LIQUID CRYSTALS, 2002, VOL. 29, NO. 9, 1151–1159

Synthesis and lyotropic liquid crystalline behaviour of a taper-shaped phosphonic acid amphiphile

SCOTT R. HAMMOND, WEN-JING ZHOU, DOUGLAS L. GIN*
Department of Chemistry, University of California, Berkeley, CA 94720-1460, USA

and JAMSHID K. AVLYANOV
Eeonyx Corporation, 750 Belmont Way, Pinole, CA 94564, USA

(Received 9 November 2001; accepted 24 April 2002)

A taper-shaped phosphonic acid, 3,4,5-tris(dodecyloxy)phenylmethylphosphonic acid (**1**), was synthesized; its lyotropic liquid crystalline (LLC) behaviour and its ability simultaneously to order and acid-dope polyaniline were examined. It was found that the ability of **1** to form LLC phases in the presence of several hydrophilic solvents is restricted by strong intermolecular interactions between the phosphonic acid head groups (presumably H-bonding). The amphiphile exhibits poor miscibility with pure water and even with strong H-bonding organic solvents such as DMF. However, it forms a lamellar mesophase in the presence of aqueous acid. Upon deprotonation of the phosphonic acid head group with NaOH, the resulting disodium salt of the amphiphile is able to form a well defined lamellar phase with pure water. The propensity of **1** to form lamellar phases is somewhat unusual since its tapered molecular shape should direct it to form an inverted hexagonal LLC phase. These results suggest that intermolecular head group interactions are more important in determining the overall LLC behaviour of this phosphonic acid amphiphile than are the hydrophobic character and shape of the organic tail system. Compound **1** was also found to be sufficiently acidic to act as an acid dopant for the conjugated polymer polyaniline in the emeraldine base form. LLC acid **1** induces the resulting polymeric salt to form an electrically conductive LLC complex with an extended lamellar microstructure. The bulk conductivity of the resulting nanostructured polyaniline salt was found to be only in the semiconducting regime (10^{-5} S cm^{-1}), due to an unfavourable polyaniline chain conformation in the LLC complex.

1. Introduction

In recent years, there has been a great deal of interest in the use of lyotropic liquid crystal (LLC) (i.e. amphiphile) assemblies for materials applications (figure 1) [1]. For example, LLC assemblies have been used as templates for forming inorganic mesoporous sieves [2] and self-ordering surfactant-polyelectrolyte complexes [3]. Polymerizable or crosslinkable LLC phases have also been used as matrices for ordered nanocomposites [4, 5] and as catalytic organic molecular sieve analogues [6, 7]. Of particular interest in our research group is the development of LLC systems with different functional properties via design of the hydrophilic head group. Previously, we showed that polymerizable LLC mesogens can be synthesized with ionic head groups containing transition-metal and lanthanide cations that afford stabilized inverted hexagonal (H_{II}) assemblies with paramagnetic and photoluminescence properties [8, 9]. We have also recently demonstrated that enhanced Brønsted base catalysis and Lewis acid catalysis can be performed using crosslinked H_{II} phases through appropriate functional head group design [6, 7]. Although a number of functional properties can be incorporated into these LLC mesogens, one property that seems to have remained fairly elusive in surfactant and LLC design is Brønsted acidity. Thermotropic liquid crystals (LCs) containing acidic groups that interact and dimerize through hydrogen bonding are well known in the literature [10]. However, to our knowledge only a very small number of LLC mesogens (and surfactants) containing a relatively strong Brønsted acid head group have been documented. For example, *p*-dodecylbenzenesulphonic acid (DBSA) is known to form a lamellar (L) phase in the presence of acidic water [11]. However, it is typically the salt of a long chain organic acid (e.g. a carboxylic, sulphonic, or phosphonic acid) that behaves as a surfactant or LLC, not the parent acid itself.

---

*Author for correspondence. Current address: Departments of Chemistry & Biochemistry, and Chemical Engineering, University of Colorado, Boulder, CO 80309-0424; USA;
e-mail: gin@spot.colorado.edu

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2002 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290210157857

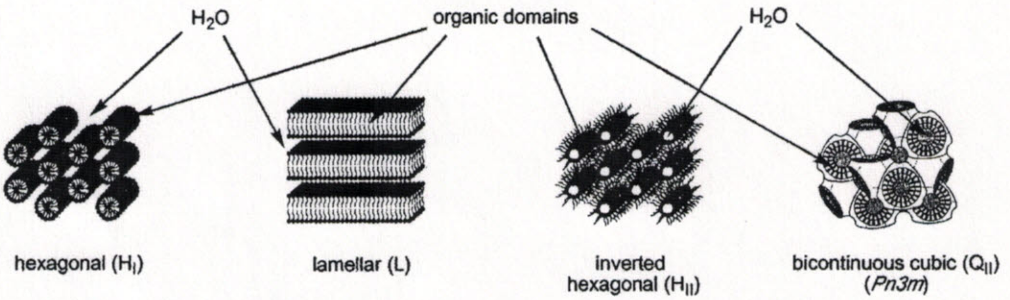
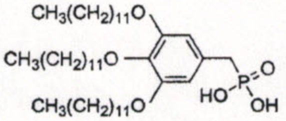


Figure 1. Schematic representations of some common LLC phases formed by amphiphilic molecules in water.

Our group is interested in designing a LLC mesogen with a relatively strong Brønsted acid head group for two reasons. The first reason is to develop nanostructured organic assemblies capable of size-selective, heterogeneous Brønsted acid catalysis (analogous to acidic zeolites). The second reason is that acidic surfactants have recently been employed as both dopants and processing aids (i.e. 'dopant-induced processability') for the intrinsically conductive polymer, polyaniline [12]. Several of these functionalized acid dopants simultaneously induce LC order and superior processing properties into the resulting electrically conductive polyaniline complexes [13–16]. However, with the exception of DBSA [11], the organic acid dopants that form LC polyaniline complexes have not been reported to exhibit intrinsic LLC properties [13–16]. The synthesis of other acidic amphiphiles with well-defined LLC properties may help in elucidating the effect of these amphiphiles on the LC order of the doped polymer. To our knowledge, the only other examples of amphiphiles containing a relatively strong Brønsted acid head group which exhibit intrinsic LLC properties are single chain phosphonic acid amphiphiles. Kose *et al.* reported that *n*-octyl- and *n*-hexylphosphonic acid form widely spaced L phases in the presence of water over a relatively broad composition and temperature range [17]. Pillai and co-workers also reported that 3-pentadecylphenylphosphoric acid induces polyaniline to form an phase upon doping; however, the intrinsic LLC properties of the pristine amphiphile were not investigated [16]. Consequently, very little is actually known about the effect of Brønsted acid head groups on general LLC design, or on their coupled mesogenic and acid-doping behaviour.

In order to investigate these effects further, we present here the synthesis and characterization of a multi-tailed, taper-shaped LLC mesogen (**1**) containing a phosphonic acid head group. Compound **1** can be considered a nonpolymerizable phosphonic acid analogue of sodium 3,4,5-tris(11′-acryloxyundecyloxy) benzoate, a taper-shaped LLC monomer [4, 18] which exhibits a strong tendency to form the H_{II} phase based on its molecular shape and packing preferences [19]. The effect of the phosphonic acid head group on LLC phase formation with respect to monomer shape will be discussed. We also present preliminary data showing the ability of this protonic LLC simultaneously to dope and induce order in polyaniline to form an electrically conducting, nanostructured polymer complex.



1

2. Experimental

All reagents and solvents were purchased from commercial suppliers and used as received, unless otherwise specified. Polyaniline emeraldine base was synthesized at Eeonyx Corporation according to the procedures outlined in U.S. Patent 5,008,041 [10]. Reactions were monitored by thin layer chromatography (TLC) using EM Science 250 micron Silica Gel F_{254} plates. ^1H NMR spectra were acquired using a Bruker AMX-300 or a Varian Inova-500 spectrometer. FTIR spectra were obtained with a Perkin-Elmer 1616 series spectrometer at a resolution of $4\,cm^{-1}$ using KBr disks as support substrates. Powder X-ray diffraction (XRD) spectra were obtained using an Inel CPS 120 powder X-ray diffractometer system equipped with a programmable capillary oven. Polarized optical microscopy (POM) was performed using a Leica DMRXP microscope equipped with a Linkam THMSE 600 hot/cold stage. UV-visible spectroscopy was performed using a Perkin-Elmer Lambda 9 UV-VIS-NIR spectrophotometer on samples mounted on quartz slides. Elemental analyses and high resolution mass spectrometry were performed by the Micro-Mass Facility (University of California, Berkeley). Bulk conductivity values were measured using a four-in-line probe apparatus equipped with an automatic Loresta AP meter (Mitsubishi Petrochemicals). Molecular lengths were calculated using CS Chem3D Std employing MM2 energy minimization parameters.

Compound **1** was synthesized as depicted in the scheme. Methyl gallate was first reacted with three equivalents of 1-bromododecane under basic S_N2 conditions to form the three-tailed platform **2**. Subsequent $LiAlH_4$ reduction of **2** affords the benzyl alcohol intermediate **3**. Reaction of **3** with PBr_3 in ethyl ether yielded the corresponding benzyl bromide **4**, which was then treated with trimethylphosphite at high temperatures to form the dimethylphosphonate intermediate **5** [21]. Treatment of **5** with triethylamine and bromotrimethylsilane, followed by methanol and aqueous acid workup [22], afforded phosphonic acid **1** as a polycrystalline powder with 34% overall yield.

2.1. *Methyl 3,4,5-tris(dodecyloxy)benzoate (2)*

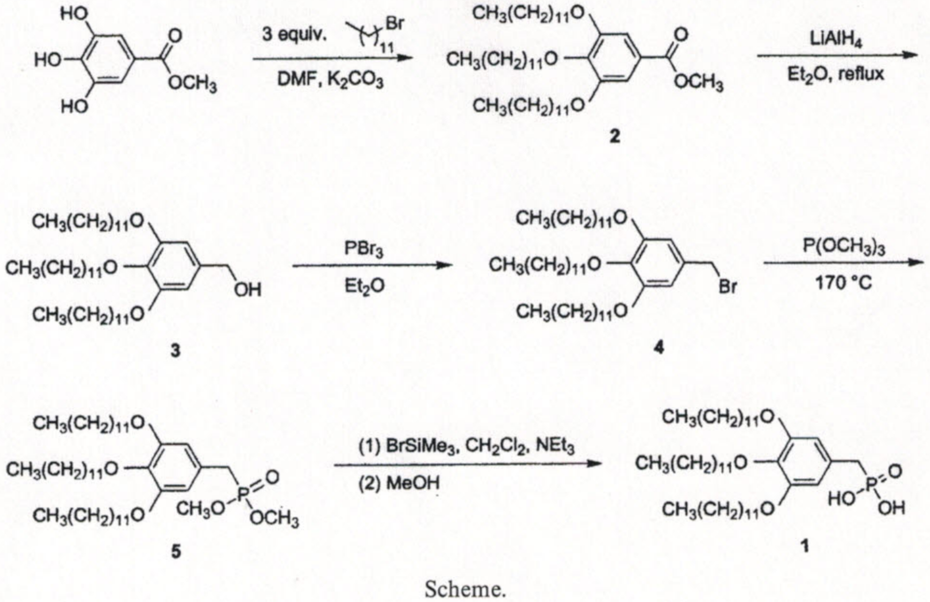
To a solution of methyl gallate (8.28 g, 0.045 mol) in DMF (300 ml) was added K_2CO_3 (70.0 g, 0.546 mol). The solution was mechanically stirred at 75°C under N_2 for 1 h, and then 1-bromododecane (41.0 g, 0.165 mol) was added. The resulting mixture was heated at 75°C under a dry N_2 atmosphere with mechanical stirring for 17 h. TLC (70/30 v/v hexanes/EtOAc) indicated complete reaction. The solvent was removed by rotary evaporator, and the residue dissolved in H_2O (250 ml) and extracted with EtOAc (3 × 200 ml). The combined organic fractions were then dried over anhydrous Na_2SO_4, filtered, and concentrated by rotary evaporation. The crude product was recrystallized from EtOAc, yielding 20.36 g (66%) of **2**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 9H), 1.25–1.47 (br m, 54H), 1.76 (m, 6H), 3.88 (s, 3H), 4.00 (m, 6H), 7.25 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.68, 23.50, 26.06, 29.28, 29.38, 29.55, 29.62, 29.64, 29.68, 30.31, 31.91, 52.08, 69.13, 73.47, 107.94, 124.62, 142.32, 152.80, 166.94. FTIR (cm^{-1}): 2923, 2845, 1719, 1590, 1501, 1466, 1337, 1225, 1131, 1014, 961, 861, 761, 720. Anal. Calcd for $C_{44}H_{80}O_5$: C 76.69, H 11.70; found C 76.85, H 12.05%.

2.2. *3,4,5-Tris(dodecyloxy)phenylmethyl alcohol (3)*

To a solution of $LiAlH_4$ (0.180 g, 0.00474 mol) in diethyl ether (25 ml) was added 1.376 g (0.00200 mol) of **2** with stirring. The flask was equipped with condenser and heated at reflux for 20 h. The reaction mixture was then cooled to 0°C and slowly quenched with H_2O, followed by the addition of 3M H_2SO_4 (5 ml). The reaction mixture was extracted with diethyl ether (3 × 30 ml), and the combined extracts dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude product was recrystallized from EtOAc, yielding 1.08 g (82%) or pure **3**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 9H), 1.26 (br m, 48H), 1.77 (m, 6H), 3.95 (m, 6H), 4.59 (s, 2H), 6.55 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.68, 26.09, 26.13, 29.36, 29.40, 29.65, 29.69, 29.75, 30.31, 31.92, 65.67, 69.09, 73.42, 105.32, 136.00, 137.57, 153.27. FTIR (cm^{-1}): 3401, 2931, 2848, 1590, 1507, 1466, 1437, 1384, 1337, 1225, 1125, 808, 720. Anal. Calcd for $C_{43}H_{80}O_4$: C 78.12, H 12.20; found C 78.09, H 12.40%.

2.3. *3,4,5-Tris(dodecyloxy)phenylmethylbromide (4)*

To a 0°C solution of **3** (5.153 g, 0.00779 mol) in diethyl ether (150 ml) under N_2, was added PBr_3 (2.40 ml, 0.0253 mol) with stirring. After 10 min, the ice water bath was removed, and the reaction allowed to continue for 4 h until TLC (80/20 hexanes/EtOAc) indicated complete reaction. The reaction mixture was then cooled



Scheme.

to 0°C and MeOH (30 ml) added. After 15 min of stirring, the reaction mixture was allowed to return to room temperature, diluted with diethyl ether (50 ml), and extracted with 5% aqueous $NaHCO_3$ solution (3 × 50 ml). The aqueous fractions were then extracted with additional diethyl ether (50 ml). The combined organic fractions were dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation to afford 4.744 g (85%) of **4**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 9H), 1.26 (br m, 48H), 1.46 (br m, 6H), 1.77 (m, 6H), 3.94 (m, 6H), 4.34 (s, 2H), 6.57 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.68, 26.07, 29.35, 29.39, 29.63, 29.65, 29.69, 29.74, 30.31, 31.92, 34.63, 69.10, 73.45, 107.48, 132.49, 138.36, 153.14. FTIR (cm^{-1}): 2919, 2848, 1590, 1466, 1437, 1331, 1243, 1131, 1114, 826, 726. Anal. Calcd for $C_{43}H_{79}O_3Br$: C 71.34, H 11.10; found C 71.58, H 11.28%.

2.4. *Dimethyl 3,4,5-tris(dodecyloxy)-phenylmethylphosphonate (5)*

A mixture of **4** (1.911 g, 0.00264 mol) and trimethyl phosphite (1.00 ml, 0.00848 mol) were heated to 230°C in a 50 ml round-bottom flask under N_2 with stirring for 4 h. The reaction mixture was then cooled to room temperature, diluted with diethyl ether (25 ml), and concentrated by rotary evaporation. The crude product was purified by column chromatography using 50/50 hexanes/EtOAc as the eluent to afford 1.69 g (85%) of **5**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.87 (m, 9H), 1.25 (br m, 48H), 1.42 (br m, 6H), 1.77 (m, 6H), 3.06 (d, $J = 21.3$ Hz, 2H), 3.66 (d, $J = 10.8$ Hz, 6H), 3.93 (m, 6H), 6.47 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.06, 22.65, 26.06, 26.09, 29.33, 29.36, 29.41, 29.62, 29.66, 29.69, 29.71, 30.29, 31.89, 53.02, 69.13, 73.55, 108.28, 125.83, 137.26, 153.08. FTIR (cm^{-1}): 2923, 2856, 1586, 1502, 1463, 1435, 1378, 1328, 1249, 1109, 1059, 1031, 868, 812, 716. Anal. Calcd for $C_{45}H_{85}O_6P$: C 71.77, H 11.37; found C 71.90, H 11.74%.

2.5. *3,4,5,-Tris(dodecyloxy)phenylmethylphosphonic acid (1)*

To a solution of **5** (3.107 g, 0.00412 mol) in dry CH_2Cl_2 (75 ml) under N_2, was added NEt_3 (2.50 ml, 0.0179 mol) and $BrSiMe_3$ (2.50 ml, 0.0189 mol) with stirring. After 10 h of stirring at ambient temperature, the solvent was removed *in vacuo*, and MeOH (75 ml) was added to the residue. The mixture was allowed to stir for another 20 h, and was then concentrated by rotary evaporation. The residue was acidified with 1M HCl solution (120 ml) and dissolved in diethyl ether (120 ml). The combined organic solutions were then extracted with 1M HCl (3 × 30 ml), followed by back-extraction of the aqueous solution with diethyl ether (2 × 50 ml). The combined organic fractions were then dried over anhydrous $MgSO_4$, filtered, and concentrated by rotary evaporation; yield 2.558 g (86%) of **1**. ^1H NMR (300 MHz, $CDCl_3$): δ 0.88 (m, 9H), 1.26 (br m, 48H), 1.43 (br m, 6H), 1.73 (br m, 6H), 2.88 (d, $J = 21.9$ Hz, 2H), 3.89 (m, 6H), 6.41 (s, 2H), 9.40 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.10, 22.69, 26.13, 26.21, 29.34, 29.48, 29.56, 29.66, 29.72, 29.78, 30.31, 31.94, 69.10, 73.55, 108.34, 126.66, 136.70, 152.88. FTIR (cm^{-1}): 3401, 3119, 2919, 2848, 2285, 1713, 1590, 1505, 1467, 1437, 1390, 1337, 1249, 1119, 996, 837, 720. Anal. Calcd for $C_{43}H_{81}O_6P$: C 67.86, H 11.25; found C 67.82, H 11.52%.

2.6. *Sodium 3,4,5-tris(dodecyloxy)-phenylmethylphosphonate*

To a stirred solution of **1** (0.305 g, 0.41 mmol) in methanol (15 ml) was added a 1M stock solution of NaOH also in methanol (0.82 ml, 0.82 mmol). The resulting mixture was allowed to stir for 15 min at ambient temperature, and then the solvent was removed by rotary evaporation to afford the disodium salt as a colourless solid; yield 0.322 g (quantitative). ^1H NMR (500 MHz, CD_3OD): δ 0.90 (m, 9H), 1.30 (br m, 48H), 1.49 (m, 6H), 1.72 (br m, 6H), 2.81 (d, $J = 19.5$ Hz, 2H), 3.89 (m, 2H), 4.01 (m, 4H), 6.69 (s, 2H). FTIR (cm^{-1}): 2923, 2853, 1586, 1502, 1468, 1439, 1334, 1241, 1118, 982.

2.7. *Doping of polyaniline emeraldine base with 1*

1-Doped polyaniline solutions were made by dissolving **1** in pure *m*-creasol, and then slowly adding polyaniline emeraldine base as a powder with stirring at ambient temperature to afford light green solutions. Films were then made by dip-casting or drop-coating glass or quartz slides from the *m*-cresol solution. Gentle heating on a hot plate in the fume hood was employed to drive off the residual *m*-cresol.

3. Results and discussion

3.1. *LLC phase behaviour of 1*

The LLC behaviour of **1** in the presence of three hydrophilic solvents (water, *N*,*N*-dimethylformamide (DMF), and 1.0M aqueous HCl) was characterized by POM and variable-temperature XRD. Differential scanning calorimetry (DSC) was also performed on the samples but was not very informative. Only broad, non-reversible thermal changes were observed, which can be attributed to solvent evaporation from the mixtures during the heating runs.

Initial mixing studies of **1** with water did not result in the formation of a homogeneous LLC phase. All attempts to mix **1** with water (from 5 to 80 wt % water) resulted in heterogeneous mixtures containing crystallites of **1** and water, even with sonication and/or heat treatment (up to 70–80°C). This water immiscibility can be rationalized as due to two factors: (1) the increased hydrophobic character of the three-tailed system, and/or (2) strong intermolecular H-bonding between the phosphonic acid head groups in the solid state. Although shorter, single-tailed phosphonic acids have been found to form L phases in the presence of water [17], it was noted that strong H-bonding between the head groups in these mono-*n*-alkylphosphonic acids causes them to strongly aggregate and form stable lamellae even at high water dilution [17]. The more extensive hydrophobic tail section in **1** may contribute in part to reduction of water penetration into the initial crystallites, but it appears that the majority of the water immiscibility in our system arises from strong intermolecular H-bonding of the acid groups. When **1** is neutralized with NaOH, the corresponding disodium salt readily mixes with pure water to form a very well defined L phase over a wide concentration range (figure 2). The L phase is characterized by XRD *d*-spacings that proceed as 1, 1/2, 1/3, 1/4. … The position of the primary *d* peak (d_{100}) indicates that the layer spacing in this phase is *c.* 46 Å, which is almost exactly twice the calculated extended molecular length of **1** (22–23 Å). The observed interlayer spacing is thus consistent with a bilayer structure in which there is little or no interdigitation of the tails or molecular tilt in the layers. Apparently, the loss of H-bonding ability upon deprotonation of the phosphonic acid groups alleviates the water miscibility problems, despite the large organic tail section. This result suggests that intermolecular interactions between the phosphonic acid head groups of **1** are primarily responsible for the inability of this molecule to form LLC phases in water.

In order to induce LLC behaviour in **1**, it was hoped that DMF, a polar organic solvent capable of interrupting H-bonding, would be more compatible with **1** in forming homogeneous mixtures. DMF is known to form LLC phases with several ionic surfactants [23]. Unfortunately, DMF was also found to be mostly immiscible with **1** over a range of compositions and temperatures.

LLC behaviour with **1** was finally observed when a solution of 1.0M HCl was employed as the hydrophilic solvent. Previous work with DBSA in water and methanesulphonic acid suggested that acidic surfactants can also form LLC phases in the presence of aqueous acid [11]. Commercial 1.0M aqueous HCl solution showed very good miscibility with **1**; up to 50 wt % HCl solution can be accommodated in the mixture. The LLC phase behaviour of **1** in aqueous HCl is summarized as a simplified phase diagram in figure 3. Between 50 and 90 wt % **1**, the resulting mixtures exhibited a well-defined L phase melting to an isotropic phase at approximately 59°C. The corresponding POM image of the L phase of **1** in HCl solution (figure 4) shows a well mixed sample with no phase-separated crystallites. As can be seen in figure 5, the XRD profile of a sample of **1** containing 30 wt % 1.0M HCl at ambient temperature (21°C) exhibits a single diffraction peak at *c.* 30 Å, indicative of an L phase. The width of the primary diffraction peak

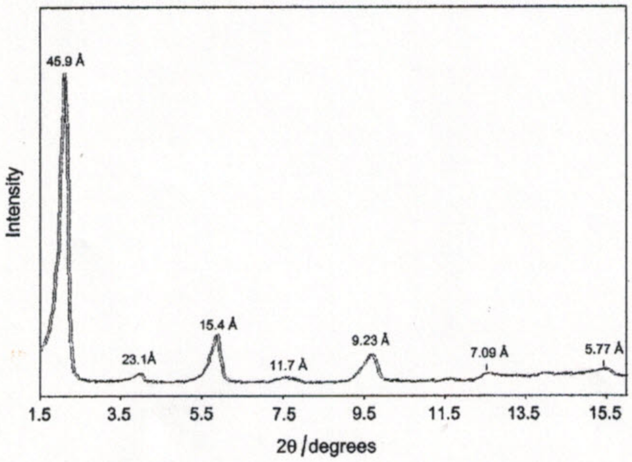


Figure 2. XRD profile of the L phase of the disodium salt of **1** in pure water: composition 51/49 (w/w) LLC/water.

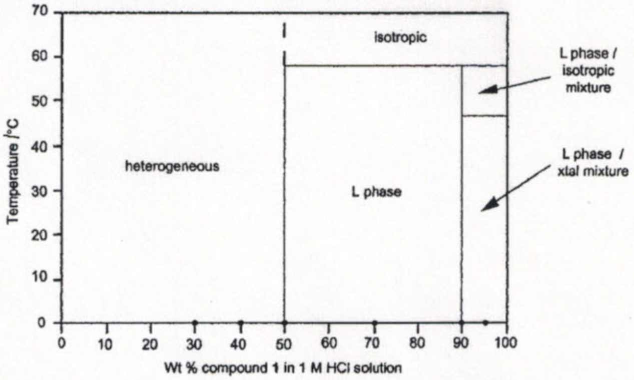


Figure 3. Simplified phase diagram of **1** with 1.0M aqueous HCl solution.

Figure 4. POM optical texture of a mixture of 70/30 (w/w) **1**/1.0M HCl at ambient temperature.

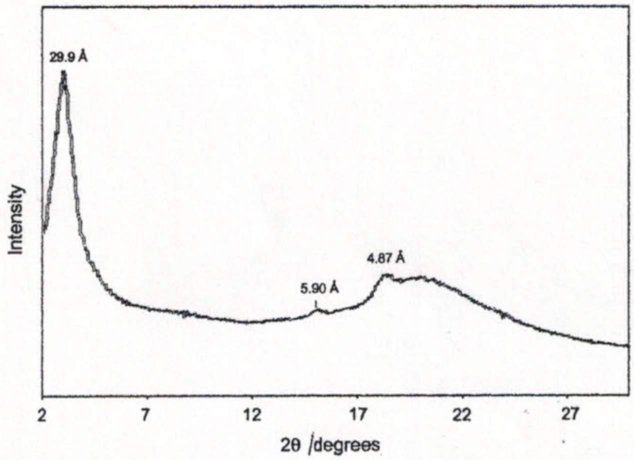


Figure 5. XRD profile of a mixture of 70/30 (w/w) **1**/1.0M HCl solution.

and the absence of secondary peaks indicates that this L phase is not as highly ordered as that of the corresponding L phase for the disodium salt of **1** in water (cf. figure 2). The fact that the observed layer spacing (30 Å) is much smaller than twice the calculated molecular length of **1**, suggests that there is also significant alkyl chain interdigitation and/or tilt of the molecules in the bilayers for this particular L mesophase. Above *c.* 90 wt % **1**, the samples exhibit a mixture of crystallites of **1** and the L phase. Below 50 wt % of **1** in the mixture, the system phase-separates to varying degrees. It should also be noted that within the L phase regime of **1**, increasing the amount of 1.0M HCl in the mixture appears to produce no significant change in the interlayer spacing, as determined by XRD.

A survey of the small number of known Brønsted acidic amphiphiles (i.e. DBSA, *n*-alkylphosphonic/phosphoric acids) shows that the L phase is the only LCC mesophase that has been observed in these materials, either as the pure materials in solvent [11, 16], or as complexes with polyaniline [17]. The tendency of these single chain organic acids preferentially to form the L phase may be a consequence of packing preferences arising from their cylindrical molecular shapes [19]. However, our current study shows that the incorporation of a phosphonic acid head group onto a taper-shaped LLC with a strong preference for the H_{II} phase, results in formation of L mesophases as either the parent acid or the salt. This phenomenon suggests that in these acidic amphiphiles, molecular shape/packing is not the overriding factor in determining overall mesogenic behaviour. Rather, it appears that the intermolecular interactions between the acid head groups (e.g. H-bonding) and with the solvent are more important in determining the overall LLC behaviour of the system than the hydrophobic character and shape of the organic tail system. The importance of head group interactions in this system is illustrated by the fact that acidic water but not pure water is required to form a LLC phase with **1**, and that deprotonation of the phosphonic acid moiety is required before any phases can form in pure water. Preliminary work in our group with sulphonic acid derivatives of other taper-shaped amphiphiles also revealed a strong preference for the parent Brønsted acids to adopt the L phase, although their sodium salts tend to form the H_{II} phase [7].

3.2. *Simultaneous acid-doping and ordering of polyaniline*

A number of functionalized organic Brønsted acids have been used as dopants and processing aids for polyaniline, including camphorsulphonic acid [13], DBSA [12, 24], the di(ethylhexyl) ester of phthalosulphonic acid [15], sulphosalicylic acid [25], and several phosphoric acid derivatives [16, 20–30]. However, there has only been one report of the use of organic phosphonic acids as dopants for polyaniline. Chan and co-workers found that *n*-butyl-, *n*-decyl-, and benzyl-phosphonic acid dopants were sufficiently acidic to dope polyaniline emeraldine base to produce polyaniline salts with greatly enhanced thermal stability compared with samples doped by HCl [31]. However, the resulting complexes were not reported to have order; and these doped materials exhibited moderate to low bulk conductivity, depending on the amount and the nature of phosphonic acid dopant used [31]. The fact that phosphonic acid **1** exhibits intrinsic LLC behaviour in aqueous acid, suggested that it should not only be able to dope polyaniline but also induce the system to order in a predictable manner.

For complete doping of the emeraldine base form of polyaniline to the conducting emeraldine salt form, the two imine N atoms in the tetrameric repeat unit of the polymer must be protonated (i.e., an optimal 2/1 acid/tetramer ratio) (figure 6) [32]. In order to examine the doping and ordering behaviour of **1** on polyaniline, samples of **1** and polyaniline emeraldine base were prepared in a 2-to-1 acid-to-tetramer ratio using *m*-cresol as the solvent. The solution conformation of the resulting polyaniline salt was examined by UV-visible spectroscopy. The LLC and bulk electrical properties of the resulting complexes were then examined by POM, XRD, and four-point-probe conductivity measurements, as solid films cast from *m*-cresol solution. The UV-visible spectrum of the 2-to-1 doped polyaniline salt in *m*-cresol solution showed a rise in absorbance in the 800–1000 nm region, indicative of a free electron carrier tail, figure 7 (*a*). This spectroscopic feature in doped polyaniline implies that the individual polyaniline chains are not only doped by **1** but that they also adopt an extended conformation that affords high electron mobility along the chains

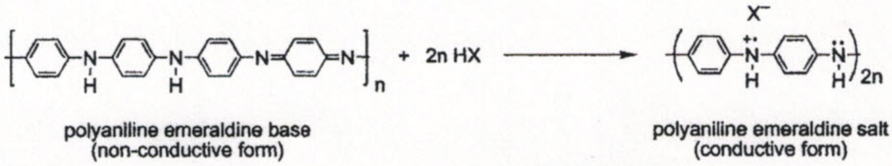


Figure 6. Acid-doping of polyaniline emeraldine base into its electrically conductive salt form.

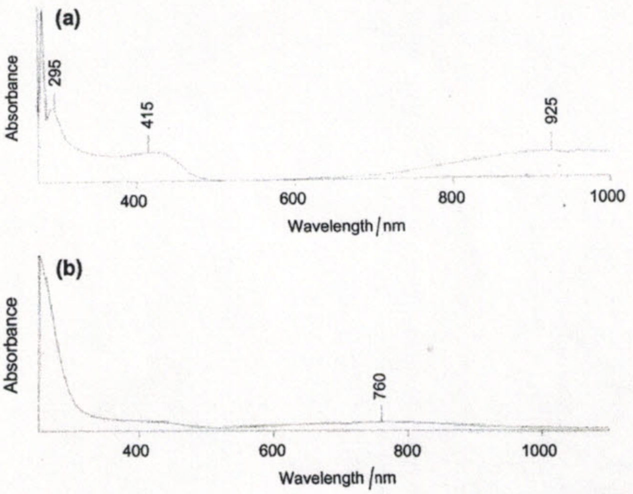


Figure 7. UV-visible spectra of (*a*) **1**-doped polyaniline in *m*-cresol solution; (*b*) **1**-doped polyaniline as a thin film after removal of *m*-cresol (doping level: 2-to-1 acid-to-tetramer).

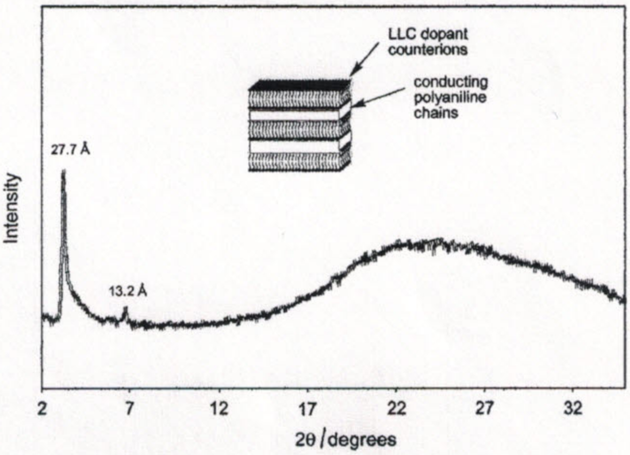


Figure 8. XRD profile of a film of **1**-doped polyaniline (2-to-1 acid to polyaniline tetramer) case from *m*-cresol.

[33]. Extended chain conformations are manifested in a number of solvents such as *m*-cresol and $CHCl_3$ when polyaniline is doped with an appropriate functionalized organic acid [33]. When the polymer complex was cast into thin films from the *m*-cresol solution, the resulting films were viscous pasty solids. XRD analysis revealed that the **1**-doped polyaniline complex in the solid state forms a nanostructured material with a lamellar architecture, as indicated by the observed *d*-spacing ratio of 1, 1/2, ... (figure 8). The value of the primary diffraction peak (*c*. 28 Å) is consistent with a bilayer structure in which the protonated polyaniline chains reside between ordered layers of dopant anions that are either significantly interdigitated and/or tilted with respect to the layer normal (figure 9). Unfortunately, the **1**-doped polyaniline films do not display a free-carrier tail in their UV-visible spectra, figure 7(*b*). Upon evaporation of the *m*-cresol solvent, the **1**-doped polyaniline chains apparently lose their extended chain conformation. The bulk conductivity of the solvent-evaporated doped films was found to be only in the semiconducting regime, on the order of 10^{-5} S cm^{-1}. This value is consistent with the loss of the extended chain conformation because doped polyaniline samples with extended polymer chain conformations typically exhibit high bulk conductivities on the order of 10^0–10^2 S cm^{-1} [33]. The modest bulk conductivity observed may also be due in part to the presence of the large organic tail section on dopant **1**, which acts as an insulator between the conductive polymer chains, thereby minimizing interchain conduction in the ordered solid. Although the liquid crystalline **1**-doped polyaniline complex is processible so that it can be spread and sheared into thin films, it was not possible to obtain sufficiently macroscopically aligned samples via shearing to detect any anisotropic bulk conductivity in the samples.

We are at present exploring methods for inducing these phosphonic acid LLC mesogens to adopt different non-lamellar LLC phases, such as tail length modification and blending with other LLC mesogens. We are also attempting to prepare polymerizable derivatives of these phosphonic acid LLC mesogens, as well as their sulphonic acid analogues.

4. Conclusions

A taper-shaped phosphonic acid amphiphile **1** has been synthesized, and its LLC behaviour in several polar solvents has been examined. It was found that the ability of **1** to form LLC phases is hindered by strong intermolecular interactions between the phosphonic acid head groups (presumably H-bonding). The amphiphile is able to form a lamellar LLC phase only in the presence of aqueous acid, but exhibits poor miscibility with pure water and even strong H-bonding organic solvents such as DMF. However, upon deprotonation of the phosphonic acid head group with NaOH, the resulting

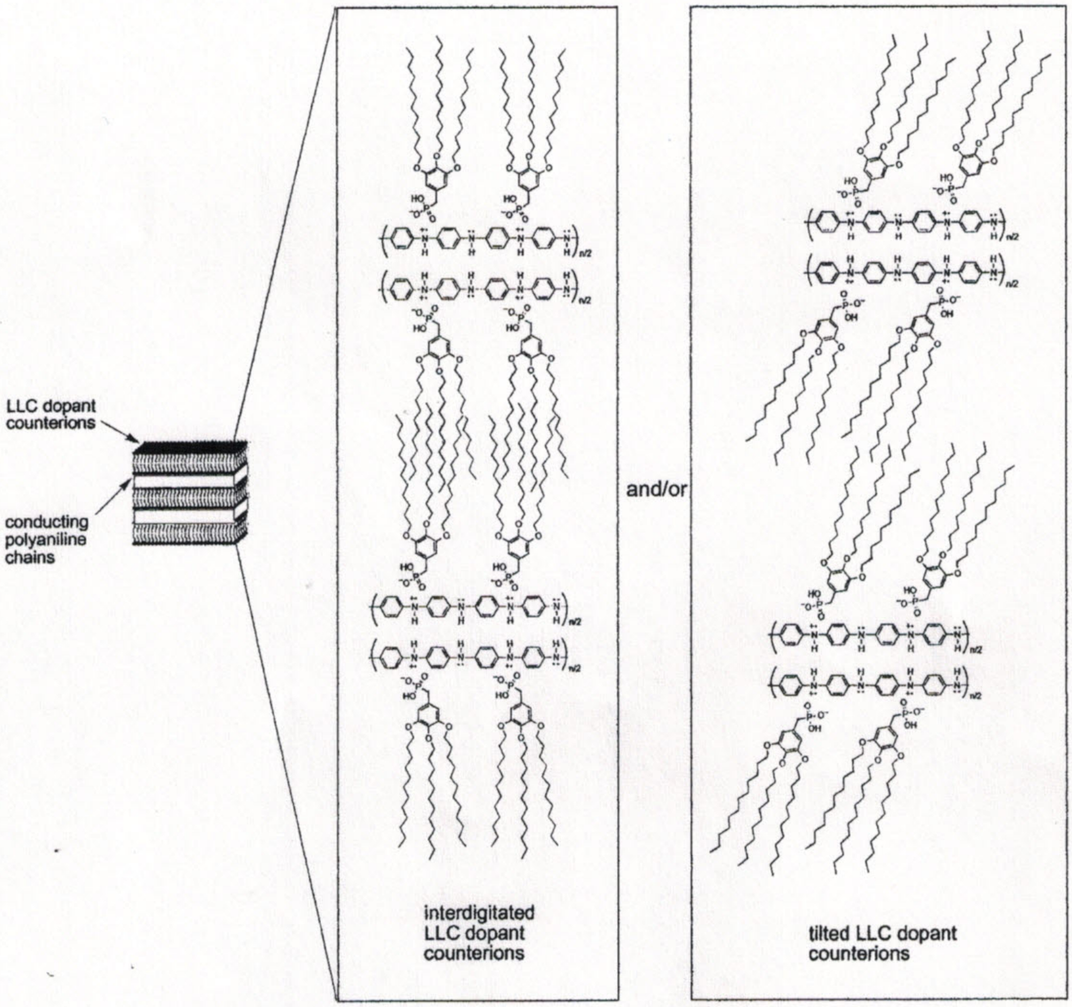


Figure 9. Schematic representation of the lamellar LLC **1**-doped polyaniline complex.

disodium salt of the amphiphile readily forms a well defined L phase with pure water. These results suggest that intermolecular head group interactions are more important in determining the overall LLC behaviour of these amphiphiles than the hydrophobic character and shape of the organic tail systems. LLC acid **1** was also found to be sufficiently acidic to act as an acid dopant for the conjugated polymer, polyaniline. It induces the resulting polymeric salt to form a mesogenic material with an extended L microstructure. However, the bulk conductivity of the polyaniline salt is only in the semiconducting regime (*c.* $10^{-5}\,\mathrm{S\,cm^{-1}}$), due to an unfavourable chain conformation in the dry LLC complex.

Partial financial support for this research was provided by the National Science Foundation in the form of a summer REU grant for S. R. H. and grants to D. L. G. (DMR-9625433 and DMR-0111193). Additional partial support from the Office of Naval Research (N00014-00-1-0271) and a Research Fellowship from the Alfred P. Sloan Foundation is also gratefully acknowledged. The authors thank Dr T. J. Kidd for performing additional characterization studies, and Dr B. P. Hoag and Mr. J. S. Yu for their help in the initial design of the phosphonic acid LLC.

References

[1] TIDDY, G. J. T., 1980, *Phys. Rep.*, **57,** 1.
[2] YING, J. Y., MEHNERT, C. P., and WONG, M. S., 1999, *Angew. Chem. int. Ed.*, **38,** 56.
[3] OBER, C. K., and WEGNER, G., 1997, *Adv. Mater.*, **9,** 17.
[4] SMITH, R. C., FISCHER, W. M., and GIN, D. L., 1997, *J. Am. chem. Soc.*, **119,** 4092.
[5] SELLINGER, A., WEISS, P. M., NGUYEN, A., LU, Y., ASSINK, R. A., GONG, W., and BRINKER, C. J., 1998, *Nature*, **394,** 256.
[6] MILLER, S. A., KIM, E., GRAY, D. H., and GIN, D. L., 1999, *Angew. Chem. int. Ed.*, **38,** 3021.
[7] GU, W., ZHOU, W.-J., and GIN, D. L., 2001, *Chem. Mater.*, **13,** 1949.

[8] Deng, H., Gin, D. L., and Smith, R. C., 1998, *J. Am. chem. Soc.*, **120,** 3522.

[9] Gray, D. H., and Gin, D. L., 1998, *Chem. Mater.*, **10,** 1949.

[10] Paleos, C. M., and Tsiourvas, D., 1995, *Angew. Chem. int. Ed. Engl.*, **34,** 1696.

[11] Krishnamurti, D., and Somashekar, R., 1981, *Mol. Cryst. liq. Cryst.*, **65,** 3.

[12] Cao, Y., Smith, P., and Heeger, A. J., 1992, *Synth. Met.*, **48,** 91.

[13] Cao, Y., and Smith, P., 1993, *Polymer*, **34,** 3139.

[14] Levon, K., Ho, K.-H., Zheng, W.-Y., Lasko, J., Kärnä, T., Taka, T., and Österholm, J.-E., 1995, *Polymer*, **36,** 2733.

[15] Olinga, T. E., Fraysse, J., Travers, J. P., Dufresne, A., and Pron, A., 2000, *Macromolecules*, **33,** 2107.

[16] Paul, R. K., Vijayanathan, V., and Pillai, C. K. S., 1999, *Synth. Met.*, **104,** 189.

[17] Klose, G., Petrov, A., Volke, F., Meyer, H. W., Foerester, G., and Rettig, W., 1982, *Mol. Cryst. liq. Cryst.*, **88,** 109.

[18] Resel, R., Thiessl, U., Gadermaier, C., Zojer, E., Kriechbaum, M., Amenitsch, H., Gin, D., Smith, R., and Leising, G., 2000, *Liq. Cryst.*, **27,** 407.

[19] Israelachvili, J. N., 1985, *Intermolecular and Surface Forces with Applications to Colloidal and Biological Systems* (London: Academic Press), pp. 249–257.

[20] Cameron, R. E., and Clement, S. K., 1991, U.S. Patent 5 008 041.

[21] Bhattacharya, A., and Thyagarajan, G., 1981, *Chem. Rev.*, **81,** 415.

[22] Petruska, M. A., and Talham, D. R., 1998, *Chem. Mater.*, **10,** 3672.

[23] Auvray, X., Perche, T., Petipas, C., and Anthore, R., 1992, *Langmuir*, **8,** 2671.

[24] Österholm, J. E., Cao, Y., Klavetter, F., and Smith, P., 1994, *Polymer*, **35,** 2902.

[25] Tzou, K., and Gregory, R. V., 1993, *Synth. Met.*, **53,** 365.

[26] Pron, A., Österholm, J. E., Smith, P., Heeger, A. J., Laska, J., and Zagorska, M., 1993, *Synth. Met.*, **55–57,** 3520.

[27] Pron, A., Laska, J., Österholm, J. E., and Smith, P., 1993, *Polymer*, **34,** 4235.

[28] Laska, J., Pron, A., and Lefrant, S., 1995, *J. polym. Sci., Polym. Chem. Ed.*, **33,** 1437.

[29] Kulszewicz-Bajer, I., 1995, *Macromolecules*, **28,** 610.

[30] Kulszewicz-Bajer, I., Sobczak, J., Hasik, M., and Pretula, J., 1996, *Polymer*, **37,** 25.

[31] Chan, H. S. O., Ng, S. C., and Ho, P. K. H., 1994, *Macromolecules*, **27,** 2159.

[32] MacDiarmid, A. G., and Epstein, A. J., 1991, in *Science and Applications of Conducting Polymers*, edited by W. R. Salaneck, D. T. Clark, and E. J. Samuelson (Bristol: IOP Publishers), p. 117.

[33] Avlyanov, J. K., Min, Y., MacDiarmid, A. G., and Epstein, A. J., 1995, *Synth. Met.*, **72,** 65.