Influence of hydrogen bonding on the generation and stabilization of liquid crystalline polyesters, poly(esteramide)s and polyacrylates

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Abstract. Induction and stabilization of liquid crystallinity through hydrogen bonding (HB) are now well-established. Interesting observations made on the influence of HB on LC behaviour of amido diol-based poly(esteramide)s, poly(esteramide)s containing nitro groups and azobenzene mesogen-based polyacrylates will be discussed. The use of amido diol as an important precursor for the synthesis of novel PEAs containing inbuilt di-amide linkage enabled generation of extensive hydrogen bondings between the amide–amide and amide–ester groups which stabilized the mesophase structures of the PEAs. The contributions of hydrogen bonding to the generation and stabilization of mesophase structures were plainly evident from the observation of liquid crystallinity even in PEAs prepared from fully aliphatic amido diols. Replacement of terephthaloyl units by isophthaloyl moiety totally vanquished liquid crystalline phases while biphenylene and naphthalene units did only reduce the transition temperatures as expected. The occurrence of the smectic phases in some of the polymers indicated possibly self-assembly through the formation of hetero intermolecular hydrogen bonded networks. A smectic polymorphism and in addition, a smectic-to-nematic transition, were observed in the monomers and polymers based on 1,4-phenylene[bis-(3-nitroanthranilidic acid)] containing nitro groups. A smectic polymorphism was also observed as a combined effect of hydrogen bonded carboxyl groups and laterally substituted alkyl side chains in the case of azobenzene mesogen containing side chain polyacrylates. It was further shown that the presence of the mesophase enhances the non-linear optical (NLO) response of these polymers.

Keywords. Hydrogen bonding; polymer liquid crystals; smectic; thermal properties; polymer.

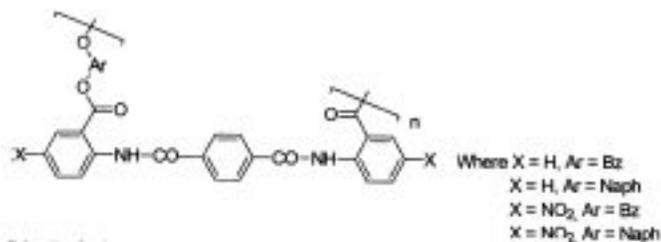**PACS Nos** 82.30.Rs; 61.30.Vx; 61.30.Eb; 67.80.Gb; 61.82.Pv

1. Introduction

Intermolecular hydrogen bonds play an important role in the design and engineering of architectures of many polymeric materials [1–4]. Hydrogen bonding can affect the chain length, chain packing, rigidity and molecular order. A systematic study of these polymers can address the fundamental question of mesophase transitions and ordering driven by the formation and destruction of such interactions in condensed phase. The induction and stabilization of liquid crystallinity by hydrogen bonding in a series of polymers containing ester–amide and acrylate moieties and azobenzene mesogens and nitro groups were studied in this laboratory, the results of which are discussed in this paper.

Three groups of polymers were selected for the study. (1) The first group consists of poly(esteramide)s (figure 1a) prepared through the amido diol route. These polymers contain di-amide linkages that favour extensive hydrogen bonding. The PEAs prepared in the laboratory [5–7] through polymerization of amido diols obtained by the aminolysis of lactones exhibited liquid crystallinity due mainly to contributions from the extensive hydrogen bonding from the amide–amide and amide–ester linkages coupled with the presence of rigidity arising from the double bond character of the amide group. (2) PEAs based on 1,4-phenylene[bis-(3-nitroanthranilidic acid)] containing nitro groups (figure 1b) exhibited a smectic polymorphism due to the additional ordering of the layer structures through hydrogen bonding of the carboxylic acid groups [8]. Nitro group plays an important role in NLO and electro-optical (EO) polymers as an electron acceptor group. (3) The effects of hydrogen bonding on the stabilization of liquid crystallinity were again observed in the case of polyacrylates containing azobenzene mesogens (figure 1) for the general structure of the polyacrylate) [9–11].
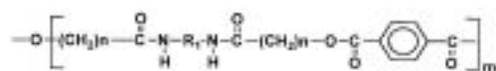
(a) Poly(esteramide) prepared from amidodiol

(b) Poly(esteramide) containing nitro group

Where X = H, Ar = Bz
X = H, Ar = Naph
X = NO$_2$, Ar = Bz
X = NO$_2$, Ar = Naph
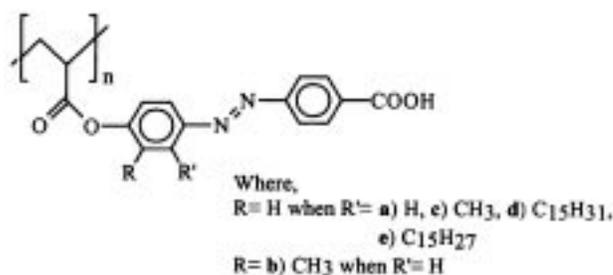
(c) **Side Chain Azobenzene Polymers**

Where,
R = H when R'= a) H, c) CH$_3$, d) C$_{15}$H$_{31}$,
e) C$_{15}$H$_{27}$
R= b) CH$_3$ when R'= H

Figure 1. General structures of PEAs containing (**a**) di-amide groups, (**b**) nitro groups and (**c**) polyacrylates containing azobenzene mesogens.

2. Experimental part

The PEAs containing diamide linkages were prepared from polycondensation of the corresponding amido diols obtained from the aminolysis of the lactones with diamines. The procedures are as reported earlier [5–7]. H-bonded liquid crystalline PEAs were also obtained from 1,4-phenylene[bis(3-nitroanthranilidic acid)] or 1,4-phenylene[bis(anthranilidic acid)] (with and without nitro groups respectively) by condensing each with hydroquinone (HQ)/dihydroxy naphthalene (DHN) separately [8]. The dicarboxylic monomers were synthesized starting from 2-aminobenzoic acid. The polyacrylates were synthesized by free radical polymerization of the respective monomers, 4-[(4-acryloyloxyphenyl)azo]benzoic acid, 4-[(4-acryloyloxy-3-methylphenyl)azo]benzoic acid, 4-[(4-acryloyloxy-2-methylphenyl)azo]benzoic acid and 4-[(4-acryloyloxy-2-pentadecylphenyl)azo]benzoic acid [9–11]. The monomers were obtained by acryloylation of the azo derivative prepared by the diazo coupling reaction between *p*-aminobenzoic acid and the respective phenolic derivatives with varying hydrocarbon substituents.

The FTIR spectra were recorded with a spectrometer of model Nicolet, 150 FTIR. Phase transitions were observed under Nikon Optiphot polarized light microscope (PLM) equipped with Linkam THMS 600 heating stage connected to TP 92 temperature programmer. DSC scans were performed using DuPont DSC 2010 differential scanning calorimeter attached to Thermal Analyst 2100 data solution under nitrogen.

3. Results and discussion

3.1 *Hydrogen bonding in PEAs prepared through the amido diol route*

The presence of hydrogen bonding in PEA was studied using FTIR technique by measuring the IR spectra (figure 2) in the temperature range 30–240°C [5]. The infrared spectra of all PEAs showed a broad dominant band in the range 3283 and 3061 cm^{-1} and the peak position of this band changes slightly with the structure of PEAs. This broad band is characteristic of hydrogen bonded *trans* form of the amide group. The decrease in the band at 1712 cm^{-1}, with simultaneous increase in the bands at 1638 and 1533 cm^{-1} confirms the fact that during heating some of the amide–ester hydrogen bonds change into amide–amide hydrogen bond. The band at 1268 cm^{-1} can be taken as the deformation vibration due to the amide–amide bonded N–H (amide III) band. This possibly indicates that the hydrogen bonding might take place between the ester carbonyl and the N–hydrogen of the amide linkage. The transition from mesophase to the isotropic phase is accompanied by a substantial decrease of hydrogen bonds. The existence of the broad band with overlaying shoulders between 3400–3313 cm^{-1} indicates that various types of hydrogen bonds, with different bond distances for N–H groups, are present. The spectrum of the polymer recorded at room temperature had two different maxima at 3310 cm^{-1} and 3423 cm^{-1}. During heating, a decrease in the band at 3423 cm^{-1} is observed. The structure of the polymers even in the mesophase is dominated by hydrogen bonds between the amide–ester and amide–amide groups in the adjacent chains formed by self-organization through the formation of hetero intermolecular hydrogen bonded networks. In other words the birefringence is due to the presence of H-bonded sheets in the form of clusters, layers or lamellae (figure 3).
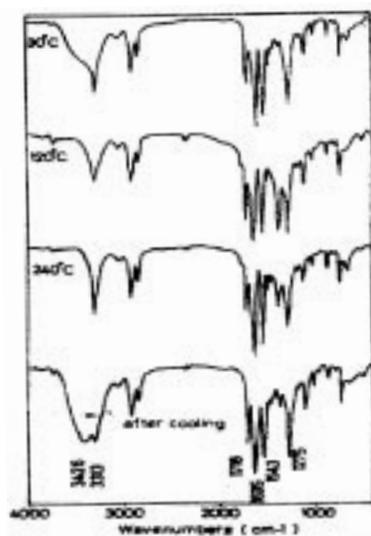
Figure 2. FTIR spectrum of the PBTBH at temperatures 30, 120, 240°C and after cooling.
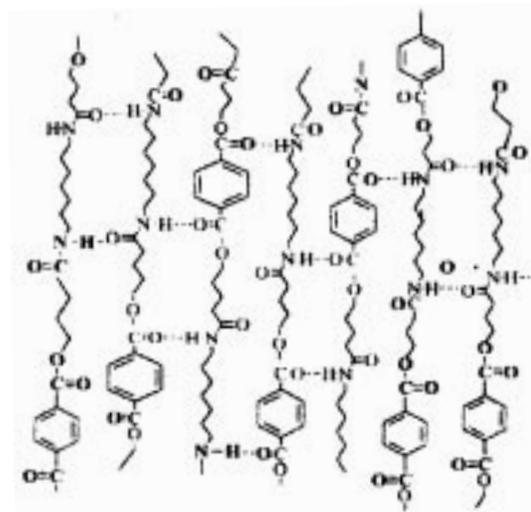

Figure 3. Hydrogen bonding in PEA.

The thermal and phase behaviour were investigated by PLM and DSC. PEA containing odd number of methylene groups exhibited mostly spherulitic structures whereas PEA containing even number of methylene groups gave nematic textures. Increasing the aromatic content alters this behaviour. Mostly smectic phases are observed [6,7]. Hydrogen bonding that induces layer formation facilitates the formation of the smectic phases. The use of non-linear monomer bends (kink or crankshaft) such as isophthaloyl moiety and naphthyl

Figure 4. Texture of a smectic phase.

moiety can disrupt the lateral interactions in the solid state, lower the persistence length of the polymer chain and decrease the liquid crystalline phase transition temperature and also influences crystallinity. Increasing the aromatic content, thus, alters liquid crystalline behaviour. While replacement of terephthaloyl units by isophthaloyl moiety totally vanquished liquid crystalline phases, biphenylene and naphthalene units did only reduce the transition temperatures as expected.

3.2 *Intermolecular hydrogen bond and the influence of nitro groups*

The influence of nitro groups on the phase behaviour of LC polymers has not been studied except a reference to the additional ordering of the layer structures, which might give rise to a smectic polymorphism (see figure 4 for smectic phase). This phenomenon and in addition a smectic to nematic transition were observed by us in the monomers and polymers based on 1,4-phenylene[bis-(3-nitroanthranilidic acid)] containing nitro groups [8]. While intermolecular hydrogen bonds stabilize the mesophases, the orientational order of a liquid crystalline (LC) system enhances the alignment of non-linear optical (NLO) chromophores. This has been achieved through the synthesis of two types of PEAs, from dicarboxylic monomers 1,4-phenylene[bis-(3-nitroanthranilidic acid)] (containing nitro groups) and 1,4-phenylene[bis(anthranilidic acid)] (H-atom in the place of nitro groups) by condensing each one with hydroquinone (HQ) or 2,6-dihydroxynaphthalene (DHN) separately.

The hydrogen bonded (H-bonded) structure of the PEAs can be explained by IR spectra of the polymers taken at various temperatures: room temperature, at 250°C and at 300°C. At room temperature the IR spectrum of the polymers showed a broad peak in the range 3350–3065 cm^{-1} which is characteristic of the H-bonded $-$NH group. Peaks of $-$C$=$O stretching vibrations were observed in the range 1700–1720 cm^{-1} for both polymers at room temperature. The lower value of C$=$O stretching in IR spectra is explained by their H-bonding. Both the polymers retained the broad peak of the range 3350–3065 cm^{-1} in the IR spectra at 250°C, which indicates that a considerable amount of H-bonding prevails at this temperature. A decrease in the intensity of the sharp peak around 3098 cm^{-1} at 300°C exhibited by both the polymers indicated considerable decrease in H-bonds.

3.3 *Hydrogen bonded liquid crystalline polymers containing azobenzene mesogen*

LCPs containing azobenzene mesogen are emerging as an attractive area because of their potential applications in LC displays, NLO materials, information storage devices etc. [12]. Recently, we have shown that a main chain polymer containing azobenzene mesogen to which a long alkyl substituent is laterally attached is potentially a

NLO material. The combined effects of the laterally substituted alkyl and the hydrogen bonded carboxyl groups on the phase behaviour of azobenzene mesogen containing side chain polymers were investigated through the synthesis of a series of side chain liquid crystalline (LC) polyacrylates containing substituted (methyl/long alkyl) azobenzene mesogens attached directly to the polymer backbone by free radical polymerization of the respective monomers, 4-[(4-acryloyloxyphenyl)azo]benzoic acid, 4-[(4-acryloyloxy-3-methylphenyl)azo]benzoic acid, 4-[(4-acryloyloxy-2-methylphenyl)azo]benzoic acid and 4-[(4-acryloyloxy-2-pentadecylphenyl)azo]benzoic acid [9–11].

The polyacrylates containing azobenzene mesogen exhibited stir opalescence and low viscosity characteristic of nematic phase on melting under a hot stage polarized light microscope [9]. However, the polymer with the long alkyl side chain ($C_{15}H_{31}$) was polymorphic with a smectic phase besides nematic phase. The methyl substituted polymers showed only nematic phases. The carboxylic acid groups of the azophenyl mesogen are found to exist as hydrogen bonded dimers as indicated by IR, NMR and finally confirmed by WAXD. It is proposed that the long alkyl substituent might be involved in the stabilization of the mesophase through its alignment parallel to the long axis of the molecule and might probably be supporting the formation of smectic phase by reducing the transition temperature low enough to maintain the layered arrangement of hydrogen bonded dimers.

3.4 *Hydrogen bonding favours smectic phase formation*

A very interesting observation of this study was the formation of smectic A phase by the polymer having the lateral side chain [11]. It is well-known that the length of the flexible spacer determines the nature of the mesophase with long spacers favouring smectic phases and short spacers favouring nematic phases. In the present case, the mesogen is directly attached to the backbone and a C_{15} *n*-alkyl substituent is present which may be supporting the formation of smectic phase by reducing the transition temperature low enough to maintain the layered arrangement of hydrogen bonded dimers. Since short spacers generally preclude smectic layering (in the present case there is no spacer at all) and the polymers with methyl substituents exhibited only nematic phase, it can be inferred that the long alkyl C_{15} substituent influence the formation of the smectic phase. In the present case, the C_{15} *n*-alkyl group is laterally substituted on the azobenzene mesogen. It has been discussed earlier that the 4,4'-hydroxycarboxylic acid-based compounds from which the monomers and polymers were prepared form intermolecular hydrogen bonding giving rise to carboxylic acid dimers (IR spectra) and that the azobenzene has a *trans* conformation (UV–vis. spectra). These intermolecularly hydrogen bonded carboxylic acid dimers aid the formation of networks which exhibit smectic A phase due to the dynamic nature of the non-covalent interaction (figure 5). Further evidence for the layered structure was obtained from WAXD which showed two diffraction peaks at $\theta = 2.8°$ and $20°$ for the polymer with the lateral side chain.

4. Conclusions

The extensive hydrogen bonding between amide–amide and amide–ester coupled with the rigidity due to the double bond character of the amide group influences the ordering of aliphatic dominated PEAs, inducing liquid crystallinity and enhancing the phase stability.
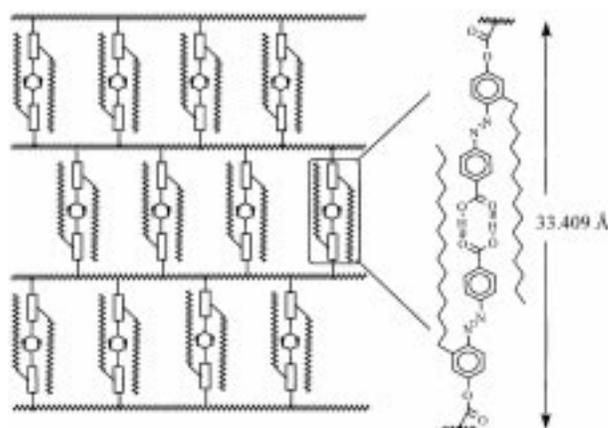
Figure 5. Hydrogen bonded layered structure.

Increasing the aromatic content alters this behaviour. Mostly smectic phases are observed. Hydrogen bonding induces layer formation. Direct attachment of phenyl moiety to NH–CO group prevents LC phase formation.

The introduction of nitro groups has induced a layer ordering into PEAs by which the smectic order with layer structure has been exhibited. This been aided and stabilized by the presence of hydrogen bonding by the carboxylic acid groups.

The LC transitions of side chain polyacrylates containing substituted azobenzene mesogen attached directly to the polymer backbone are largely influenced by the nature of the substituent and the intermolecularly hydrogen bonded carboxylic acid dimers. The $-C_{15}$ alkyl chain, thus, was found to favour stabilization of the LC phase possibly by aligning along the long molecular axis of the mesogen.

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