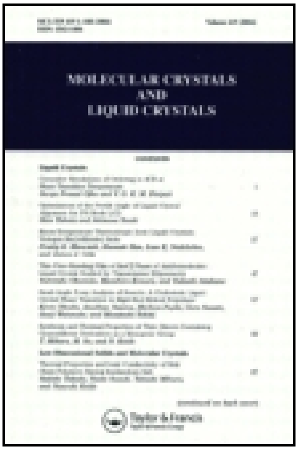


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Influence of Lithium Perchlorate on Discotic Liquid Crystals and the Ion Conduction of their Mixtures

L. Brunsveld [a] , J.A. J.M. Vekemans [a] , H. M. Janssen [a] & E. W. Meijer [a]

[a] Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600, MB Eindhoven, The Netherlands

To cite this article: L. Brunsveld, J.A. J.M. Vekemans, H. M. Janssen & E. W. Meijer (1999): The Influence of Lithium Perchlorate on Discotic Liquid Crystals and the Ion Conduction of their Mixtures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 331:1, 449-456

To link to this article: http://dx.doi.org/10.1080/10587259908047545

Mol. Cryst. Liq. Cryst., 1999, Vol. 331, pp. 449-456
Reprints available directly from the publisher
Photocopying permitted by license only

The Influence of Lithium Perchlorate on Discotic Liquid Crystals and the Ion Conduction of their Mixtures

L. BRUNSVELD, J.A.J.M. VEKEMANS, H.M. JANSSEN
and E.W. MEIJER*

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

A C_3-symmetric trimesic amide derivative with peripheral oligo(ethylene oxide) side chains (compound **1**) shows discotic mesomorphism in a broad temperature range due to stacking of the extended core ($T_g \sim -50°C$; $T_{cl} \sim 240°C$). Mixtures of **1** and lithium perchlorate ($LiClO_4$) also exhibit liquid crystalline (LC) properties as shown by polarization microscopy, DSC and X-ray diffraction studies. An increase of the T_g as well as a decrease of the clearing temperature are observed with increasing salt concentration. The ion conducting properties of the $LiClO_4$-mixtures of **1** have been measured by complex impedance spectroscopy; promising levels of conductivity, up to 10^{-6} S/cm at room temperature, have been recorded.

Keywords: discotic; ion conduction; mesophase; liquid crystals

INTRODUCTION

Ion solvating polymers such as poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) have been elaborately used as ion conductive materials.[1] It has been shown that the ion transport in these polymeric systems is three-dimensional and occurs in the amorphous regions of the polymer. In fact, the ion transport in polymeric materials is directly related to

---

* To whom correspondence should be addressed

the segmental motion of the polymer chains. Ion conducting matrices have usually been based on polymeric systems, although also a limited number of liquid crystalline (LC) materials[2a-c] have been studied.

LC compounds chargeable with salts are promising ion conducting materials, since they contain flexible regions in which solvated ions are mobile. The liquid crystalline systems that have been studied up to date all show relatively low conductivities at room temperature, mainly due to the high melting or glass-transition temperatures of the materials investigated. Recently, we have developed a new class of molecules that display discotic behavior.[3] The compounds consist of a C_3-symmetrical extended core with three hydrogen bonded 3,3'-di(acylamino)-2,2'-bipyridine units and bear nine peripheral aliphatic chains. The molecules are observed to associate into columns *via* stacking and hydrogen bonding interactions resulting in columnar mesophases with broad temperature ranges. Their liquid crystallinity at room temperature makes them highly attractive targets for ion transport studies, provided the peripheral chains are replaced by oligo(ethylene oxide) chains.

Here we present the synthesis, phase-characterization and bulk ion conductivity of a new member in the aforementioned class of C_3-symmetrical molecules: molecule **1**. The tetra(ethylene oxide) peripheral chains in this new component enable ion solvation. Mixtures of **1** and $LiClO_4$ in various molar ratios have been studied to investigate the influence of the salt concentration on the mesophase behavior and on the ion conducting properties.

EXPERIMENTAL

Methods

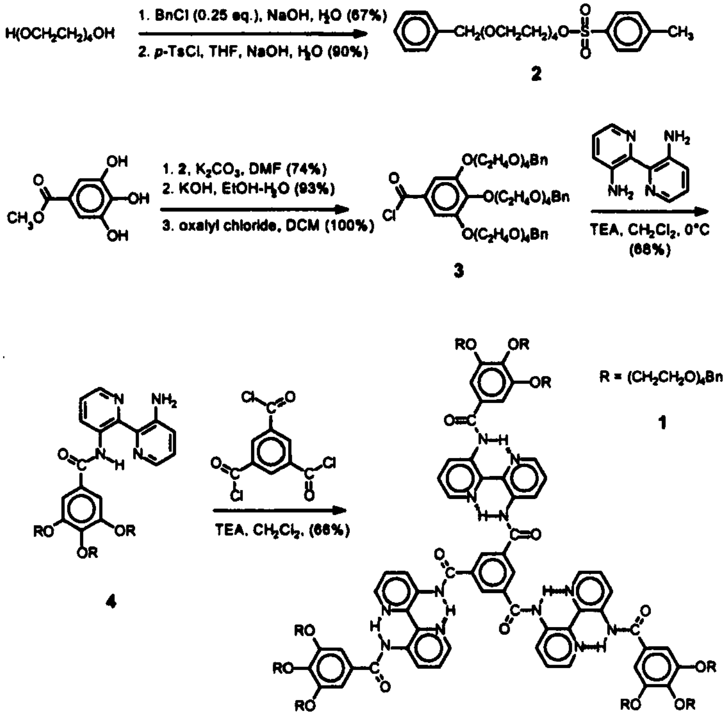
^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker AM or on a Varian Gemini. IR-spectra were measured on a Perkin Elmer 1600 FT-IR. GC/MS measurements were performed on a Shimadzu GC/MS-QP5000. Elemental analyses were carried out using a Perkin Elmer 2400. Optical properties and melting points were studied using a Jeneval polarization microscope equipped with a Linkam THMS 600 heating device with crossed polarizers. TGA measurements were performed with a Perkin Elmer TGA 7. DSC spectra were recorded on a Perkin Elmer Pyris 1 DSC. The glass transition temperatures were taken at half ΔC_p. X-ray diffraction patterns were recorded using a multiwire area detector X-1000 coupled with a graphite monochromator. Ion conductivity measurements were performed on a Hewlett Packard 4194A impedance/gain-phase analyzer using a Mettler FP82HT Hot Stage and a FP80 central processor. Samples for the impedance measurements were prepared in the glovebox and had thicknesses of 140 μm and surfaces of 2 cm^2.

Materials

The experimental details of the synthesis 1 will be published elsewhere. The structure and purity of all the products was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR and elemental analysis and/or mass spectrometry. For compound 1, the spectral data are as follows: ^{1}H-NMR ($CDCl_3$): δ = 15.53 (s, 3H, inner-N*H*CO); 14.52 (s, 3H, outer-N*H*'CO); 9.60 (dd, *J* = 8.0 and 1.1 Hz, 3H, H-4); 9.38 (dd, *J* = 7.8 and 1.0 Hz, 3H, H-4'); 9.22 (s, 3H, *ortho*-H); 9.06 (dd, *J* = 4.4 and 1.2 Hz, 3H, H-6'); 8.48 (dd, *J* = 4.4 and 1.4 Hz, 3H, H-6); 7.55 (m, 6H, H-5 and H-5'); 7.34-7.24 (m, 51H, all trisalkoxybenzoyl and benzyl ring protons); 4.56 (s, 6H, *para*-C*H*$_2$Ph); 4.54 (s, 12H, *meta*-C*H*$_2$Ph); 4.28 (t, 18H, ArOC*H*$_2$); 3.90 (t, 12H, *meta*-OCH$_2$C*H*$_2$); 3.84 (t, 6H, *para*-OCH$_2$C*H*$_2$); 3.77-3.61 (m, 108H, ethylene oxide protons). ^{13}C-NMR ($CDCl_3$): δ = 165.6 and 163.8 (2 x CO); 152.5 (C-3 benzoyl); 142.1; 141.8; 141.2; 140.5; 138.0; 137.3; 137.2; 135.7; 130.3; 129.6; 128.0-127.4 (multiple signals); 124.6; 124.2; 107.8 (C-2 benzoyl); 72.9 (*C*H$_2$ benzyl); 72.3-69.2 (ethylene oxide carbons). IR (neat): ν = 3580; 3514; 2865; 1669; 1571; 1495; 1446; 1372; 1299; 1241; 1104; 800; 742. MALDI-TOF Matrix: Sudan Orange; [M + Na$^+$] = 3590.5 (calcd. 3590.7). Anal. Calcd. for $C_{195}H_{240}O_{51}N_{12}$ (MW 3568.14): C 65.64, H 6.78, N 4.71. Found: C 65.39, H 6.81, N 4.62.

RESULTS AND DISCUSSION

Disc-shaped molecule **1** was synthesized *via* a convergent approach similar to our described method.[3] The acid chloride **3** was prepared in a five-step sequence starting with tetra(ethylene glycol) and methyl gallate. Remarkably, the acylation of 2,2'-bipyridine-3,3'-diamine with acid chloride **3** is highly selective: a ratio of mono-acylated : di-acylated product as high as 98 : 2 has been achieved. The final step in the convergent synthesis is the coupling of trimesic chloride with the mono-acylated 2,2'-bipyridine derivative **4** (see Scheme 1). The structure and purity of all the products was confirmed by ^{1}H-NMR, ^{13}C-NMR, IR and elemental analysis and/or mass spectrometry.



SCHEME 1

Compound **1** has been mixed with $LiClO_4$ in different ratios of lithium to ethylene oxide units (Li^+:EO) (see Table 1) to obtain mixtures with low and high concentrations of salt (**1a-e**). The mixtures have been studied using polarization microscopy, TGA, DSC,[4] X-ray diffraction and impedance spectroscopy. The phase behavior of compound **1** and the salt-mixtures **1a-e** are listed in Table 1. Compound **1** does not exhibit a melting temperature, but it displays a T_g. The T_g is located at -50°C, which is *ca.* 60°C lower than the melting temperature of the corresponding LC-molecule with dodecyloxy peripheral side-chains.[3] Apparently, the tetra(ethylene oxide) chains prevent crystallization and introduce an amorphous character to the molecule. The high clearing temperature of the mesophase (244°C) is due to the large aromatic core, which stabilizes the packing of the molecules. Addition of $LiClO_4$ to the LC-system has a dramatic influence on the temperature range in which the mixture is liquid crystalline. The T_g increases up to 14°C and the clearing temperature drops to 145°C at the highest salt concentration investigated (**1e**). The rise in the T_g is not surprising since the ion-dipole interactions between the solvated cations and the ethylene oxide chains suppress the segmental motion of the ethylene oxide chains. The drop in the clearing temperature seems to arise from an increased disorder in the packing of the aromatic cores presumably due to the presence of the large perchlorate anions. This increased disorder upon salt addition is confirmed by polarization microscopy and X-ray diffraction (*vide infra*).

TABLE 1: Phase behavior of compound **1** and its mixtures with $LiClO_4$.

Compound / Mixture	Li^+ ions per molecule	Li^+:EO ratio	T_g (°C)	Mesophase	T_{cl} (°C)
1	0	0	-50	D_{ho}	244
1a	1	1:36	-42	D_{ho}	242
1b	2	1:18	-29	D_{ho}	230
1c	3	1:12	-16	D_{ho}	222
1d	6	1:6	3	D_{hd}	182
1e	9	1:4	14	D_{hd}	145

The mesophase of the pure compound **1** is a D_{ho} phase as can be derived from the typical flower-like textures that were grown from the melt and that were clearly visible with the optical microscope (Figure 1). The presence of a D_{ho} phase can also be derived from the X-ray diffraction pattern, that exhibit the typical small-angle reflections (100; 110; 200; 210) at distances of 1, √3, √4 and √7. In the wide-angle area, the halo ring is visible as well as the 001 reflection, which is oriented perpendicular to the 100 reflection. The 100 reflection has a *d*-spacing of 36.8Å, corresponding to an intercolumnar distance of 42.5Å. The 001 reflection, accounting for the disc-disc distance, has a *d*-spacing of 3.5Å.

The addition of salt greatly influences the order in the LC-system as is apparent from optical microscopy and X-ray diffraction data. In Figure 2, a picture is shown of mixture **1d**. The sample has been prepared in the same way as that shown in Figure 1 (the same magnification is used in both pictures). It is clearly visible that the size of the monodomains has decreased considerably and that the typical flower-like texture has disappeared in Figure 2. The same phenomenon can also be derived from the X-ray diffraction pattern recorded for mixture **1d**, which shows significant broadening of all reflections. Especially the 001 reflection has merged from a sharp peak into a very broad and weak peak. The broadening of all lines indicates a more disordered packing mode in the salt containing samples.

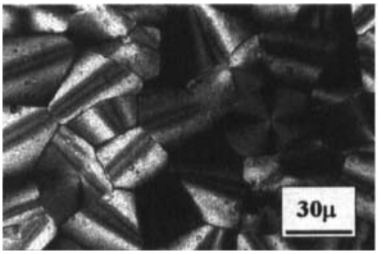


FIGURE 1: Flower-like D_{ho} texture of **1** after cooling from the melt
(See Color Plate III at the back of this issue)

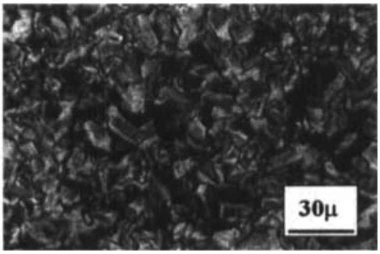


FIGURE 2: Distorted texture of **1d** after cooling from the melt
(See Color Plate IV at the back of this issue)

The temperature dependency of the ionic conductivity of the mixtures is depicted in Figure 3. The mixtures with low salt concentrations (**1a-c**) show promising levels of conductivity at room temperature, up to 10^{-6} S/cm. The increase of the conductivity of these mixtures with increasing temperatures is not very strong, since the low amount of charge carriers present, limits the conductivity at higher temperatures. The mixtures with high salt concentrations (**1d,e**) show similar high conductivities at high temperatures, but the conductivity at room temperature is very low. This is probably due to the high T_g of these mixtures (Table 1).

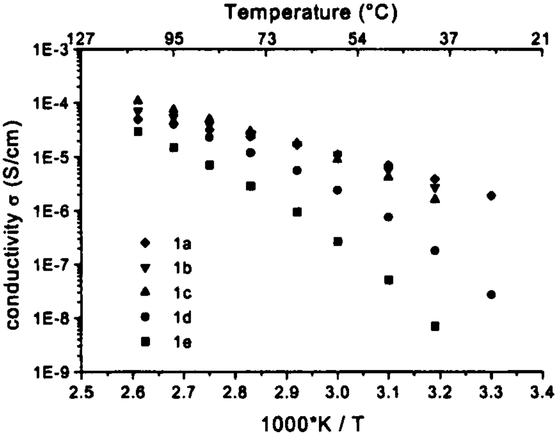


FIGURE 3: Ion conductivity of mixtures **1a-e** as a function of temperature. The pure compound **1** displays conductivities not higher than 10^{-9} (S/cm).

CONCLUSIONS

We have developed a C_3-symmetric disc-shaped molecule (**1**) that shows discotic mesomorphism in a broad temperature range due to strong stacking interactions of the hydrogen bonded extended core. The compound bears tetra(ethylene oxide) side chains capable of ion solvation. Mixtures of **1** with lithium perchlorate exhibit liquid crystalline properties, although upon increasing the salt concentration the T_g increases and the clearing temperature decreases. The ion conducting properties of the mixtures showed promising levels of conductivity, up to 10^{-6} S/cm at room temperature for some mixtures. This value for the room temperature conductivity is about one magnitude of order higher than for previously reported liquid crystalline ion conducting media,[2a-c] but still two orders of magnitude remote from that of the best solid polymer electrolytes.[5]

Currently, we are investigating the properties of compounds containing longer ethylene oxide chains that are not terminated with a benzyl end group. Additionally, the possibilities for anisotropic ion conduction in these materials is addressed, since the columns formed by **1** can easily be macroscopically aligned by shearing.

Acknowledgments

The authors would like to thank R.A. Hikmet for valuable discussions and H. Fischer for X-ray measurements and discussions.

References

[1] For an overview: F.M. Gray, *Solid Polymer Electrolytes,* VCH Publishers, New York, 1991.

[2] G. Ungar, S.V. Batty, V. Percec, J. Heck and G. Johansson, *Adv. Mater. for Opt. and Electr.*, **4,** 303 (1994), b. F.B. Dias, S.V. Batty, P. Voss, G. Ungar and P.V. Wright, *Solid State Ionics,* **85,** 43 (1996). c. K. Kimura, H. Motokau and M. Yokoyama, *J. Mater. Chem.*, **1,** 293 (1991).

[3] A.R.A. Palmans, J.A.J.M. Vekemans, H. Fischer, R.A. Hikmet and E.W. Meijer, *Chem. Eur. J.*, **3,** 300 (1997).

[4] It was not possible to determine the melting enthalpies of the mixtures due to degradation of the perchlorate anion above 100°C.

[5] H.R. Allcock, S.J.M. O'Connor, D.L. Olmeijer, M.E. Napierala and C.G. Cameron, *Macromolecules,* **29,** 7544 (1996).