Journal of Non-Crystalline Solids 357 (2011) 1745–1749

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Liquid crystalline G phase of self assembled donor–acceptor molecules by intermolecular hydrogen bonding

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ARTICLE INFO

Article history:
Received 20 October 2010
Received in revised form 23 December 2010
Available online 25 February 2011

Keywords:
PNBA;
NHB;
FTIR;
Intermolecular hydrogen bonding;
Crystal G phase

ABSTRACT

The interaction with donor p-*n*-alkylbenzoic acid and acceptor nonyl-*p*-hydroxy benzoate molecules was studied. The likely association of these molecules to complexes is studied by intermolecular hydrogen bonding. The textures are observed by polarizing optical microscope with corresponding transitions confirmed by differential scanning calorimetry. The molecular complexes exhibited enantiotropic crystal G phases in both heating and cooling cycles. The relevant functional groups C O, C–O and OH in formation of molecular complexes are attributed with spectral shifts in infrared spectra and further with absorption studies. The proton NMR studies convinced the structural aspects of hydrogen bonded structure. Crystal parameters were studied with powdered X-ray diffraction. The results show that constituent molecules self organize through intermolecular hydrogen bonding in the formation of crystal G phase.

1. Introduction

It is evident that a new class of liquid crystals was initiated with hydrogen bonding [1–5] that gained importance by self assembling process [6,7]. A great deal of work is reported on hydrogen bonded liquid crystals either with mesogenics, non mesogenics or with their combination in generation of new phases leading to supramolecular structures [6–9] due to its stability[10] and directionality [11].These include the doubly hydrogen bonding systems [6], the side chains [8], Schiff bases [12], smallest possible molecules [13], polyoxometalates [14], donor–acceptor groups [15], organic acids[16], benzoic acid derivatives [17], oxadiazole derivatives and dicarboxylic acid [18] and dimers of 4-alkoxy-4^1 stilbazole [19]. In all these processes an intermediate state is reached either minimizing the energy or connected with higher energy that participates in hydrogen bonding leading to supramolecular structures. Considerable progress has been made between the donor–acceptor [15,20,21] molecules cross linked by non covalent interactions [5,22,23] with intermolecular hydrogen bonding and its compatibility to its optical property inducing new thermo dynamical phases [24–27]. Herein we report crystal G phase between the donor COOH group p-*n*-alkylbenzoic acid where *n* is alkyl chain from 5 to 10 and acceptor group nonyl-*p*-hydroxy benzoate with intermolecular hydrogen bonding is shown in Fig. 1.

2. Materials and methods

The preparation is performed by dissolving in 1:1 ratio the compounds p-*n*-alkyl benzoic acids (PNBA) mesogenic in nature and nonyl-*p*-hydroxy benzoate (NHB) in pyridine under constant stirring for about 4 h approximately at 80 °C. The volume of resultant homogenous mixture was reduced to solid powder by removing excess pyridine by fractional distillation. The crystalline products were dried and re-crystallized by using dichloro-methane and the yield obtained is approximately up to 90%.

The free and synthesized molecular complexes (PNBA:NHB) were characterized with texture using Hertel Reuss super-pan II polarizing optical microscope (POM) equipped with optical display (DP10) at scan rate of 0.1°°C/min. Confirmations of transition temperatures and thermal studies involve use of differential scanning calorimeter (DSC) with thermograms recorded by SDT Q600 V8.1 under nitrogen atmosphere at scan rate of 5°°C/min with enthalpies measured in W/g and entropies in W K^{-1} Mol^{-1}. The solid state (KBr) FTIR-spectra was recorded on Perkin-Elmer (spectrum bX) series at room temperature from 400 to 4400 cm^{-1} with resolution 8 cm^{-1}. The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on the Brucker Avance 400 MHz instrument in $CDCL_3$ with chemical shifts in ppm. X-ray studies were performed at room temperature using Phillips powdered XRD system in determining interplanar spacing(Angstrom units), intensity(arbitrary units) and thickness (Angstrom units) using Scherrer's formula [28].

3. Results

The understanding of phase transition in liquid crystalline complexes is emphasized involving non covalent cross linked

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doi:10.1016/j.jnoncrysol.2010.12.076

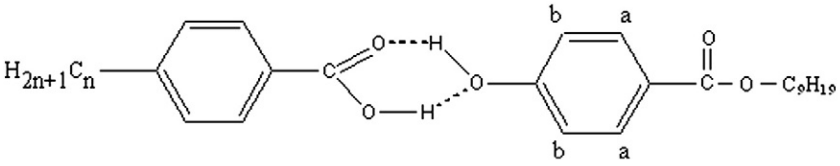

Fig. 1. Intermolecular hydrogen bonded molecular complex PNBA: NHB.

Table 1
Observations of free p-n-alkyl benzoic acids PNBA.

Free molecules	Transition temperatures in °C in heating and cooling				$DSC_{N\ phase}$ (ΔH) W/g		$(\Delta S)\times 10^{-3} W K^{-1} mol^{-1}$	
	Cr to N	N to I	I to N	N to Cr	Heating	Cooling	Heating	Cooling
P5BA	91.2	126.4	124.0	084.0	87.89(0.1031)	117.24(1.13)	0.2856	2.8956
P6BA	99.5	116.5	112.5	094.5	95.76(0.1666)	112.5(1.15)	0.4517	2.983
P7BA	105.7	123.2	121.7	102.2	102.6(0.6495)	117.5(0.75)	1.729	1.9206
P8BA	98.3	114.3	110.3	98.90	100.29(0.5517)	109.6(1.53)	1.4779	3.9989
P9BA	99.8	118.6	115.8	90.10	96.71(0.5854)	111.5(2.04)	1.5834	5.3055
P10BA	95.6	111.3	108.8	93.30	96.07(1.075)	103.9(2.45)	2.9127	6.5003

network. In the absence of the acid group the complexes do not exhibit liquid crystalline transition. The free p-*n*-alkyl benzoic acids [29] with n = 5 to 10 exhibit a threaded nematic and further transformed to nematic droplets texture in entire homologous series with clearing temperatures extending from 126.4 to 111.3°°C. These molecules with terminal chains provide the flexibility to stabilize molecular alignment with the endothermal peaks in heating and exothermal peaks in cooling. The observed texture and transition temperatures in heating and cooling with thermal quantities enthalpy (ΔH) and entropy (ΔS) values in order of 10^{-3} are depicted in Table 1 and phase diagram in Fig. 2.The textural studies with nematic (N)–Isotropic (Iso) narrates even odd behavior and contrast behavior with crystal (Crys) to nematic in chain lengths from n = 5 to 7 and 8 to 10 of homologous series. The enthalpies at the expense of energy during transition are responsible in the orientational order of the rigid rods forming nematics with second order transition. These nematics are sensitive allowing the scattering of rigid rods in interactions with the addition of the nonyl-*p*-hydroxy benzoate resulting in formation of crystal G phase [30].

FTIR analysis confirms the presence of specific interactions between the constituents under consideration and suitable technique for identification of changes of during bond formation. The solid state IR spectral studies with the representative octyl-*p*-benzoic acid (P8BA), nonyl-*p*-hydroxy benzoate and molecular complexes with respective functional groups (in cm^{-1}) are listed in Table 2. The infrared spectral studies [31–33] are convinced with respective functional groups of donor C O at 1644, 1289 and 3441 of C–O and OH and acceptor with its in plane bend (IPB), out plane bend (OPB) at 1397, 620 and 1221 of C–O in their respective regions.

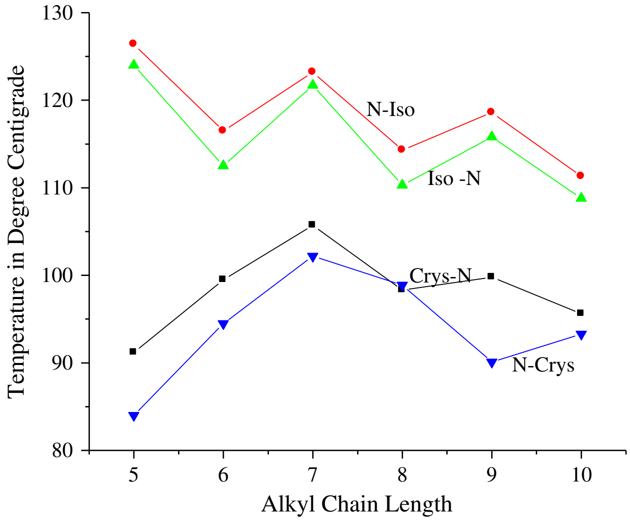

Fig. 2. Phase diagram of free mesogen in heating and cooling process.

The proton magnetic resonance spectral studies [34] of the free benzoic acids exhibit a doublet at 7.5 to 7.7 equivalent to 2H is due to aromatic protons, a doublet at 8.1 equivalent to 2H is due to aromatic protons and a singlet at 12.7 equivalent to 1H is due to carboxylic acid proton. The free nonly-p-hydroxy benzoate exhibits doublet at 6.9 equivalent to 2H is due to aromatic protons [a–a], a doublet in range at 7.9–8.0 equivalent to 2H is due to aromatic protons [b–b], a doublet between 1.2 and 1.3 equivalent to 3H indicates methyl protons, a multiplet between 1.2 and 1.4 of $(CH_2)_n$ indicates methylene protons and a triplet at 1.7 to 1.8 equivalent to 2H indicates methylene protons beside COO. The peak at 4.1 ppm attributed for phenolic OH of NHB.

The crystal parameters of molecular complexes with the constituents were performed by powdered X-ray diffraction with CuKα radiation of wavelength λ = 1.54056 AU .These include interplanar spacing d = n λ/sin θ and thickness<t> = 0.94 λ/FWHM Cos θ_B measured in angstrom units(AU) with FWHM as full width half maximum and θ_B is the corresponding Bragg angle in degrees.

4. Discussion

Crystal G exhibit herringbone packed structure with orientational disorder and maintaining continuous translational symmetry. The molecular centers are arranged in layers delimited by equidistant planes leading to long range positional order characterized by C–centered monoclinic cell with molecules having hexagonal packing. This texture is formed with projected growth of elongated molecules that is viscous and sheared leading to textures rectangular in shape.

The molecular complexes PNBA: NHB exhibit a high degree of thermal and chemical stability transform to phase at reduced temperature range with thermal quantities listed Table 3 further with phase diagrams in Fig. 3. The heating process is realized in two steps i.e. from crystal (Cr) to G phase and to isotropic (I) phase and its reverse in cooling process. The cooling process narrates even odd behavior in addition to Cry to G in heating process. A feature of complexes is enantiotropic behavior due to the addition of benzoate group and the cooperative nature of acid group invokes the fluctuations in nematics with increased mobility allowing displacing