Synthesis, characterization, and phase transition studies on some N-(4-butyloxy benzylidene)-4-alkoxy anilines, 4O.Om compounds – A dilatometric study

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Abstract

Dilatometric studies are carried out on the synthesized N-(4-butyloxy benzylidene)-4-alkoxy anilines, 4O.Om compounds with the m = 3 to 7 and 9. Characterization of these compounds is done using the polarizing microscope attached with a hot stage. The differential scanning calorimeter is employed to find out the transition temperatures as well as the heats of transitions. All the compounds exhibit nematic phase with varying thermal ranges with the clearing temperatures are above 100 ^{O}C as unlike the case of the well known N-(4-butyloxy benzylidene)-4-alkyl anilines, 4O.m compounds which exhibit rich poymorphysim and the clearing temperatures are well below 100 ^{O}C.   As expected the isotropic to nematic transition exhibited first order nature and the results are discussed with the body of the data available in literature.

Key words: nO.Om compounds, Phase transitions, Dilatometry, Order of the transition.

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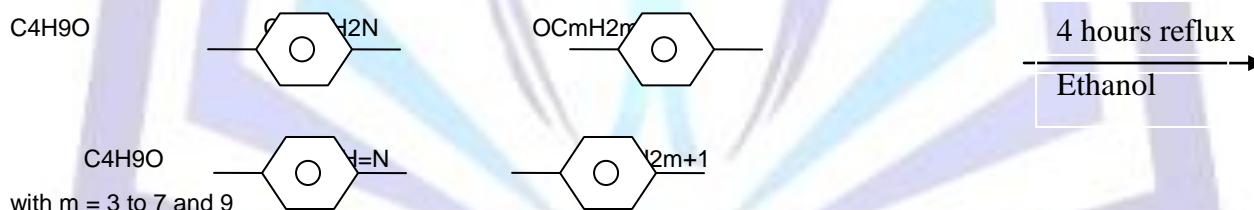**E-mail :** venkata_pisipati@hotmail.com (V. G. K. M. Pisipati).

Introduction

The N-(4-alloxybenzylidene)-4-alkyl anilines, nO.m and N-(4-aloxy benzylidene)-4-alkyloxy anilines, nO.Om compounds are well studied [1 – 6]. Systematic studies on nO.Om compounds reveal that these compound exhibit thirteen different types of phase variants stating from the mono variant (N, SmA and SmC) to penta variant NSmASmCSmISmG [2 – 4, 7]. Different physical property measurements such as birefringence, viscosity, dielectrics at different frequencies are necessary to understand the material and its viability in application side. In addition to these properties, the density studies will provide the nature of the phase transitions across different liquid crystalline phases and the isotropic to first liquid crystalline phase. Further, the density studies will provide the complimentary results to the polarizing microscopic and DSC data. The systematic studies on these Schiff's base compounds reveal that the position of the electronegative oxygen in the liquid crystal moiety plays an important role on the exhibition of the liquid crystalline phases as well as on the magnitude of the clearing temperature [8, 9]. Different researchers have carried out dilatometric studies on a number liquid crystal materials to understand the different phase transitions and the pretransitional effects [10, 11]. The important parameter like thermal expansion coefficient, $\alpha = (1/\rho)(d\rho/dT)$ can be obtained from density studies which is being used to evaluate the very interesting thermodynamic parameters, the molecular free length and the moleculau radius of the liquid crystal material [12].

The present manuscript reports the synthesis, characterization through polarizing microscope and DSC and the phase transition studies through dilatometry of N-(4-butoxybenzylidene)-4-alkyloxy anilines, 4O.Om with m = 3 to 7 and 9.

Experimental

The liquid crystal compounds are synthesized following the standard procedure described in literature [9], and the compounds are synthesized by the condensation of 4-butoxy benzaldehyde (0.1 mol) and the corresponding alkoxy anilines (0.1 mol) in refluxing absolute ethanol on the presence of few drops of glacial acetic acid. The reactants are refluxed for 3–4 h. Then, the solvent is removed by distillation under reduced pressure. The obtained crude sample is recrystallized from absolute ethanol in cold until the transition temperatures are constant. The purity of the compounds tested using DSC are shown in the table 1. A U-shaped bi-capillary pyknometer in conjunction with the cathetometer (an indigenously developed experimental setup) was used for the density measurements. The absolute error in the measurement of density is ±10-4 g cm-3. The cooling rate during the measurement was 0.5 OC. For the textural characterization and the determination of phase transition temperatures, polarizing microscope (S. D. Tech, India) attached with the hot stage is used. The liquid crystalline phases of the compounds are characterized by observing the standard optical textures of nematic (threaded marble texture). The temperature accuracy in the measurement is ±0.1OC. The heats of transitions are measured using Perkin Elmer Diamond DSC. The reaction route for the compounds is as follows.

C4H9O ⬡ C 2N   OCmH2m ⬡   4 hours reflux
                                 Ethanol

C4H9O ⬡ H=N   ⬡ 2m+1

with m = 3 to 7 and 9

Results and discussion

The compounds in this study only exhibit mono variant nematic phase with the characteristic threaded marble texture which is shown in figure 1. The heats of transition along with the transition temperatures obtained from DSC and Polarizing optical microscope (POM) and the purity of the compounds is given in the table 1. The DSC plots for the compounds 4O.O3, 4O.O5, 4O.O7 and 4O.O9 are shown in figures 1 to 4. All these six LC compounds exhibit nematic phase with varying thermal ranges and in all the cases the clearing temperatures are above 100OC. As expected in other homologues, these compounds also exhibit an odd-even effect in the case of clearing temperatures and are depicted in the figure 5.

The following observations are made from the earlier studies on Shiff's base compounds [2-4, 7-10].When the oxygen atom is on the left side of the rigid core (nO.m) compounds, generally, the clearing temperatures are below 100O C, no compound exhibits smectic-I phase and only few compounds show smectic-A to smectic-C (AC) transition.When the oxygen atom is on the right side of the rigid core (n.Om), the situation is more or less same as the case of nO.m compounds except in the exhibition of phase variants. When the oxygen atom is on both sides of the rigid core (nO.Om), the clearingtemperatures are elevated to more than 100O C, and we see the presence of nematic phase even in compounds with high alkoxy chain number and the exhibition of phases such as smectic-I and the phase transitions such as smectic-A to smectic-C((SmA-SmC) and smectic-C to smectic-I (SmC-SmI) andWhen the oxygen atom is quenched from the molecular moiety (n.m), the clearing emperatures are lowered to around 50O C, the liquid crystalline nature in some cases goes below room

temperature and, as a result, the thermal range of nematic phase is reduced.The density of a substance is defined as the mass per volume and is generally determined by measuring the volume (V) of a known mass (m) of a substance. The thermal expansion coefficient, [α = 1/Mv) (dMv/dT)] of the material can also be obtained from the dilatometric studies. The density measurement is useful in determining the order of phase transition, pre transition behavior and critical exponent. Fundamentally, the density is related to the derivatives of Gibb's free energy (G). The first-order transition is characterized by a discontinuity or a steep change in specific volume/density associated with thermal expansion coefficient. It is found that density decreases with the increase of temperature in the liquid crystalline phases except in the vicinity of phase transitions where it shows a steep increase, before it attains equilibrium value of the next (lower temperature) phase. The density, ρ and estimated thermal expansion coefficient, α with temperature for the above four compounds are exhibited in figures 6 to 9. The variation of molar volume per methylene is found to be 15.90 x 10-6 m3.mol-1 and agrees with the literature data available on nO.m compounds whose values vary between 15 to 17 x 10-6 m3.mol-1. Figure 10 illustrates the variation of molar volume with the chain number.

Isotropic-Nematic (IN) transition

The slope of the density variation with temperature (dρ/dT)iso in the equilibrium isotropic phase for these compounds is 7.21, 7.62, 7.68, 7.87, 8.23 and 8.63 g.cm-3 OC-1 for the six compounds respectively. The values are found to be in agreement with the density measurements on nO.m [13, 14], PBnA [15] and nO.O4 [10] compounds. The IN transition observed in these compounds are accompanied by distinct jumps ($\Delta\rho$/ρ) x 100 and the thermal expansion coefficient maxima, αmax values are given in the Table 2. The values of density jumps vary around 0.4 ± 0.05 which are on the higher side compared to those values observed in other LC compounds which exhibit IN transition but are slightly less magnitude with those of nO.O4 [10] compounds. The distinct density jumps and the thermal expansion coefficient maxima suggest the IN transition nature is first order and are found to be in agreement with the body of the data available in other compounds [8, 10, 13, 14].   For the sake of comparison the density jumps data of other LC compounds along with these compounds are presented in Table 3. The smaller jump in the case of 6O.O4 like in other compounds (Table 3) is not uncommon. The higher values of slopes of density variation with temperature in equilibrium nematic phase in these compounds (Table 2) than in the isotropic region indicate in the molecular packing in the nematic phase and the accompanying growth of long range orientational order from a completely disordered molecular arrangement in the isotropic phase.

5. Acknowledgements

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Captions

Table 1. The transition temperatures, the heats of transition in heating and cooling cycles from DSC and the transition temperatures from POM in cooling cycle along with the purity og the compounds.

Table 2. Slopes of density in different phases, Thermal expansion coefficient maxima in nematic phase of N-(p-n-butyloxy benzylidene)-p-n-alkoxy anilines (4O.Om)

Table 3. The Density jumps, Thermal expansion coefficient maxima, across IN phase transition in different LC compounds.

Figure 1. DSC plot of the compound 4O.O3.

Figure 3. DSC plot of the compound 4O.O5.

Figure 3. DSC plot of the compound 4O.O7.

Figure 4. DSC plot of the compound 4O.O9.

Figure 5. Variation of clearing temperatures with the chain length.

Figure 6. Variation of density, ρ (gm.cm-3) and thermal expansion coefficient, α (10-4 oC-1) with temperature in 4O.O3.

Figure 7. Variation of density, ρ (gm.cm-3) and thermal expansion coefficient, α (10-4 oC-1) with temperature in 4O.O5.

Figure 8. Variation of density, ρ (gm.cm-3) and thermal expansion coefficient, α (10-4 oC-1) with temperature in 4O.O7.

Figure 9. Variation of density, ρ (gm.cm-3) and thermal expansion coefficient, α (10-4 oC-1) with temperature in 4O.O9.

Figure 10. Variation of Molar volume with the chain length.

Table 1

Compound	Phase Variants		Scan Rate	IN	Melting	Solid	Solid	Purity from DSC
4O.O3		Heating	10°C/min					99.32 ± 0.32
			ΔH J/gm					
	N	Cooling	10°C/min	112.61		111.10		
			ΔH J/gm	0.9323		0.2763		
		TM	Cooling	112.5		109.2		
4O.O4		Heating	10°C/min	126.71		109.03		99.45 ± 0.24
			ΔH J/gm	102.4507		13.8692		
	N	Cooling	10°C/min	120.50		115.54		
			ΔH J/gm	0.5107		89.50		
		TM	Cooling	120.0		115.8		
4O.O5		Heating	10°C/min	115.89		85.01		97.45 ± 0.21
			ΔH J/gm	88.8584		2.3190		
	N	Cooling	10°C/min	111.43		108.78		
			ΔH J/gm	2.6964		82.7652		
		TM	Cooling	111.0		108		
4O.O6		Heating	10°C/min	117.20		103.11		98.62 ± 0.15
			ΔH J/gm	1.5168		48.5446		
	N	Cooling	10°C/min	115.61		98.38		
			ΔH J/gm	2.9453		49.3164		
		TM	Cooling	115.5		98.5		
4O.O7		Heating	10°C/min	---		89.5		96.28 ± 0.43
			ΔH J/gm	----		101.45		
	N	Cooling	10°C/min	105.3		88.0		
			ΔH J/gm	2.985		98.55		
		TM	Cooling	103.5		89.0		
4O.O9		Heating	10°C/min	110.13		97.69	87.75	98.41 ± 0.46
			ΔH J/gm	3.1076		64.6844	13.3320	
	N	Cooling	10°C/min	108.82		90.40	60.49	
			ΔH J/gm	3.39		57.02810	1.1452	
		TM	Cooling	109.0		91.0		

Table 2

Compound	$(d\rho/dT)_{Iso}$ x 10^{-4} $^oC^{-1}$	$(d\rho/dT)_N$ x 10^{-4} $^oC^{-1}$	α_{I-N} x10^{-4} $^oC^{-1}$	% of $(\Delta\rho/\rho)_{I-N}$
4O.O3	7.21	8.26	52.22	0.34
4O.O4	7.62	8.20	64.44	0.40
4O.O5	7.68	8.93	71.08	0.39
4O.O6	7.87	9.05	76.00	0.40
4O.O7	8.23	12.64	73.62	0.42
4O.O9	8.63	17.65	91.94	0.38

Table 3

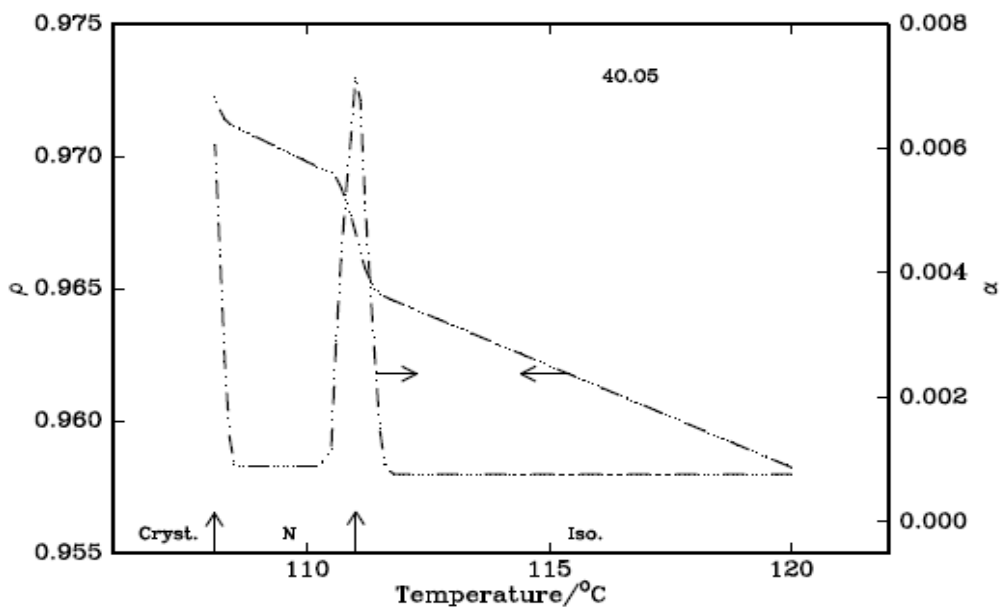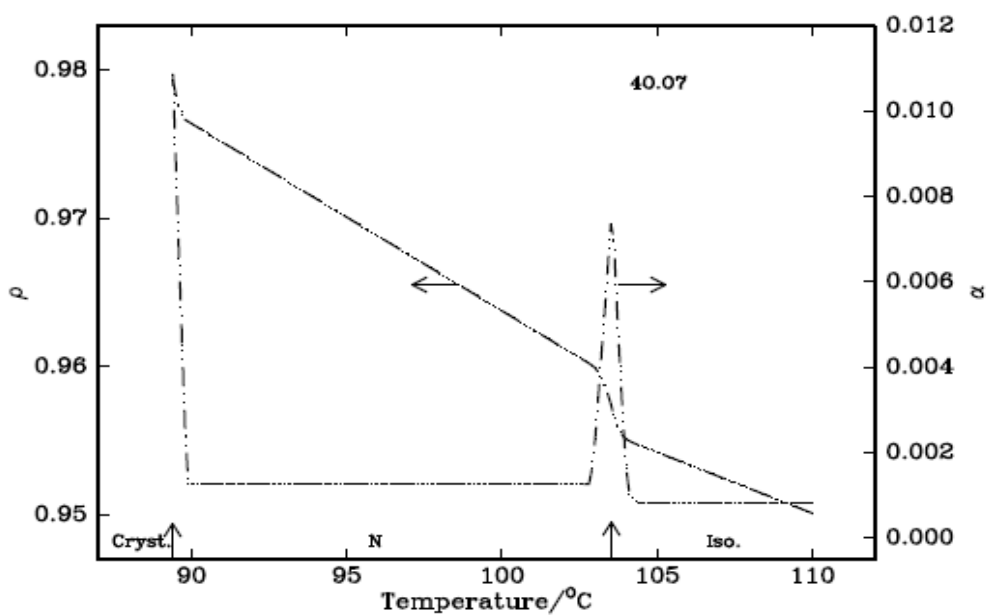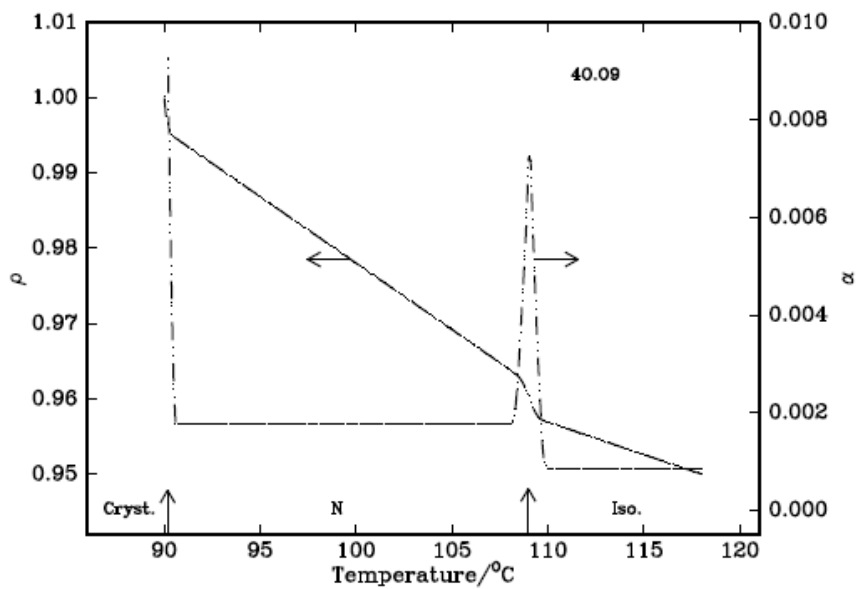| Compound	$(\Delta\rho/\rho) \times 100$	$(\alpha_{max.}) \times 10^{-4}\ {}^{O}C^{-1}$	Ref.
4O.O3	0.34	52.22	
4O.O4	0.40	64.44	
4O.O5	0.39	71.08	
4O.O6	0.40	76.00	pw
4O.O7	0.42	73.62	
4O.O9	0.38	91.94	
7O.O3	0.48	65.92	
7O.O5	0.52	69.56	
7O.O6	0.46	70.40	16
7O.O7	0.51	60.19	
7O.O9	0.54	76.11	
1O.O4	0.46	71.75	
3O.O4	0.47	73.12	
6O.O4	0.17	42.86	10
7O.O4	0.51	85.19	
10O.O4	0.51	72.96	
7O.1	0.20	133.0	
7O.2	0.27	96.00	
7O.3	0.32	119.0	17-21
7O.4	0.28	58.00	
7O.5	0.34	140..0	
7O.7	0.51	182.0	

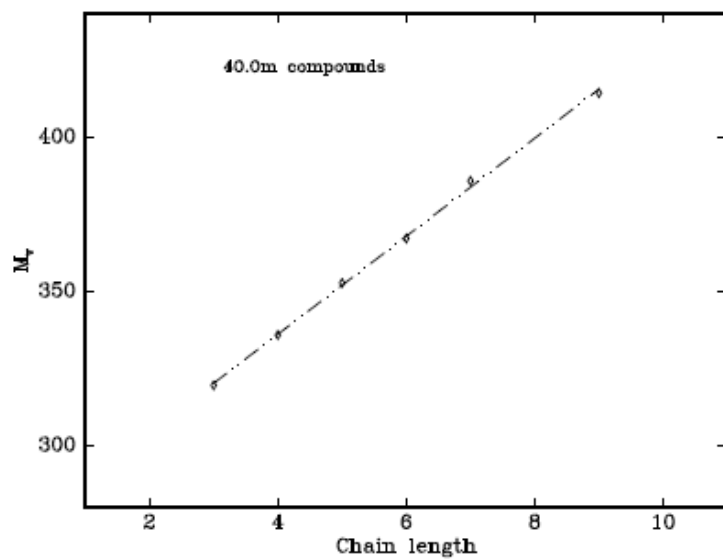Figure 1

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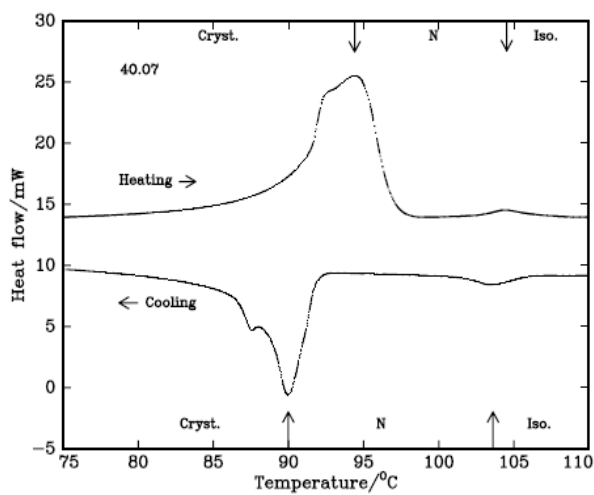
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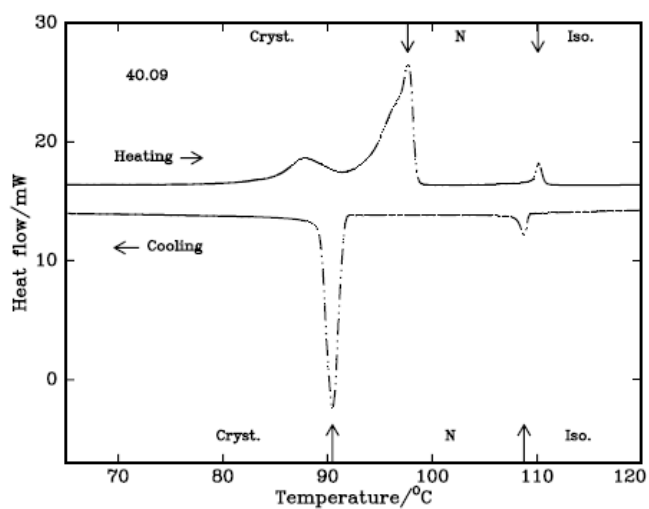
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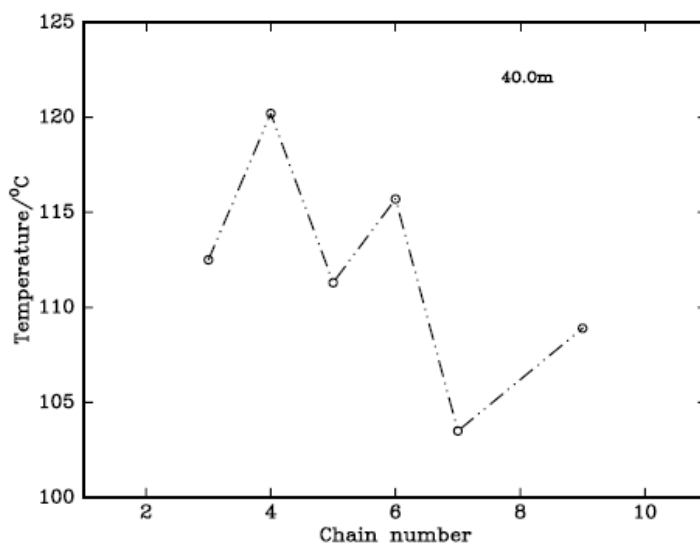
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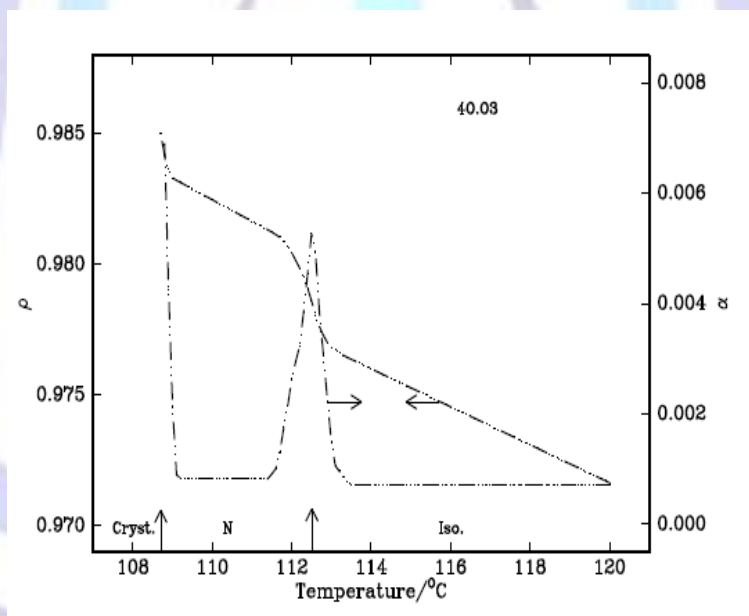
Figure 6

Figure 7

Figure 8

Figure 9

Figure 10.