

Mesomorphic Properties Of Structure Related Ester Homologous Compounds : P-(P'-N-Alkoxy Benzoyloxy) Ter-Butyl Cinnamates

Patel B.K.¹ Chauhan M.L.*²

¹Pacific Academy of Higher Education And Research University, Udaipur, Rajasthan, India

²Chemistry Department, Sheth P. T. Arts & Science College, Gujarat University, Gujarat, India

ABSTRACT

A novel homologous series of p-(p'-n-Alkoxy Benzoyloxy) ter-Butyl Cinnamates was synthesized and studied for mesophase behavior dependence on molecular structure. The nematogenic mesophase is exhibited from the Pentylloxy to the last member hexadecyloxy derivative and the smectogenic mesophase from the pentylloxy to the tetradecyloxy member of the series. The nematic mesophase is of a threaded or Schlieren type, and the smectic mesophase is of a focal conic fan of the type A or C. Mesomorphic properties of the present novel homologous series are compared with other structurally similar homologous series. The average smectic and nematic thermal stabilities are 172.33 °C and 202.14 °C, respectively. Smectogenic phase lengths vary from 22 °C (C₁₄) to 58 °C (C₈) and the nematogenic phase lengths vary from 10 °C (C₁₆) to 50 °C (C₅). The series is partly nematogenic and smectogenic with considerable mesophase length. It is a middle ordered melting type series, whose relative group efficiency order for nematic derived.

Keywords : Liquid Crystal, Mesomorphic, Monotropic, Nematic, Smectic

I. INTRODUCTION

The number of liquid crystals compounds consisted of rigid part as two or three phenyl rings bridged through central bridge or bridges and flexible part as varying left polar terminal, alkyl or alkoxy (1–10) end group keeping right terminal end group intact of fix polarity with or without lateral substitution . In continuation of the same, presently a homologous series with two phenyl rings bridged through carboxylate linkage and ter-butyl cinnamates fixed end group with n-alkoxy as left terminal end group, is synthesized to investigate the effect of varying molecular structure by varying molecular rigidity and flexibility on mesogenic property. The present investigation is planned with a view to establish and

to understand the effect of molecular structure on liquid crystalline behavior of a substance.(11-15)

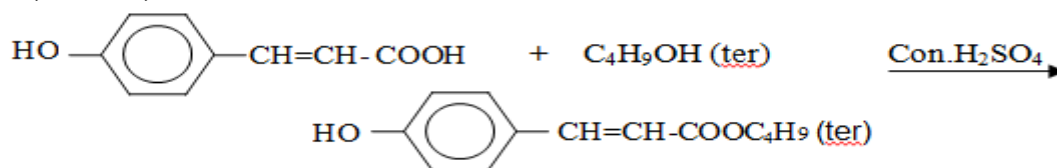
II. EXPERIMENTAL

Synthesis Experimental :

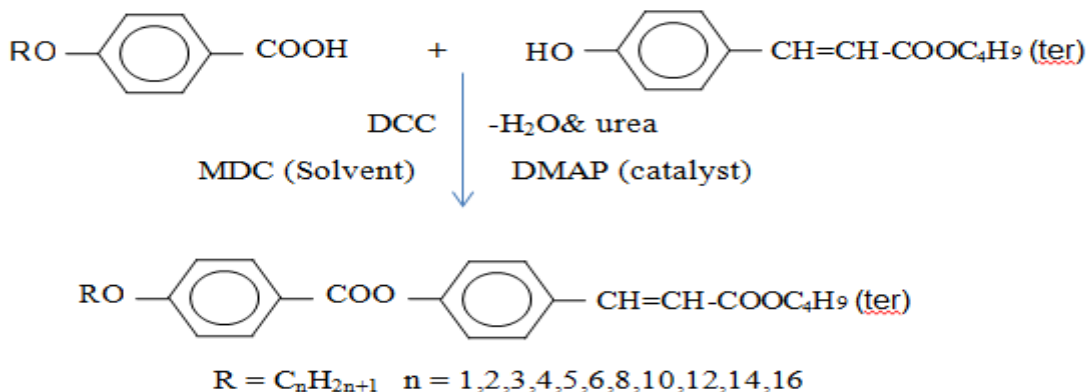
- p-n-alkoxy benzoic acids were prepared by the method of Gray and Winsor (16), Vora and Dave (17), Vogel (18).
- p-hydroxy ter-butyl cinnamates is prepared by reacting p-hydroxy cinnamic acid with corresponding freshly distilled ter-butyl alcohol in presence of concentrated sulphuric acid mixture.
- p-n-alkoxy benzoic acids dissolved in MDC with p-hydroxy ter-butyl cinnamates is in portions with DCC & DMAP as catalyst by stirring reaction mixture. (19-21) Products were

decomposed, filtered, washed, dried and purified, till the constant transition temperatures obtained. p-Hydroxy cinnamic acid, alkyl halides (R-X), tert-butanol, KOH, DCC, DMAP, MDC etc. required

(1) p-Hydroxy ter-butyl Cinnamates.



(2) p-(p'-n-alkoxy benzoyloxy) ter-butyl Cinnamates.



(Scheme -1)

Characterization

Some homologs as representative members of the series were selected for characterization of their structures by IR and ¹H NMR techniques. IR spectra were recorded on Perkin Elmer spectrum GX and

NMR were recorded using CDCl₃ as solvent. Microanalysis was performed on Perkin Elmer PE 2400 CHN analyzer. Transition and melting temperatures and liquid crystal properties were investigated by using optical polarizing microscopy.

Table 1. Elemental analysis for some derivatives.

Sr. No.	R = n-alkyl chain	Molecular Formula	Calculated %		Observed %	
			C	H	C	H
1	Propyl	C ₂₃ H ₂₆ O ₅	71.87	6.77	71.33	6.90
2	Pentyl	C ₂₅ H ₃₀ O ₅	73.17	7.31	73.33	7.30

Analytical Data

NMR: in ppm. Octyloxy Homologue : 1.11 – CH₃, 3.99 – OCH₂, 4.01 – OCH₂ of OCH₂-CH₂, 4.44 and 4.02 – OCH₂ of C₁₆H₃₃, 5.64 & 5.8 –CH=CH-, 6.89, 6.92, 8.00, –p-di-sub. phenyl 8.02 – p-di-sub phenyl two p-sub benzene.

Decyloxy Homologue : 0.99 –CH₃, 1.22 –CH₂, 2.49 – OCH₂-CH₂, 3.5, 3.31 – OCH₂ of –C₈H₁₇, 4.99 & 5.2 –CH=CH-, 6.9 and 6.8 two p-di-sub phenyl ring, 7.85 and 7.98, two p-di-sub phenyl ring.

IR in cm⁻¹. Hexyloxy Homologue : 2850 alkyl group, 1100, 1150, and 1730 COO ester group, 860 p-sub

phenyl ring, 3000 aromatic ring, 1640 alkene group, 750 polymethylene of C₁₄H₂₉

3080 aromatic ring, 1660 alkene group, 750 polymethylene of C₆H₁₃,

Octyloxy Homologue: 2900.0 alkyl group, 1050,1150, and 1710 COO ester group, 850 p-sub phenyl ring,

Table 2. Transition temperatures

Sr. No.	n-alkyl group	Transition temperatures in °C		
		Smectic	Nematic	Isotropic
1	Methyl	-	-	215
2	Ethyl	-	-	172
3	Propyl	-	-	180
4	Butyl	-	-	130
5	Pentyl	119	142	192
6	Hexyl	129	172	198
7	Octyl	112	170	200
8	Decyl	135	170	198
9	Dodecyl	138	180	210
10	Tetradecyl	178	200	215
11	Hexadecyl	-	192	202

III. RESULT AND DISCUSSION

4-Hydroxy cinnamic acid is dimeric, which on linking through the nonmesomorphic ester component resulted in the formation of mesomorphic products. Pentyloxy to tetradecyloxy homologues are enantiotropic nematogenic and smectogenic manner, hexadecyloxy homologue is only nematic .. A phase diagram (Fig. 1) shows the number of carbon atoms present in *n*-alkyl chain of the left *n*-alkoxy terminal end group versus the transition temperatures (**Table 2**) of the homologues showing mesophase behavior of the novel series. A solid-mesomorphic transition curve follows a zigzag path of rising and falling values with alternation of transition temperatures and behaves in normal manner. The smectic-nematic transition curve initially rises and then descends after passing through a maxima and further rise at the last number homologue. Hence, the smectic-nematic transition curve behaves in a usual manner. The nematic-isotropic transition curve descends as the

series is ascended with a sudden steep rise at the hexadecyloxy homologue. The single curve propagated until the last hexadecyloxy homologue of the series and generally behaves in a normal manner except for the hexadecyloxy for the novel homologous series under discussion. Smectogenic phase lengths vary from 22 °C (C₁₄) to 58 °C (C₈) and the nematogenic phase lengths vary from 10 °C (C₁₆) to 50 °C (C₅), respectively. The novel series under present investigation is partly nematogenic and partly smectogenic and is of a muddle order melting type. The methoxy to butoxy homologues sharply transform into isotropic state on heating and cooling . The molecules arrange themselves in a statistically parallel orientational order under a floating condition with favorable molecular rigidity and flexibility, which causes the molecular disalignment on the plane of a surface at an angle less than 90° under the influence of suitable magnitudes of anisotropic forces of intermolecular adhesion resisting thermal environment. ,The remaining homologues, i.e.,

pentoxy to hexadecyloxy of the novel homologous series resist externally exposed thermal vibrations for a definite range of temperature causing nematic and/or smectic mesophase formation by arranging the molecules as statistically parallel orientational order of molecular and/or in a sliding layered molecular arrangement in a floating condition. The butoxy, pentyloxy, and hexadecyloxy homologues do adopt only parallel orientational order of molecules within definite temperature range giving rise to only nematic mesophase formation, while the hexyloxy to tetradecyloxy homologues show a sliding layered arrangement of molecules due to the lamellar packing of molecules in their crystal lattices at first, for definite temperature range showing smectic mesophase formation and then they arrange themselves in a statically parallel orientational order in floating condition for another higher temperature range showing nematogenic mesophase formation [9,10]. Every substance does have the capacity to resist thermal vibrations exposed upon it up to a definite temperature, limit depending upon energy stored (ΔH) due to its mass and characteristics. However, since its heat resisting capacity crosses the limit, the molecules of a substance under thermal energy exposure loses intermolecular attractions and molecules are randomly oriented in all possible directions without any ordered manner. Thus, high order of molecular disorder or molecular randomness or entropy ($\Delta S = \Delta H/T$) occurs from and beyond isotropic temperature, i.e., mesophase formation destabilizes and ceases to appear. Thus, the thermal behavior of a thermotropic liquid crystal substance varies with temperature giving rise to various stabilized physical states of a substance. The molecular rigidity and flexibility are reduced or ineffective. The variations in mesomorphic properties from homologue to homologue in the novel homologous series are attributed to the gradual addition of $-\text{CH}_2-$ unit at the left n -alkoxy terminal end group keeping the right side laterally substituted almost equipolar and flexible groups that contribute to increased molecular polarizability and flexibility. Thus, the intermolecular adhering anisotropic forces of

attractions are favorably enhanced to induce mesophase formation right from the first member of the series to the last member of the series. The mesomorphic behavior of the presently investigated novel series-1 is compared with structurally similar other known homologous series –A (22) as shown in **Figure 2**. The solid-nematic or isotropic transition curve follows a zigzag path of rising and falling

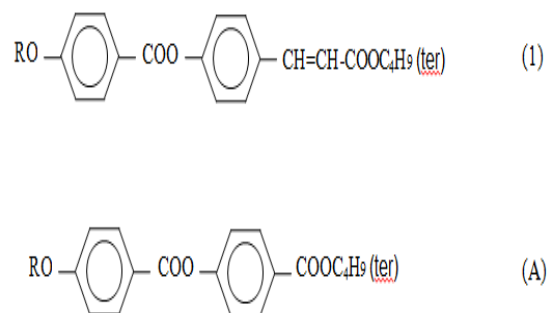


Figure 2

tendency as the series is ascended. The plot of the phase diagram (**Figure 1**) shows the presence of normal manner in the smectic-nematic and nematic-isotropic transition curve. Thus, the behavior of both smectic-nematic and nematic-isotropic transition curve of the present study suggests that, enthalpy change of the homolog from fifth up to hexadecyloxy homologue decreases Hence, a low and a high value of enthalpy correspond to a low and a high amount of heat energy requirement (low and high temperature) from surrounding to system. The opposing effects to the molecular geometry of an ter-butyl terminal group operates (1) an effect due to widening of the molecule causing a reduction in the intermolecular adhesion by increasing the intermolecular

Table 3. Thermal stabilities in °C

Series	(1)	(A)
Smectic-isotropic	172.33 (C5-C14)	–
Commencement of Smectic phase	C5	–

Nematic-isotropic	202.14 (C5-C16)	190.57 (C5-C16)
Commencement of Nematic-phase	C5	C5

distance and on the other hand (A) increased molecular width, increases molecular polarizability causing an increase in the intermolecular adhesion. Thus, closeness of molecular packing depends upon the net resultant intermolecular forces of attractions, which depend upon the predominating effect out of two opposing effects (1) and (A). In the present study, the latter effect is a predominating effect. **Table 3** summarizes the average thermal stabilities and molecular structure of the present series and other structurally related series A chosen for comparative study. The molecular geometry of all the homologous series under comparison consists of two phenyl rings linked through a carboxy or a vinyl carboxy ester central linkage with n-alkoxy group at the left terminus and $-\text{CH}=\text{CH}-\text{COO}-\text{C}(\text{CH}_3)_3$ (ter) and $-\text{COO}-\text{C}(\text{CH}_3)_3$ (ter) at the right terminus for series (1) and (A) respectively. The variation in the mesomorphic characteristics can be attributed to the combined effect of the presence of central ester and different right terminal groups, which have different molecular rigidity and flexibility related to molecular polarity and polarizability for the formation of mesophase [13,14]. On comparing the mesomorphic characteristics of series (1) with series A, it is observed that, the homologous of both the series differing in respect of central bridge only are enantiotropically nematogenic. Introduction of a polar ter-butyl group at the terminal position with $-\text{COO}-\text{C}(\text{CH}_3)_3$ in series-1 and Series-A enable considerable and significant anisotropic forces of attraction of suitable magnitude for pentyloxy to hexadecyloxy homologs, which serve to stabilize statistically parallel orientational order of molecules by end-to-end attractions conducive to the formation of a nematogenic mesophase. This effect persists even in the homologs with long n-alkoxy groups. Comparison

of series-1 with series-A indicates that the series-A has an isobutyl group at the right terminal with a vinyl carboxy central group while series-A has ter-butyl terminal group with a carboxy group. The flexible straight chained ter-butyl group with $-\text{CH}=\text{CH}-\text{COO}-$ group in series -1 adds the formation of smectic mesophase due to enhanced lateral attraction in addition to terminal attractions, which facilitates lamellar packing required for the formation of higher temperature smectic and nematic mesophase (1). Thus, series-1 exhibits smectic and nematic but series-A exhibits only nematogenic character. The nematic thermal stability of series-A being lower than series-1 is understandable because of the difference in terminal attractions arising from the $-\text{CH}=\text{CH}-\text{COO}-$ and $-\text{COO}-$ groups.

IV. CONCLUSION

The study suggests that a polar substituent at a terminal position in a homologous series with present molecular geometry gives rise to the exhibition of a smectogenic and nematogenic mesophase. Moreover, the presence of a vinyl carboxylate unit at a central and/or a terminal position favorably induce a higher temperature smectogenic and nematogenic mesophase.

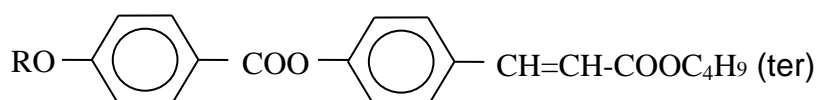
V. ACKNOWLEDGMENT

Authors acknowledge thanks to the S.P.T. Science College, Godhra for research facilities services as and when needed. Authors obliged to Dr. A. V. Doshi, ex-Principal, M.V.M. Science College, Rajkot. Authors are also thankful to Dr. N.N. Vyas, Dr. V. R. Patel for their valuable helping hand and microscopic facility. The authors are also thankful to Department of Chemistry, Saurashtra University, Rajkot. For analytical and spectral analysis.

VI. REFERENCES

- [1]. D. Demus and H. Zschke, *Flussige Kristalle in Tabellen* (Leipzig: VEB Deutscher Verlag für Grundstoffindustrie), 1984.
- [2]. P.G. de-Gennes and J. Prost., *The physics of liquid crystals*, claredon press, oxford, 1993.
- [3]. V. Vill, *Liquid crystal 2.0*, Database of liquid crystalline compounds for personal computers, Fijisu Kyushu System (FQS) Ltd. Fukuoka (Hamburg: LCI), 1996.
- [4]. A.V. Doshi and H.R. Prajapati, *J. Inst. Chemist*, 2008, 80, 14.
- [5]. K.J. Ganatra and U.C. Bhoya, *Mol. Cryst. Liq. Cryst.*, 2008, 487, 110.
- [6]. A.V. Doshi and K.J. Gantra, *Proc. Indian, Acad. Sci.*, Bangalore, 1999, 3, 563.
- [7]. A.V. Doshi and U.C. Bhoya, *J. Indian chem. Soc.*, 2002, 79, 249.
- [8]. N.D. Jadav et al, *Mol. Cryst. Liq. Cryst.*, 2003, 399, 53.
- [9]. A.K. Prajapati and H.M. Pandya, *Mol. Cryst. Liq. Cryst.*, 2003, 393, 31.
- [10]. J.S. Dave et al, *Mol. Cryst. Liq. Cryst.*, 2002, 378, 1.
- [11]. R.A. Vora and A.K. Prajapati, *Liquid Crystals*, 1998, 25, 5, 567.
- [12]. U.J. Al-Hamdani, T.E. Gassim, and H.H. Radhy, *Molecules*, 2010, 15, 5620.
- [13]. Lohar, J. M. and Dave Jayrang. (1983). *Mol. Cryst. Liq. Cryst. (Eng.)*, 103(1-4), 181.
- [14]. Baumeister, U., Kosterkiewiez, Z., Hartungs, H., Weissflos, W., and Demus, D. (1990). *Liquid Crystal*, 7, 241.
- [15]. Chauhan, M. B., Bhoi, D. K., Machhar, M. T., Solanki, D. K., and Solanki, Dhaval. (2010). *Der Pharma Chemica*, 2(4), 30-37.
- [16]. (a) Gray, G.W. (1962). *Molecular Structure and Properties of Liquid Crystals*, Academic Press: London (b) Gray, G. W. and Winsor, P. A. (1974). *Liquid Crystals and Plastic Crystals*, Eillis Harwood: Chichester.
- [17]. Dave, J. S. and Vora, R. A. (1970). *Liquid Crystals and Ordered Fluids*, Plenum Press: New York.
- [18]. Vogel, A. I. (1989). *Textbook of Practical Organic Chemistry*, Longmann: London.
- [19]. Patel B. H. & Doshi A.V. "Mesomorphism and Molecular Structure Novel Homologous Series - 4-(4'-n-alkoxy Cinnamoyloxy)-4''methoxy Benzyl Benzoates". *Mol. Cryst. Liq. Cryst.*, Vol-607, PP. 78-86 (2015).
- [20]. Patel B.H., V.R.Patel & Doshi A. V. "Mesomorphism Dependence on Molecular Flexibility by -OCH₃ And -H Terminal Units" *Mol. Cryst. Liq. Cryst.*, Vol-609, PP. 10-18 (2015).
- [21]. Rajesh B. Marathe, N.N. Vyas and Doshi A. V. "Molecular Flexibility Operated Mesomorphism" *ILCPA, Scipress Ltd*, Vol-52, PP. 163-171, (2015).
- [22]. Chauhan, M. L., Patel,B.K., (2016). *Der Pharma Chemica*, 8(11), 104-109.

Homologous Series : p -(p'-n-alkoxy benzoxyloxy) ter-butyl Cinnamets



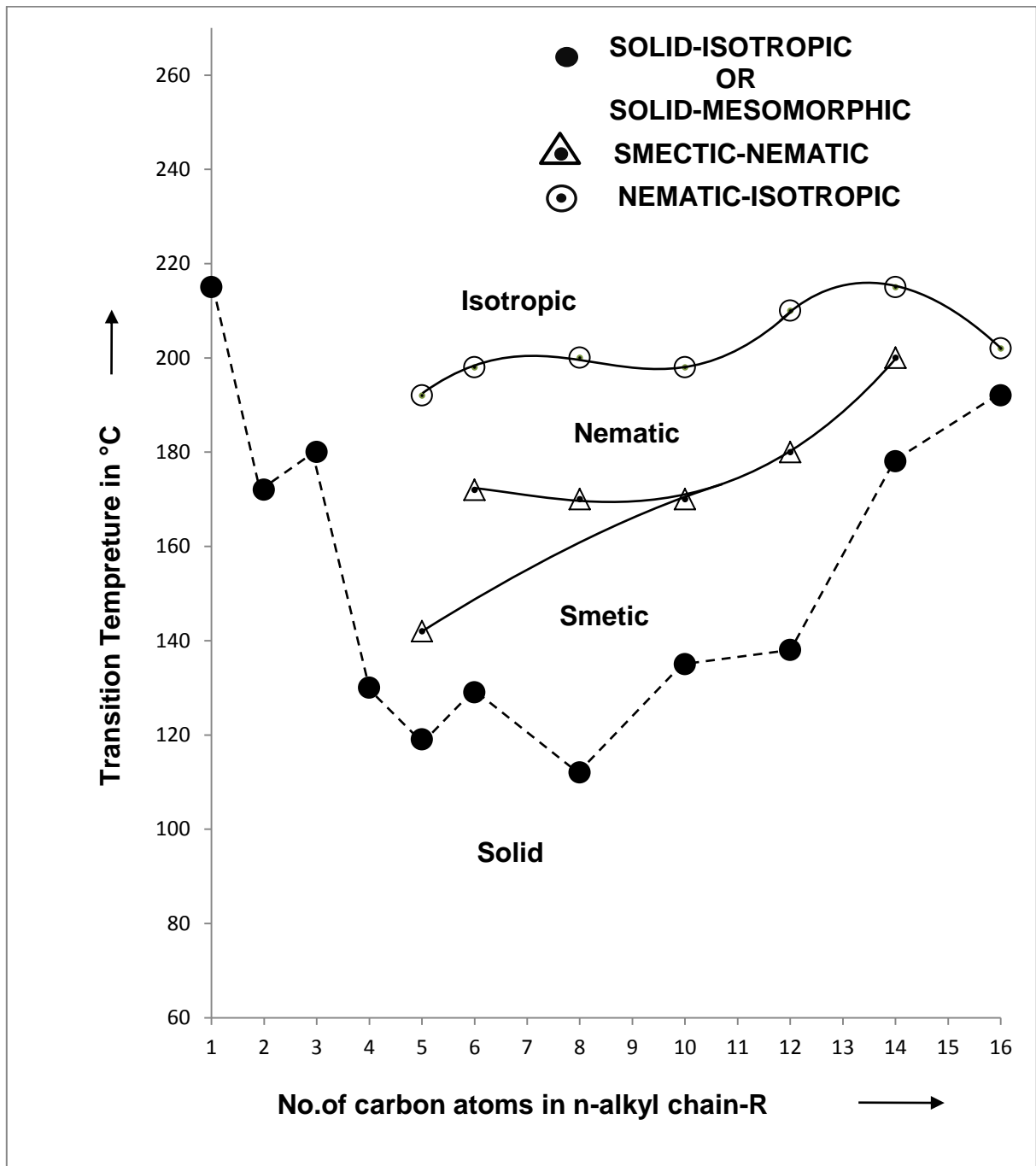


Figure 1. Phase Behavior of Series