/mol)
[IV]	Cr 107 I
[V]	Cr 119 (35.25) SmA 184 (15.46) N 223 (1.70) I
[VI]	Cr 121 I
[VII]	Cr 145 (11.28) N > 350 (a) I
[VIII]	Cr 171 (9.17) N 329 (a) I
[IX]	Cr > 350 I
[X]	Cr 325 I
[XI]	Cr 222 (27.15) SmA 250 (2.21) I
[XII]	Cr 306 I

(a) = Not detected; Cr = Crystal; N = Nematic; SmA = smectic A; I = Isotropic transition.

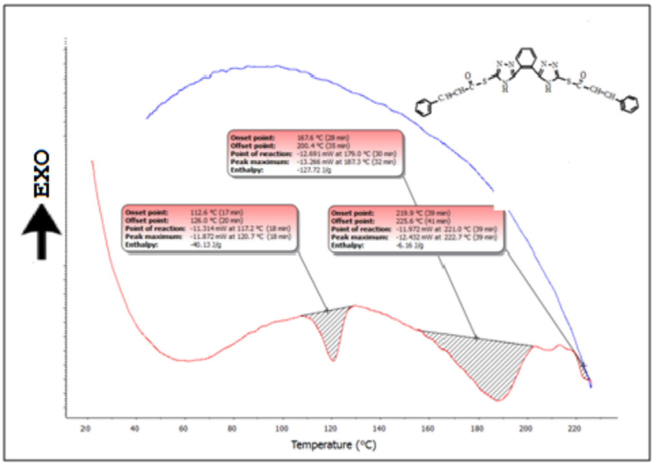


Fig. 1. The DSC thermogram of monomer [V].

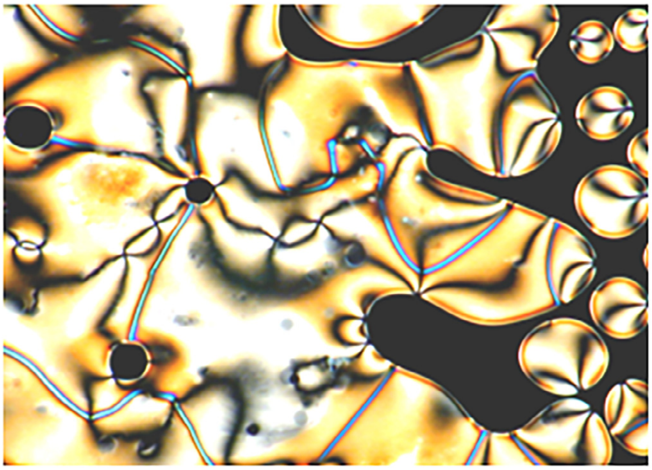


Fig. 2. Mesophase optical texture of the nematic phase obtained on cooling. A thread-like texture and the typical nematic droplets (200 × magnification) for the monomer [V] at 211°C.

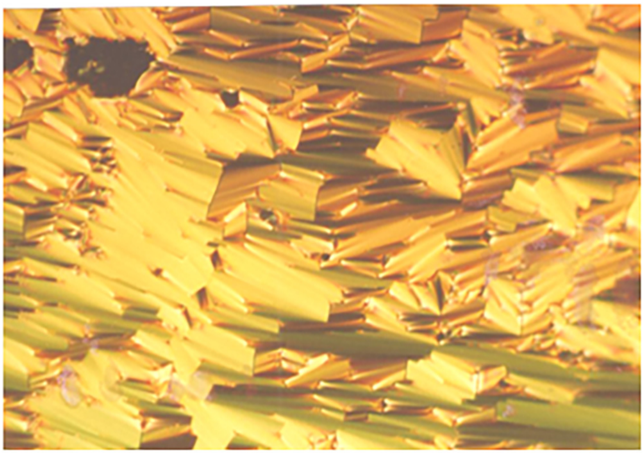


Fig. 3. Mesophase optical texture of the SmA phase obtained on cooling. A typical focal conic fan texture (200 × magnification) for the monomer [V] at 167°C.

liquid, thread-like texture developed which is characteristic of nematic phase (Fig. 2). On further cooling focal conic fan texture displayed as showed in Fig. 3 which is characteristic of smectic A (SmA) texture. The presence of thio cinnamate and phenyl ring in the compound [V] could be increase rigidity and polarizability of the core and extends the molecular length [39] leading to the formation of liquid crystalline mesophese.

The thermal data of the polymers of series B are gathered in Table 1. Among the three polymers, [VII], [VIII] and [IX], polymers [VII] and [VIII] display liquid crystalline behavior. The DSC thermogram of polymers [VII] and [VIII] show two endothermic transitions between 145 °C, >350 °C and 171 °C and 329 °C, respectively corresponding to solid crystalline-liquid crystalline and high temperature one is liquid crystalline-isotropic liquid transitions, confirming the formation of liquid crystalline phase. This may be explained based on the formation of macromolecular structure allow the terminal molecular interaction between the polymer chains [40]. On heating under POM of these two polymers, they are exhibited a uniform worm-like texture [41]. The representative POM photograph of polymer [VII] was shown in Fig. 4. The polar–polar interaction between triazole rings in [IV] and [V] monomers (consider as a model to polymers [VII] and [VIII]) is restricted in polymers [VII] and [VIII] systems lead to nematic like-character than SmA texture of their models [18].

The phase transition temperatures of the compounds in series C are given in Table 1. Compound [XI], is the only compound in this series showing liquid crystalline behavior. Reference to the geometry of compounds [X], [XI] and [XII], compound [XI] derive from phthaloyl chloride forming bent core mesogene due to angle

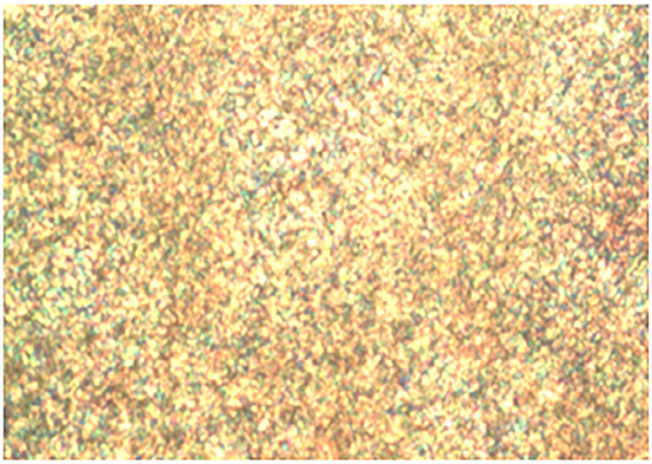


Fig. 4. Mesophase optical texture of the nematic phase obtained on cooling. A worm-like texture (200 × magnification) for the polymer [VII] at 159°C.

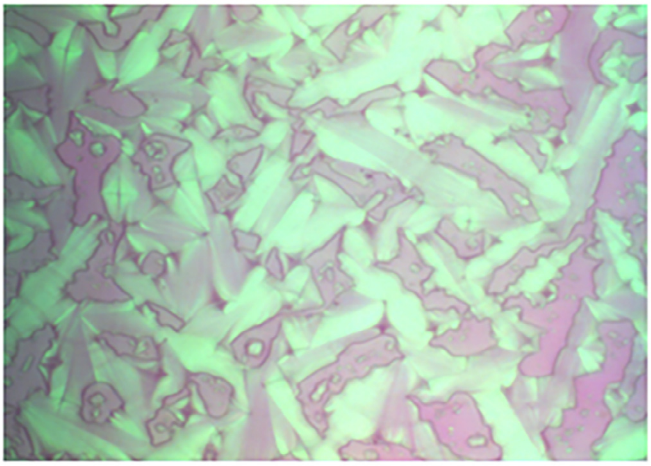


Fig. 5. Mesophase optical texture of the SmA phase obtained on cooling. A batonnets texture (200 × magnification) for the compound [XI] at 237°*C*.

between 1,2-disubstituted phenylene ring is 60° comparing with 1,3- and 1,4-disubstituted phenylene, 120° and 180°, respectively [14] which are the favor of forming cyclic shape. It seems that the lateral molecular interaction between the phenylene ring along with the 1,2,4- triazole heterocyclic in bent core structure favored the formation of smectic layer mesophase, which does not appear in the compounds of 1,3- and 1,4-disubstituted phenylene ring with cyclic shape. The texture of compound [XI] under POM showed a series of dark-lines, when further cooled; the bands expanded, melt and eventually coalesce to produce a batonnets texture typical character of SmA (Fig. 5) [42].

4. Conclusions

In this article three series A, B and C containing 4H-1,2,4-triazol-3-thiol unit were synthesized and their liquid crystalline properties were analyzed with respect to their chemical structure. Monomer of series A derived from phenylacryloyl chloride show dimorphism liquid crystalline behavior with SmA and nematic mesophases, comparing with other two monomers derived from acryloyl and methacryloyl which are not showing liquid crystalline character. The polymers of series B were synthesized by free radical polymerization of monomers of series A. Polymers of acryloyl and phenylacryloyl monomers display liquid crystalline properties with nematogen character. The restricted of lateral molecular interaction between 1,2,4-triazole in monomers comparing with polymeric system lead to formation of nematic texture rather than smectic layer texture. Compound derived from terephtaloyl chloride in series C forming bent-core structure showed SmA mesophase. The other two compounds of this series derived from isophtaloyl and terephtaloyl chloride do not show liquid crystalline behavior. This could be attributed to structural geometry of these two compounds.

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