Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: Anselm C. Griffin, Thomas R. Britt & Glenn A. Campbell (1982): Mesogenic Polymers. 5. [1]Thermotropic Polyamide Liquid Crystals and Analogous Small Molecule Diamides, Molecular Crystals and Liquid Crystals, 82:4, 145-150

To link to this article: http://dx.doi.org/10.1080/01406568208070174

Mol. Cryst. Liq. Cryst. Vol. 82 (Letters), pp. 145-150
0140-6566/82/8204-0145$06.50/0

MESOGENIC POLYMERS. 5.[1] THERMOTROPIC POLYAMIDE LIQUID CRYSTALS AND ANALOGOUS SMALL MOLECULE DIAMIDES

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(Submitted for Publication May 27, 1982)

Abstract: The use of substituents ($X \neq H$) ortho to the amide nitrogen in both aromatic polyamides and analogous diamides renders these compounds to be enantiotropic mesogens by lowering the solid → mesophase temperature. At the molecular level this is understood as a reduction in interchain hydrogen bonding through either a steric blocking effect and/or through formation of intramolecular hydrogen bonds (when X = Cl, OCH_3). DSC, optical microscopy and infrared data are presented for the eight compounds reported.

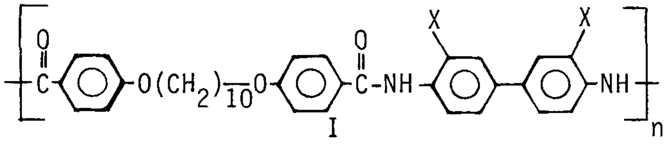
INTRODUCTION

The search for thermotropic polymeric mesogens for potential use as ultra-high strength fibers (and also as plastics) has centered on polyester materials. Although polyamides are known to form liquid crystalline solutions,[2] there are, to our knowledge, no reports in the literature of stable, thermotropic polyamides. Recently however Chapoy[3] has reported on polyamides for which preliminary data indicate possible thermotropic mesophase behavior. The amide linkage seems an excellent candidate for the construction of durable liquid crystalline polymers since polyamides are usually quite stable to hydrolysis, are photochemically stable, are resistant to thermal degradation, and can be prepared with reasonably high molecular weights.[4] The most offending characteristic of aromatic polyamides (and small molecule amides as well) is that they are high melting - to such an extent that mesomorphic behavior is often not observed. The usual explanation of the high melting points is that strong intermolecular hydrogen bonds are formed which require elevated temperatures to be overcome.[5] Aharoni[2] has however reported on mesogenic imine-amide materials with reasonably low melting temperatures.

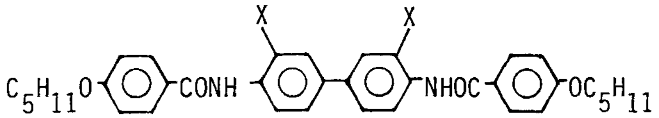
One assumes that reducing hydrogen bonding in amides (polyamides) would result in lowered melting temperatures. McIntyre[6] has performed experiments in which polyesteramides containing a substituent on nitrogen (replacing H) are compared to their unsubstituted analogue. The N-methyl amides indeed melt lower than the unsubstituted amides. In the same report, lateral substituents at various positions on aromatic rings were also used to obtain lower melting points by, it was assumed, reducing crystallinity of the compound. Another approach to lowered melting points of polyamides, which we wish to report here, is the use of substituents, not on nitrogen, but specifically on proximal ring carbons (ortho to amide nitrogen) to reduce the effective interchain hydrogen-bonding. In addition we wish to report the synthesis and characterization of analogous small molecule diamide mesogens.

EXPERIMENTAL

Synthesis of polyamides and diamides: Polyamides Ia-d were prepared by the solution polymerization of 4,4'-dichloroformyl-1,10-diphenoxydecane and the appropriate 3,3'-disubstituted-4,4'-diaminobiphenyl (1:1 molar ratio) in methylene chloride. The polymers precipitated from the reaction mixture and were collected by vacuum filtration. After washing the resulting solid repeatedly with water, ethanol, and finally, acetone, the polymers were dried under vacuum for several hours. All 3,3'-disubstituted-4,4'-diaminobiphenyls were commercially obtained products except the dimethoxy compound which was purchased as the dihydrochloride salt. Treatment of this salt with aqueous base (NaOH) afforded the 3,3'-dimethoxy-4,4'-diaminobiphenyl. (CAUTION: All 4,4'-diaminobiphenyls are to be used only with the utmost care due to the known carcinogenicity of some members. Protective clothing and adequate ventilation (hood) was used throughout this study.) The diamides on the following page were prepared in the same manner as the polymers and were recrystallized from chloroform. Infrared spectroscopy (Perkin-Elmer model 257) was used to characterize both polyamides and diamides and in all cases the resulting spectra were consistent with assigned


I

$X \equiv (a = H,\ b = Cl,\ c = CH_3,\ d = OCH_3)$



II

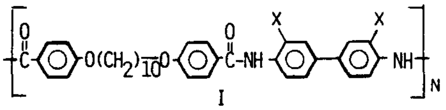
X ≡ (a = H, b = Cl, c = CH_3, d = OCH_3)

structures. Viscosity measurements were obtained on two of the polymers (Ic and Id) using a Cannon-Finske viscometer at 30.0°C in a constant temperature bath. A 60:40 (v:v) phenol/tetrachloroethane solution of the polymers was employed to obtain intrinsic viscosities by extrapolation using several polymer concentrations below 0.5 gdl^{-1}. The following intrinsic viscosities were obtained: Id(X = OCH_3), 0.49; Ic(X = CH_3), 1.11. Differential scanning calorimetry (DSC) experiments were carried out using a du Pont 990 DSC unit and optical microscopy was performed on a Reichert Thermovar microscope equipped with a Mettler FP5/52 heating accessory.

It is for convenience only that we have shown both X substituents up ("cis"). There is of course a dynamic equilibrium between "cis" and "trans" conformations of these substituents caused by rotation about the C-C bond linking the aromatic rings in the biphenyl moiety.

RESULTS AND DISCUSSION

Collected into Table I are transition temperatures (DSC) and observations of phase types (microscopy) for the polyamides Ia-d. Table II contains comparable data for the diamides IIa-d. As can be seen from these tables, introduction of lateral substituents ortho to the amide nitrogen reduces the solid → mesophase temperature to the point where an enantiotropic mesophase can be seen for these materials. We attribute this lowering of the solid → mesophase temperature to a reduction in solid phase interchain hydrogen bonding. Although it is tempting to speculate as to the electronic origin of the reduction in hydrogen bonding (intermolecular; steric blocking of hydrogen on nitrogen <u>or</u> intramolecular; ortho Cl and OCH_3 hydrogen bonding with hydrogen on amide nitrogen) we are currently unable to discern between the alternatives. Infrared spectra taken in the 3600-3100 cm^{-1} region (N-H stretching frequency) revealed that ortho-substituted compounds Ib-d and IIb,d had very different infrared absorptions compared to the unsubstituted parent compounds Ia and IIa, respectively. All (X ≠ H) had much



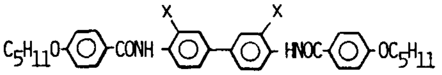
I

X: A = H, B = CL, C = CH_3, D = OCH_3

X	ENDOTHERMS (°C)	OPTICAL OBSERVATION (°C)
A(H)	138, 277, 322, DECOMPOSITION>425	NO MESOPHASE SEEN OPTICALLY UP TO 350, THE LIMIT OF MICROSCOPY
B(CL)	190, BROAD ENDOTHERM CENTERED AT 254	NEMATIC TEXTURE EVIDENT AT 250, NEMATIC PHASE COMPLETELY GONE BY 275
C(CH_3)	272, 332	SOLID → NEMATIC AT 272; NEMATIC → ISOTROPIC AT 332
D(OCH_3)	226, 256	SOLID → NEMATIC AT 276; NEMATIC → ISOTROPIC AT 256

Thermal Properties of Polyamides Ia-d

Table 1



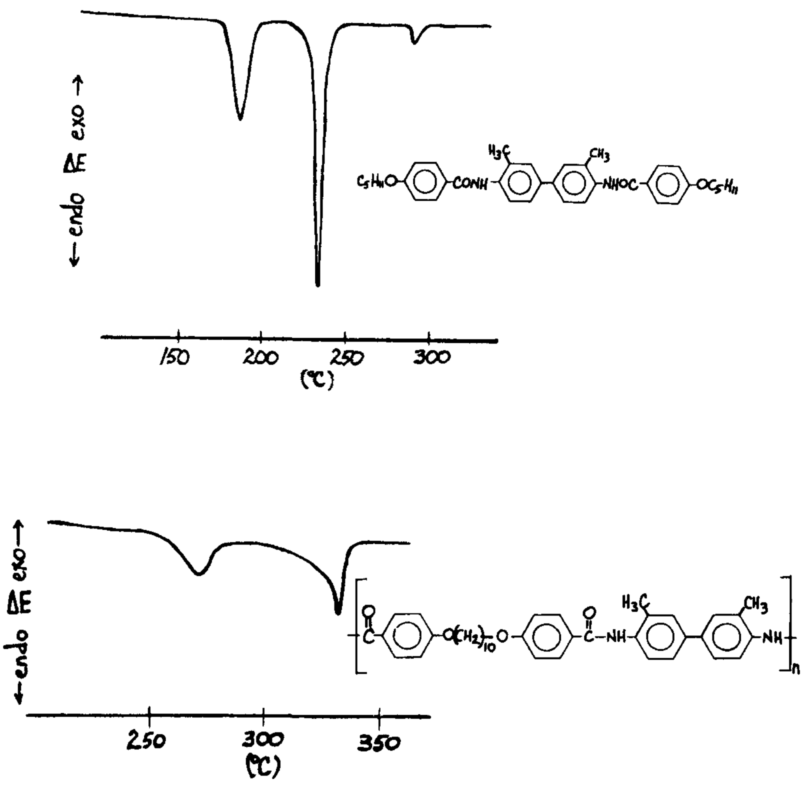
II

X: A = H, B = CL, C = CH_3, D = OCH_3

X	ENDOTHERMS (°C)	OPTICAL OBSERVATION (°C)
A(H)	298, 316, 330, 354, DECOMPOSITION>425	NO MESOPHASE SEEN UP TO 350, LIMIT OF MICROSCOPY
B(CL)	181, 210, 321	SOLID → SOLID AT 181; SOLID → NEMATIC AT 210; NEMATIC → ISOTROPIC AT 321
C(CH_3)	186, 233, 289	SOLID → SOLID AT 186; SOLID → NEMATIC AT 233; NEMATIC → ISOTROPIC AT 289
D(OCH_3)	184, 249	SOLID → NEMATIC AT 184 NEMATIC → ISOTROPIC AT 249

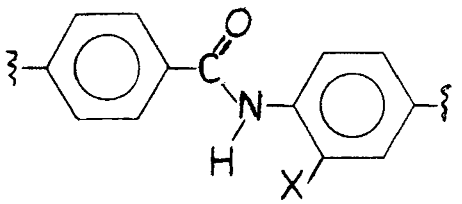
Thermal Properties of Diamides IIa-d

Table II



DSC CURVES FOR X = CH_3 POLYAMIDE AND DIAMIDE
(20°C/MIN)

FIGURE I



AMIDE LINKAGE INCLUDING ORTHO SUBSTITUENT

FIGURE II

stronger absorptions in the free (unassociated) N-H region (∿3450 cm^{-1}) than the X = H parent compounds and also much weaker absorptions in the associated (hydrogen bonded) N-H region (∿3320 cm^{-1}). The lone exception is the diamide IIc ($X = CH_3$); the only strong absorption in this region was at 3320 almost exactly coinciding with the strong hydrogen bonded N-H stretch for the parent IIa (X = H).

It is evident from the high $T_{N \to I}$ for the diamides and polyamides that the well-known polarity of the amide bond acts to strengthen intermolecular forces over those produced by most other linking groups for example azoxy, ester, and Schiff's base.[5] The introduction of ortho substituents on the 4,4'-diaminobiphenyl nucleus leads to enantiotropic nematic mesophases in our compounds both polymeric and monomeric and should, as a principle, lead to new types of polyamide liquid crystals rendered mesogenic through reduced solid phase hydrogen bonding.

ACKNOWLEDGEMENT: We wish to thank the National Science Foundation (DMR 8115703) for partial support of this work.

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