

## تأثير اربع مجاميع مثيل في الخواص الحرارية لسلسلة ازو بلورية سائلة

عصام عبد الكريم عبد اللطيف ، ايمان صبيح حسن  
قسم الكيمياء ، كلية التربية - ابن الهيثم ، جامعة بغداد

### الخلاصة

عشرون مخططا ثنائي المكون لمركبات بلورية سائلة تمت دراستها باستخدام مجهر الضوء المستقطب ، وجهاز المسح التفاضلي المسعري (DSC) . كان اربعة مخططات منها لاثبات ان الطور السمكتي هو نفسه في جميع مركبات السلسلة ،

(4-n-alkoxy -2, 3, 5, 6-tetramethyl-4-n-alkoxy azobenzene) (nPA4M).

والمخطط الخامس كان بين المركب (6PA4M) والمركب البلوري السائل المرجع (TBAA) (terephthylidene-bis(4-n-butylaniline) لاجل تشخيص الطور السمكتي ومعرفة نوعه للسلسلة المذكورة ، وقورنت النتائج مع الادبيات العلمية . اما تأثير مجاميع المثيل الاربعة الجانبية والموجودة على احدى حلقات البنزين على السلوك الحراري للسلسلة (nPA4M) فقد تمت من خلال خمسة عشر مخططا ثنائي المكون التي قسمت على ثلاث مجاميع ، كل مجموعة من المخططات تحوي على خمسة مخططات ثنائية المكون ، اذ كانت المجموعة الاولى بين مركبات السلسلة البلورية السائلة (nPA4M) مع المركب المرجع

(HPA) 4-n-hexyloxyphenyl-4-n`-hexyloxy azobenzene وكان هذا المركب لا يحتوي على اي مجموعة مثيل جانبية . اما المخططات الخمسة الثانية فكانت بين مركبات السلسلة نفسها (nPA4M) والمركب المرجعي البليوري السائل (4B2M)

4-butylpheny-4-[(4-ethyloxyphenyl)carbonyl]oxy}-3-methyl benzoate

الذي يحتوي على مجموعة مثيل جانبية واحدة ، اما المخططات ثنائية المكون الخمسة الاخيرة فكانت بين (nPA4M) والمركب المرجعي (4B2,3M)

4-butyl-2methylpheny4-[(4-ethyloxyphenyl) carbonyl]oxy}-3-methylbenzoate

الذي يحتوي على مجموعتي مثيل جانبية .

# The Effect of Four Lateral Methyl Groups on The Thermotropic Behavior of Azo Liquid Crystal Homologous Series

I. K. Latif and E.S. Hassan

Department of Chemistry, College of Education, Ibn Al-Haitham, University of Baghdad

## Abstract

Twenty binary liquid crystalline mixture diagrams were investigated with polarizing microscope and differential scanning calorimeter (DSC). Four binary mixture diagrams were constructed to identify the smectic phase which is found to be the same in all components of the homologous series (4-n-alkoxy -2, 3, 5, 6-tetra methyl-4-n-alkoxy azo benzene) (nPA4M). The fifth binary mixture diagram was between the (6PA4M) and the reference liquid crystal compound, terephthylidene-bis (4-n-butylaniline) (TBAA) to identify the type of smectic mesophase of these compounds, and the results obtained were compared with the literature. To study the effect of the 4 methyl lateral groups on the thermotropic behavior of the (nPA4M) homologous series, fifteen binary mixture diagrams were divided in to three parts, each part contains five diagrams. The first binary diagrams were (nPA4M) with reference liquid crystalline compound 4-n-hexyloxyphenyl-4-n'-hexyloxy azobenzene (HPA) (compound without lateral group). The second five diagrams were between (nPA4M) and reference liquid crystal compound 4-butylphenyl-4-[[4-ethyloxyphenyl]carbonyl]oxy}-3-methyl benzoate (4B2M) ( compound with one methyl lateral group), and the last part of binary diagrams was between (nPA4M) and reference liquid crystal compound 4-butyl-2methylphenyl-4-[[4-ethyloxyphenyl] carbonyl]oxy}-3-methylbenzoate(4B2,3M) ( compound has two methyl lateral groups).

## Introduction

A wide range of lateral groups have been incorporated into many liquid crystal systems. Initially, it may be thought that they disrupt molecular packing and reduce liquid crystal phase stability. Indeed such destabilization often occurs through lateral substituents [1, 2].

On the other hand, in many cases, this disruption may be also advantageous for mesomorphism as well as properties required for technical use. Such groups like -F, -CN, -NO<sub>2</sub>, -CH<sub>3</sub>, or -OCH<sub>3</sub> always reduce the stability of the smectic phase more than of the nematic one. In general, the depression of the nematic-isotropic transition is proportional to the size of the substituents irrespective of its polarity. For smectic phases, the lamellar packing of smectogens was destabilized by the increase in the size of lateral groups but enhanced by the increase in polarity of side groups [3]. The lateral groups mentioned above introduce strong side dipole moments altering intermolecular forces [4,5]. The methyl group often appears as lateral substituents in structures of liquid crystals and leads to a decrease of the clearing temperatures and nematic ranges and increase the viscosity [6].

To identify any liquid crystal phase it must be shown that an investigation of the behavior of binary systems with components forming liquid-crystalline modifications leads to a classification of the liquid-crystalline states [7]. The key to such a classification is the following empirical rule of selective complete miscibility. All liquid-crystalline modifications which exhibit complete miscibility in binary systems, without contradiction, can be marked with the same symbol. 'Without contradiction' means that modifications which have the same symbol in no case exhibit complete miscibility with modifications of another symbol [8]. In general, binary mesophase systems exhibit eutectic behavior in their solid-mesophase

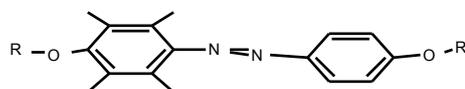
transition temperatures ( $T_m$ ), whereas their mesophase isotropic transition temperatures ( $T_c$ ) vary linearly with composition [9]. However, non-linear  $T_c$ -composition behaviors were reported for some mixtures when one component was chloro [10] or nitro [11, 12] substituted liquid crystals. In most cases, a mixed mesomorphic system is employed in order to depress the melting point ( $T_m$ ) of one, or both, of the pure components so as to obtain its mesophase over a more readily accessible temperature [13].

The aim of the present work was to study the influence of the four methyl groups in the azo core (Figure 1) on the liquid crystals thermotropic properties, these methyl groups act as broadening groups on the geometrical shape of the molecule i.e. they will change the ratio between the length and diameter ( $l/d$ ) of the molecules, at the same time the molecules have four electron – donating  $\text{CH}_3$  groups on the same azo benzene ring.

## Experimental

### 1. Preparation of materials

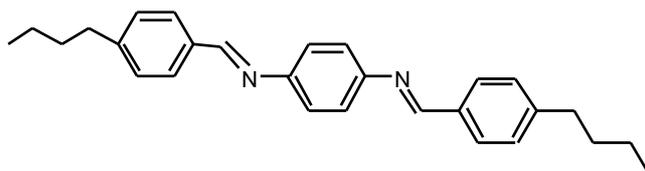
The following homologous series compounds (4-n-alkoxy-2,3,5,6-tetramethyl phenyl-4-n-alkoxy azobenzene) (nAP4M) were prepared according to the method previously described by Latif and Hassan [14]. The transition temperatures and phase behavior of this series are given in Table 1.



$$R = \text{C}_n\text{H}_{2n+1} \quad n = 4-8 \quad (n, \text{ number of carbon atoms in the terminal alkyl})$$

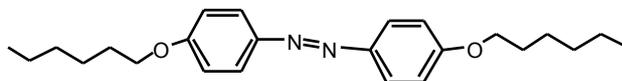
The following four reference liquid crystalline compounds were used for miscibility experiments:

- i- Terephthlylidene-bis-(4-n-butyl-anilin) (TBAA)



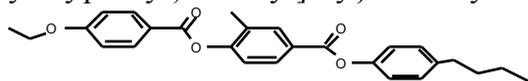
Mesophase: Cr Sm5 SmH SmG SmC SmA N I  
 Transition temp. °C: 113 74 89 144.5 172 199 233

- ii- 4-n-hexyloxy phenyl -4-n-hexyloxy azobenzene. (HPA)



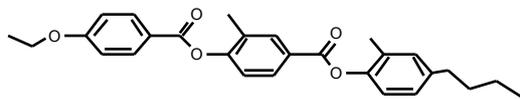
Mesophase: Cr Sm N I  
 Transition temp. °C : 102 114

- iii- 4-butylphenyl 4-[(4-ethoxyphenyl)carbonyl]oxy}-3-methyl benzoate . (4B2M).



Mesophase: Cr N I  
 Transition temp °C: 91 179

iv- 4-butyl-2-methylphenyl-4-[[[(4-ethoxyphenyl)carbonyl]oxy]-3-methylbenzoate. (4B2,3M)



Mesophase: Cr N I  
 Transition temp. °C: (143) 160

These compounds were kindly supplied by Prof Dr. Pelzl, Physical Chemistry Department, Martin Luther University, Halle, Germany. They were prepared according to the methods previously described [15-17].

## 2. Differential Scanning Calorimetry (DSC)

Calorimetric investigations were carried out on 910 differential scanning calorimeter (DSC) 1090 thermal analyzer (Phillips) by adopting a scanning rate of 10°C/min.

## 3. Preparation of binary mixtures

The binary mixtures used in this study were prepared by weighing each of the pure components adequate proportion to four places on an analytical balance into small glass vials, each mixture was heated until it became isotropic and mixed very well then allowed to crystallize. This was repeated three times to ensure a homogenous mixture.

## 4. Microscopy

The transition temperatures and the type of mesophase present in each mixture were determined by polarized light microscopy using Olympus microscope provided with a heating and cooling stage. Each mixture, mounted on a microscope slid and covered with a glass cover slip.

# Results and Discussion

## The thermal behavior and the binary systems

For the investigation of the monotropic smectic phase in the homologous series nAP4M, (n = 4-8). It is necessary to proof if all these smectic phases (Table 1) [14] which appear are the same smectic phase or not.

Figure (1) represents the phase diagrams of the four possible binary combinations made from the 6AP4M with the different alkyloxy terminal group (n = 4, 5, 7, or 8). The binary diagrams show that all the homologies components have the nematic and the same smectic phase.

On other hand our smectic phase need to be identified with other known liquid crystal component which have a smectic phase which can be miscible with it without contradiction. Figure (2) shows the binary mixture system of the compound (6AP4M) with the reference liquid crystalline compound (TBAA). The smectic phase of the compound (6AP4M) is miscible with Sm5 phase from compound (TBAA) without any contradictions and can take its symbol. The compressive of the thermodynamic transition enthalpies  $\Delta H$  values with topology of the binary systems diagrams Figure (2) and the transition enthalpies  $\Delta H$  of the pure liquid crystals compounds (6AP4M and TBAA) give an identification image for the structural situation of the mesophases.

Phase transition temperatures and transition enthalpy values of compounds (6AP4M and TBAA) are listed in Table 2. By comparing the transition between the various phases type in this table, we notify the following certain regularities:

1. The melting enthalpies possess the highest value compared with other data and it's normal [18] □□ In certain substances with low melting enthalpy, transition could be detected due to several phases in the solid state. In these cases the transition enthalpies were added to the melting enthalpies, to yield transition of  $\Delta H$ .
2. The transition enthalpies connected with the liquid crystals phases do not exceed 7.080 kJ/mol; in most cases they are considerably smaller. Certain regularities could be easily

derived by taking into consideration the various group liquid crystalline phase types. The transition enthalpies of the compound TBAA represented by small  $\Delta H$  (Sm5 / SmH and SmH / SmG), were extremely small or even vanishing value (SmC/SmA), large transition enthalpy was (SmG/SmC) more than 1.500 kJ/mol, and the compound 6AP4M showed a large  $\Delta H$  (Sm5/N).

The DSC thermograms Figure (3), show the transition enthalpies of the different mesophase with different concentrations at (95, 75, 50, 20, and 5% of compound 6AP4M). A large transition enthalpy (Sm5/SmH, SmH/SmG) at concentrations 5 and 20% of compound 6AP4M, this occurs also in the concentration 50% of compound 6AP4M between the phases (Sm5/SmG). The concentrations 75% of compound 6AP4M, the transitions (Sm5/SmG, Sm5/N) large  $\Delta H$ , and at 95% of compound 6AP4M have also a large transition  $\Delta H$  between (Sm5/N). This large  $\Delta H$  change indicates large structural change within the transitions from phase to phase. While the transition enthalpies within the same phase group are combined normally with small structural change indicated by small  $\Delta H$  value [19, 20].

Fifteen binary mixtures were represented in Figures (4, 5, 6). Figure (4) shows the binary mixtures between the (nPA4M) and HPA (this reference compound has no lateral group in its structure), this Figure displays linearly mesophase isotropic transition temperatures and appeared enantiotropic nematic phase in wide concentration in the binary mixtures and the Sm5 as monotropic in a concentration region between (75-100% of nPA4M).

The Figure 5 shows the binary mixture systems between nPA4M and 4B2M (this reference compound has one methyl lateral group in the middle core benzene ring), this also shows a linearly mesophase isotropic transition temperature, enantiotropic nematic phase wide concentration area (0-96% of nPA4M), and the monotropic Sm5 phase in the concentration region of (77-100 % of nPA4M). Figure 6 the binary mixtures were between nPA4M and 4B2,3M (this reference compound contains two methyl terminal groups on two different core benzene ring). The enantiotropic nematic phase was on small concentration region of the eutectic transition temperature ( $T_m$ ) the maximum area was in diagram (a) in concentration between (56-94% of 4PA4M) this area was small in comparison with areas of nematic phase in Figure 5, the monotropic Sm5 appeared in the diagrams (a-d), but in diagram (e) the nematic and the Sm5 phases appeared enantiotropically and around the concentration where the eutectic transition temperature of the Sm5 region was in the concentration (88-93 % of 8PA4M).

## Conclusions

Twenty phase diagrams of the all possible binary mixtures of the previously liquid crystals compounds were constructed in order to investigate the type of the smectic phase in the homologous series nPA4M. This smectic phase was (Sm5) which has a large transition enthalpy  $\Delta H$  compared to the nematic phase, which indicates that this phase has large structural changes through the transition to the nematic phase, which indicates that this smectic phase has large order parameter, this phase till now is not identified by x-ray diffraction method to decide its type.

From the thermal phase behavior and the lateral methyl groups effect on the thermotropic properties of the homologues series one can be draw the following conclusions:

1. All the systems containing HPA (a compound without a lateral methyl group) tended to possess eutectic composition in respective of the difference between terminal chain lengths of the two compounds in the binary systems.
2. With the systems containing 4B2M (a compound has one lateral methyl group) and (4B2,3M) a compound with two methyl lateral groups), the methyl lateral groups are a weak electron-releasing therefore the melting points of their eutectic composition is much

more depressed and accordingly led to the appearance of a wider composition range of nematic phase and allowed to appear the enantiotropic Sm5 in the eutectic region.

3. Figs. (4a, 5a and 6a) show the eutectic movement toward a high concentration of (4PA4M0). This phenomenon appeared in all systems by the same manner. Therefore Sm5 appeared in fig. (6e) enantiotropic with nematic phase.

## References

- Weissflog, W. and Demus, D.(1983) Cryst. Res. Technol. 18: K21.
- Weissflog, W. and Demus, D.(1984) Cryst. Res. Technol. 1955.
- Collings,P.J. ; Harid,M. and Gray, G.W.; Goodby J.W. (1997) "Introduction to liquid crystals, pp. 70-77, Tylor&Francis , London.
- Orzeszko,J.K. ; Maurin,D. and Melon-Ksyta, Z. (2001) Naturforsch. 55b, 1035
- Orzeszko,J.K.; Melon-Ksyta, K. and Czuprynski, Z. (2003)Naturforsch. 58b:1015
- Demus,D. (1985).Cryst. Res. Technol. 10:1413-1420
- Sackmann,H. and Demus,D. (1973). Mol. Cryst. Liq. Cryst. 21:239
- Sackmann, H. (1979).Pure Appli. Chem. 38: 503
- Gray, W. (1962). "Molecular Structure and Properties of Liquid Crystals", New York, Academic Press
- Sackmann, H. and Demus,D. Z. (1963).Phys. Chem., 224:177
- Sackmann, H. and Demus, D. Z. (1965). Phys. Chem., 230:285
- Dove ,S. ; Patel,P. R. and Vasnath, K. L. (1966). Indian J. Chem.,4:505
- Rushdy , M. (2006).Egypt. J. Solids, 29(2):227-240
- Latif,I. ; Hassan,E. S. (2009) Jornal of Diyala, 36 : 368.
- Goodby,J. W. ; Gray G. W. and Mosley,A. (1978).Mol. Cryst. Liq. Cryst. 41(lett.):183
- Wegand,C. ; Gabler,R. (1940).J. Prakt. Chem. 155,332
- Young,W.R. ; Haller, I. and Green, D. C. (1972) J. Org. Chem. 37:3707
- Wieggeleben,A. ; Richter,L. ; Deresch ,J. and Demus , D. (1980).Mol.Cryst. Liq. Cryst. 59:329
- Arnold,H. ; Demus,D. ; Koch,H. J. ; Nelles ,A. and Sackmann, H. (1969). Z. Phys.Chem. 240:185
- Marzotko ,A. and Demus, D. (1975). Liq. Cryst. Proc. Int. Conf., 1973: 189

**Table (1): The transition temperatures (°C) for series nAP4M**

Transition temperatures (C)					
-----					
Compound	R= C <sub>n</sub> N <sub>2n+1</sub>				
No.	n	Cr	Sm	N	I
1AP4M	1	• 129		-	-
2AP4M	2	• 126		-	-
3AP4M	3	• 103		-	-
4AP4M	4	• 89		• (83)	• (85)
5AP4M	5	• 87		• (59)	• (62)
6AP4M	6	• 80		• (48)	• (63)
7AP4M	7	• 69		• (47)	• (54)
8AP4M	8	• 65		• (45)	• (61)



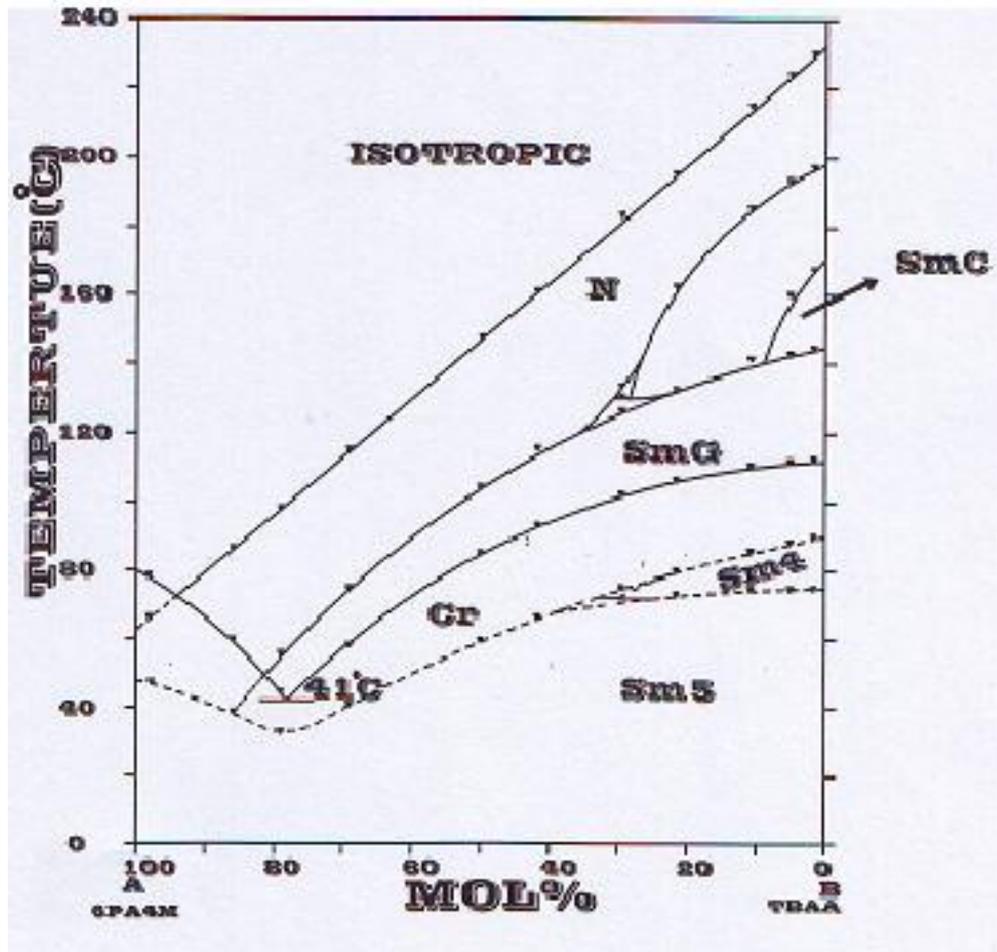


Fig.(2): The binary mixture of compound 6PA4M with the reference liquid crystalline compound TBAA.

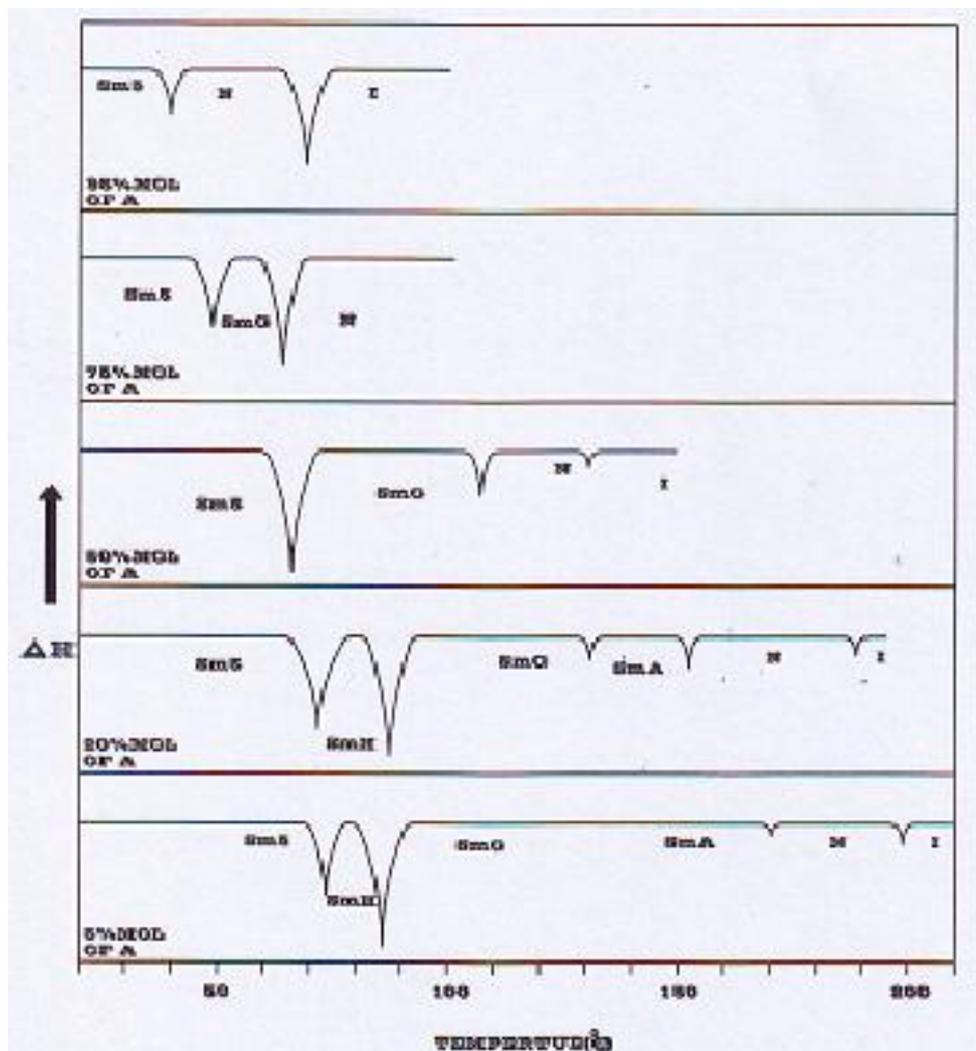


Fig.(3):DSC thermograms of the transition enthalpies of the different mesophase with different concentration 5-95% of compound 6AP4M.

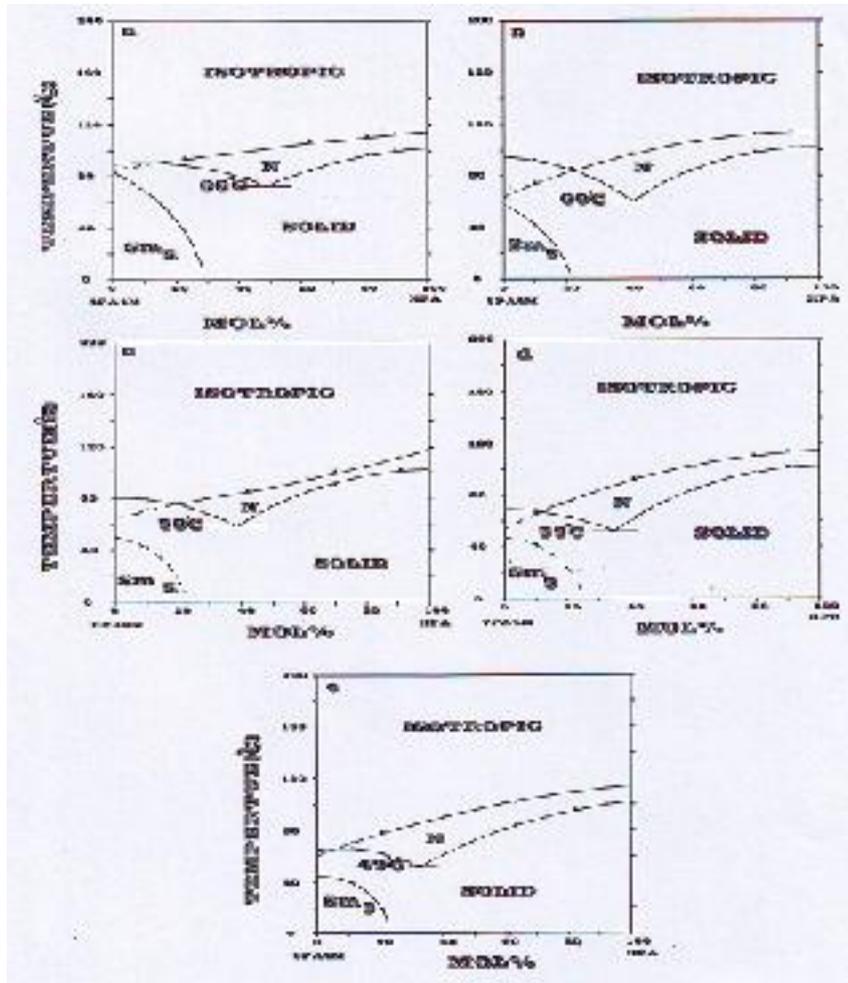


Fig.(4). The binary mixture diagrams of nPA4M and reference compound HPA, a) 4PA4M, b) 5PA4M, c) 6PA4M, d) 7PA4M and e) 8PA4M.

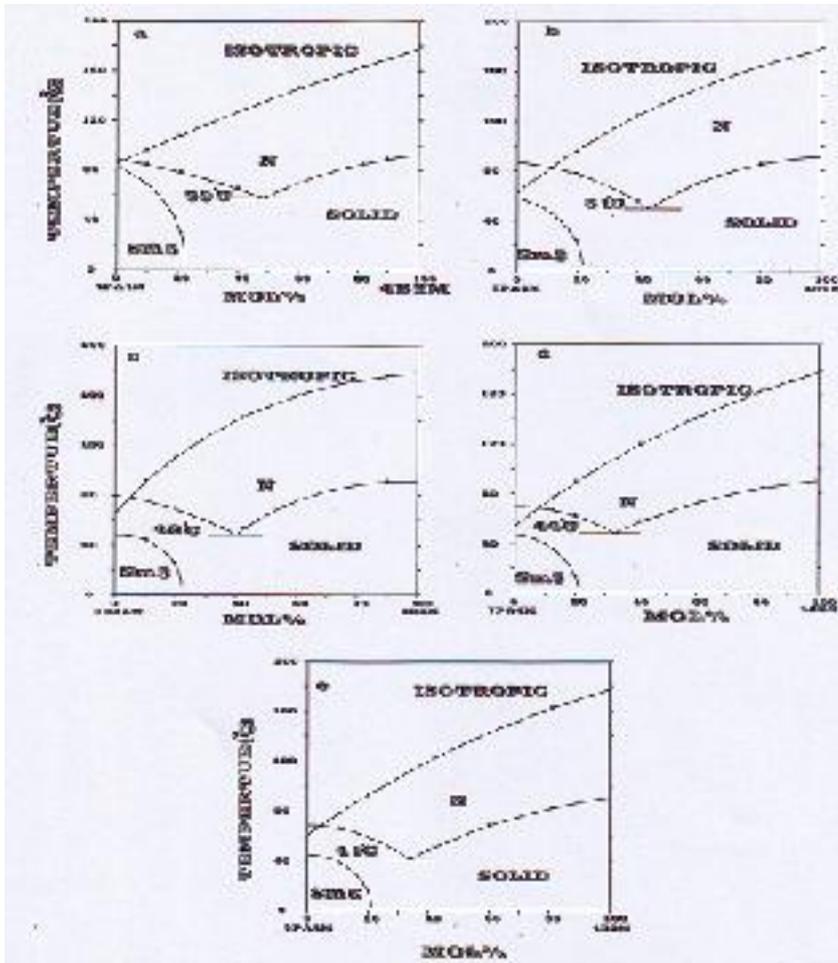


Fig.(5):The binary mixture diagrams of nPA4M and reference compound 4B2M, a) 4PA4M, b) 5PA4M, c) 6PA4M, d) 7PA4M and e) 8PA4M.

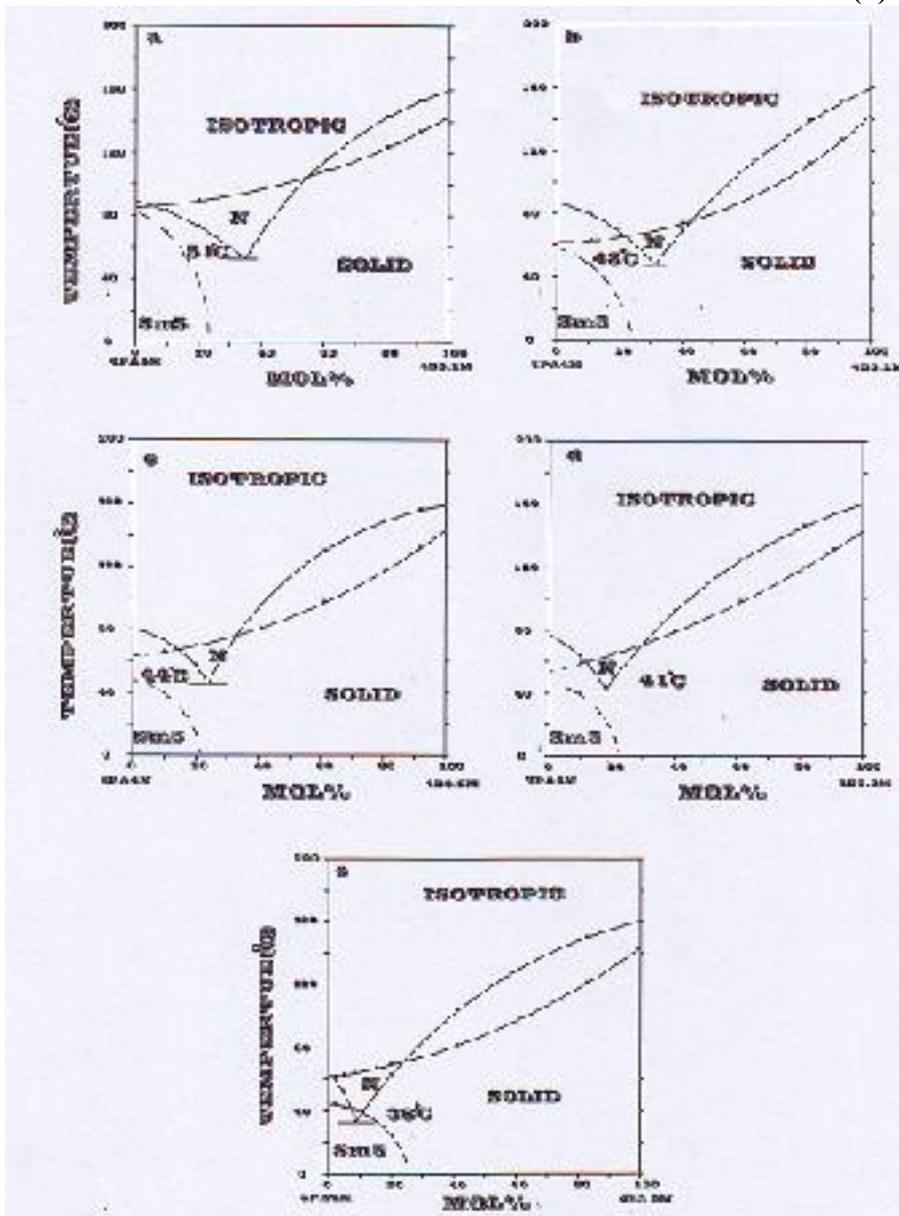


Fig.(6): The binary mixture diagrams of nPA4M and reference compound (4B3,2M) a) 4PA4M, b) 5PA4M, c) 6PA4M, d) 7PA4M and e) 8PA4M.