

Naphthoic Acid Derivatives as Hydrogen Bond Donors in Supramolecular Materials

Paul J. Riedel, Justin R. Kumpfer, Donald C. Rogness,* Kurt N. Wiegel

Department of Chemistry, University of Wisconsin-Eau Claire, Eau Claire, Wisconsin 54702

Received 17 November 2005; accepted 14 April 2006

DOI 10.1002/app.25014

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The synthesis of a series of 6-hydroxy-2-naphthoic acid derivatives is described. These have been used to form supramolecular main-chain liquid crystalline polymers. These hydrogen bond donors are complexed with a series of bisfunctionalized rigid pyridine species. These associative chain structures were analyzed through differential scanning calorimetry and polarizing light thermal optical microscopy. The liquid crystalline phases formed displayed mainly enantiotropic nematic phases that display an increase

in clearing temperature as the rigid portions of the supramolecular system increased in length. A decrease in the clearing temperature was observed as the length of the flexible spacer group increased. Both of these observations follow established trends in liquid crystalline behavior. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5890–5894, 2006

Key words: supramolecular; hydrogen bonding; liquid crystal; polymer; self-assembly; fibers; networks

INTRODUCTION

The formation of functionalized materials through noncovalent modification is an area of considerable scientific interest. One of the most prominent characteristics introduced through this process is the formation of liquid crystals from nonmesogenic precursors.^{1–7} A wide variety of mesogenic shapes (calamitic, discotic, banana-shaped, and bowlic mesogens)^{8–11} and structures (small molecule, main-chain polymers, side-chain polymers, and networks)^{12–15} have been created through these noncovalent interactions.

One of the most studied supramolecular associations is the benzoic acid/pyridine molecular complex formed through a hydrogen bond.^{16–18} Extensive work has been carried out in the formation and analysis of main-chain supramolecular polymers and small molecules from these components.^{19–21} Biphenyl acid/pyridine derivatives have also been implemented for mesogen assembly,²² but the higher melting nature of a biphenyl acid can make complexes with some pyridine derivatives difficult, especially if the pyridine is susceptible to degradation or sublimation at the temperatures needed to induce fluidity in the biphenyl acid species.

Naphthalene derivatives have long been recognized as a mesogen-forming structure.²³ Esters formed from 6-hydroxy-2-naphthoic acid produce predictable and stable mesogenic systems.²⁴ Additionally, derivatives of 6-oxyisoquinoline (structurally similar to naphthalene) have been used as hydrogen bond acceptors in supramolecular liquid crystals.²⁵ To date, there has been no study involving naphthoic acid species in the formation of supramolecular liquid crystalline materials with pyridyl hydrogen bond acceptors. Here, we report the synthesis of derivatives of 6-hydroxy-2-naphthoic acid and the formation of hydrogen bonded complexes with a series of rigid and flexible pyridyl species. These assembled chain structures display strong liquid crystalline characteristics (rigid pyridyls) or the ability to form fibers (flexible pyridyl species).

EXPERIMENTAL

Characterization

Phase transitions were observed using an Olympus BHT polarizing light microscope equipped with a Mettler-Toledo FP82-HT thermal optical hotstage connected to a Mettler Toledo FP90 control unit. Differential scanning calorimetry thermograms were obtained from a Perkin-Elmer Pyris 1 DSC. A heating/cooling rate of 10°C/min was used in both analyses. ¹H- and ¹³C-NMR spectra were recorded on a JEOL Eclipse 400 MHz FTNMR spectrometer using TMS as an internal standard.

Synthesis

Reagent grade reactants and solvents were used as received from suppliers. Spectrographic grade solvents

*Present address: Department of Chemistry, IA State University, Ames, IA 50011.

Correspondence to: K. N. Wiegel (wiegelkn@uwec.edu).

Contract grant sponsor: Research Corporation; contract grant number: CC5890.

Contract grant sponsors: The Office of Research and the University of Wisconsin-Eau Claire.

were used for all measurements. The synthesis of 4,4'-azopyridine (AZO P)²⁶ and 4,4'-(*p*-phenylenedi-1,2-ethylenediyl)bispyridyl (3RP)²⁷ have been reported previously.

Methyl-2-hydroxy-6-naphthoate

Five grams of 6-hydroxy-2-naphthoic acid was combined with 500 mL of methanol and 0.5 mL of sulfuric acid and refluxed for 24 h. The excess solvent was then removed under reduced pressure, and the oil was poured into 2 L of ice water. A white solid precipitated was isolated by filtration and recrystallized from ethanol to provide 2.80 g of a grayish-tan solid.

Yield: 52%; T_m : 153°C; ¹H-NMR: 8.52 (s, 1H), 7.94 (d, 1H), 7.75 (d, 1H), 7.68 (d, 1H), 7.38 (s, 1H), 7.22 (d, 1H), 3.98 (2, 3H).

General procedure for the preparation of ethyleneglyoxy-bis-2-(6-hydroxynaphthoic acid)

Methyl-2-hydroxy-6-naphthoate was mixed with the di-*p*-tosylate (2.2 : 1 molar ratio) of the appropriate oligomeric ethyleneglyoxy chain with cesium carbonate (2.2 eq.) in acetone and refluxed for 48 h. The mixture was cooled to room temperature, filtered, and the solvent was removed from the acetone fraction under reduced pressure. The oil was combined with 250 mL of a 10% potassium hydroxide in ethanol solution and refluxed for 3 h. The solution was cooled to room temperature, and excess solvent was removed under reduced pressure. The grayish-brown solid was then added to 4 L of water acidified with 250 mL of 12M hydrochloric acid. A gray precipitate was collected by filtration and recrystallized from ethanol to afford the pure bisacid.

3-NBA: 69% yield, T_m : 252–254°C, ¹H-NMR: 8.51 (s, 2H), 8.01 (d, 2H), 7.90 (d, 2H), 7.84 (d, 2H), 7.39 (s, 2H), 7.25 (d, 2H), 4.25 (t, 4H), 3.85 (t, 4H), 3.67 (s, 4).

4-NBA: 72% yield, T_m : 184–185°C; ¹H-NMR: 8.51 (s, 2H), 8.03 (d, 2H), 7.86 (d, 2H), 7.81 (d, 2H), 7.39 (s, 2H), 7.22 (d, 2H), 4.25 (t, 4H), 3.88 (t, 4H), 3.67 (t, 4H), 3.61 (t, 4H).

5-NBA: 68% yield, T_m : 164–165°C; ¹H-NMR: 8.52 (s, 2H), 8.01 (d, 2H), 7.90 (d, 2H), 7.85 (d, 2H), 7.38 (s, 2H), 7.22 (d, 2H), 4.22 (t, 4H), 3.80 (t, 4H), 3.55 (t, 4H), 3.51 (t, 4H), 3.33 (s, 4H).

Bis-(4-mercaptopyridine) methane

A 2.5-g amount of 4-mercaptopyridine (0.023 mol) was mixed with 1.86 g of dibromomethane (0.011 mol) and 1.26 g of potassium hydroxide (0.022 mol). The mixture was refluxed in ethanol for 2 h. The resultant

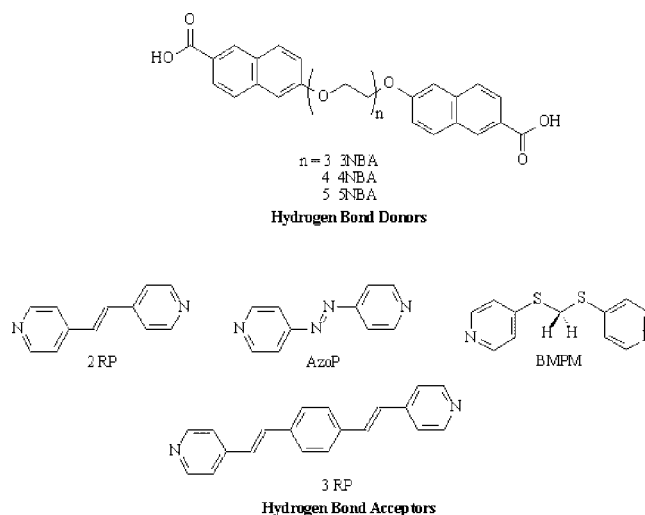


Figure 1 Materials used.

solution was poured over 1 L of a water/ice mixture to produce a white solid, which was filtered and recrystallized from ethanol to afford 1.86 g of a white, fibrous solid. BMFM: 74% yield, T_m : 93–94°C, ¹H-NMR: 8.43 (d, 4H), 7.36 (d, 4H), 4.92 (2H, s).

Complex formation

The hydrogen bond complexes were formed by thoroughly mixing equimolar quantities of the hydrogen bond donor and acceptor in the molten state for 2 min under an inert atmosphere. These mixtures were allowed to cool slowly to room temperature to form the liquid crystalline materials. Hydrogen bond formation was confirmed through infrared spectroscopy by the presence of two characteristic stretching bands (centered around 2500 and 1950 cm^{-1}).

RESULTS AND DISCUSSION

Liquid crystalline materials

The materials used in this study are provided in Figure 1. DSC data for these complexes is presented in Figures 2 and 3, and selected optical images from these complexes are seen in Figures 4 and 5. A compiled table of thermal transitions can be seen in Table I.

The 3NBA/2RP complex displayed the highest clearing temperature of the systems utilizing the 2RP hydrogen bond acceptor. The clearing temperature dropped as the systems increased the number of flexible ethylene-glyoxy units between the hydrogen bond donors. This follows the accepted liquid crystalline theory: As the flexibility of a chain increases, the molecular mobility of the mesogens also increases, leading ultimately to a lower clearing temperature. Interestingly, the only more ordered phase observed was a smectic A phase formed from the 5NBA/2RP complex.

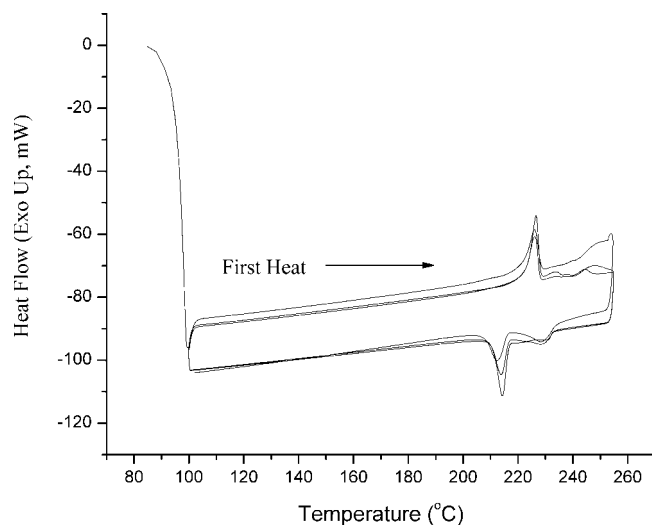


Figure 2 DSC thermogram of 3NBA 2 RP.

Utilizing the 3RP system produced a material that degraded rather than melt when complexed with the 3NBA donor. The combined species produced too high of a melting point to effectively measure before decomposition. The associative chain structure formed from the 3RP and 4NBA displayed a measurable clearing temperature that was higher than the transition observed in the 3RP/5NBA system. This also follows accepted trends, i.e., increasing the flexibility in the 5NBA species would decrease the overall clearing temperatures.

The complexation of the AZO P hydrogen bond acceptor with the 3NBA donor produced a complex that had transitions at temperatures such that the AZO P sublimed at such a rate that stoichiometric imbalance was induced into the material. The resultant material would not display accurate liquid crystalline

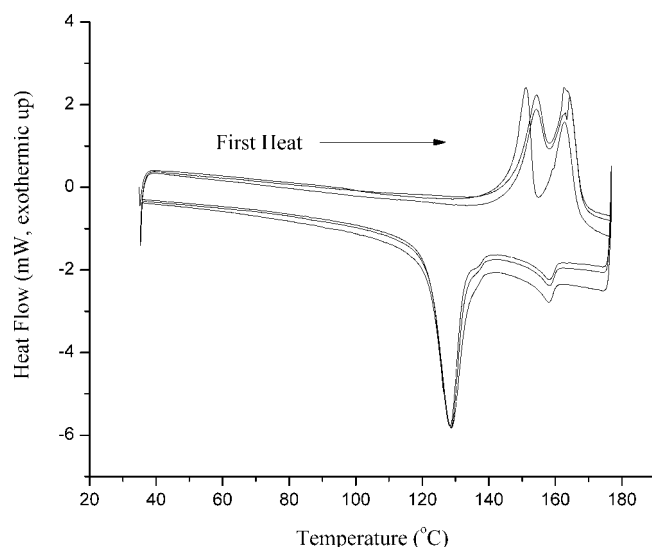


Figure 3 DSC thermogram of 5 NBA AzOP.

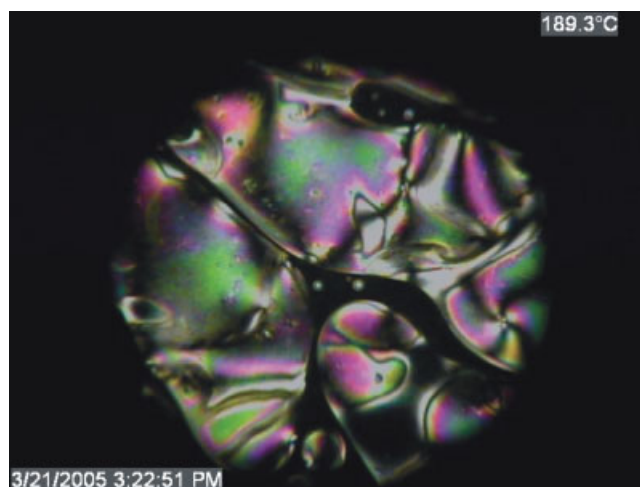


Figure 4 Optical micrograph of 5 NBA 2 RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

transitions. The associative chain structure formed from the 4 NBA and 5 NBA hydrogen bond donors, however, had transitions sufficiently low that mesogenic character could be observed. As the ethyleneglycoxy spacer increased in length, the clearing temperature subsequently decreased as well.

When the naphthoic acid species were tethered to bisfunctionalized chains, the liquid crystalline characteristics formed through hydrogen bond dimer formation disappeared, again as typified in benzoic acid species. When used to form hydrogen bonded complexes with rigid bispyridyls (2RP, 3RP and AZOP) each of the naphthoic bisacids (3NBA, 4NBA, 5NBA) displayed thermally stable, enantiotropic liquid crystalline (mainly nematic) phases. As the rigid components of the complexes increased in length (increasing

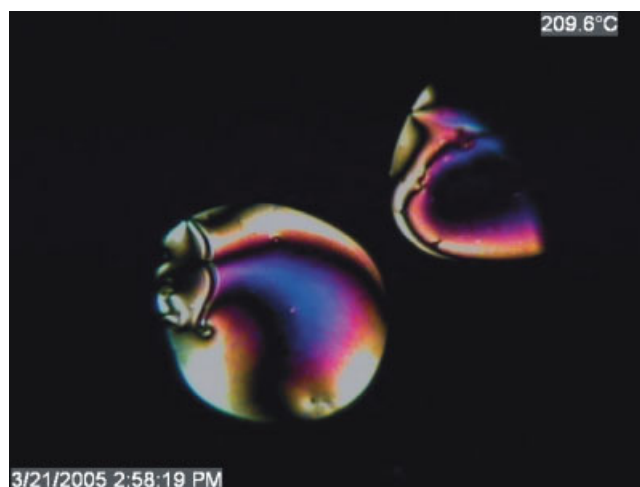


Figure 5 Optical micrograph of 4 NBA 3 RP. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE I
Summary of Thermal Analysis Data

	2 RP	3 RP	Azo P
3 NBA			
Heat	K 225.9 N 233.7 I	Dec.	Sub.
Cool	I 228.4 N 214.3 K	Dec.	Sub.
4 NBA			
Heat	K 193.9 N 215.3 I	K 195.8 N 201.6 I	K 173.4 N 180.3 I
Cool	I 214.0 N V	I 150.96 N 130.5 K	I 178.5 N 145.1 K
5 NBA			
Heat	K 163.9 S _A 184.4 N 193.3 I	K 151.3 N 173.3 I	K 151.1 N 162.7 I
Cool	I 192.2 N 182.4 K	I 131.8 N 108.8 K	I 158.2 N 128.8 K

K, crystal; N, nematic; S, smectic; I, isotropic; V, vitrification (cooling to an ordered glass); Sub., sublimation of azopyridine; Dec., decomposition.

the length of the rigid pyridyl components), the clearing temperature of the liquid crystalline phases increased. This phenomenon is in line with current liquid crystalline theory: By increasing the overall length of a mesogen, the melting temperature and therefore clearing temperature of the systems is increased.

The inclusion of the AZOP species as the hydrogen bond acceptor lowered the clearing temperature further when compared with the structurally similar 2RP. One possible explanation for these lowered clearing temperatures is the electronegativity of the azo nitrogens para to the hydrogen bond acceptor. The lower electron density on these acceptors could weaken the hydrogen bond and therefore weaken the mesogen-forming phenomenon.

As the flexibility of the spacer groups increases in the study (comparing three, four and five ethylene-glycoxy repeat units in the spacer groups), the clearing temperatures of the associative chain structures subsequently decreased. This is rational when compared with the body of understanding on liquid crystalline characteristics—higher amounts of chain flexibility impart more degrees of freedom between the mesogens, allowing for a lower melting temperature and a subsequently lower clearing temperature.

Complexes formed through the naphthoic acid species show an increase in the transition temperatures as compared to those seen using a structurally analogous bisbenzoic acid species. Although biphenyl-based complexes provide strong liquid crystalline complexes as well, the transition temperatures for assembled chain structures based on these donors tend to be very high, often above the degradation temperatures of the parent species, because of the dramatic increase of the mesogen size.²⁷ These naphthoic acid species provide an compromise between increasing the mesogen length and maintaining usable transition temperatures.

Nonmesogenic polymers

When the bisnaphthoic acids were used in the formation of supramolecular polymers from BMPM, no

liquid crystalline characteristics were observed. The aliphatic core of this species imparts enough of an angle to prevent the formation of a rigid mesogenic species. The ability of these polymers to form fibers pulled from the melt was impressive—several fibers ranging in length from 10 to 66 cm were pulled. Optical micrographs of these fibers (seen in Fig. 6) showed a consistent, smooth surface with no anisotropy present in the materials. The fibers themselves were isotropic glasses. These fibers crystallized and decomposed while kept at room temperature after 6 h. The crystallization of these components after approximately 6 h induced chain scission and fiber degradation. There was no noticeable effect in increasing the flexible spacer length in the characteristics or the lifetime of the fibers. The crystallization of the component species (bisacids and bispyridyl) was apparently delayed in the formation of the fiber, which allowed the fibers to exist instead of immediately decomposing to component crystals. Similar behavior has been observed in fibers pulled from bisacids and tetrakis-pyridyls.²⁸



Figure 6 Optical micrographs of fibers pulled from 5 NBA BMPM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

A series of main-chain liquid crystalline polymers have been synthesized through hydrogen bonding with rigid pyridyl species as the hydrogen bond acceptor and alkoxy-substituted naphthoic acid species as the hydrogen bond donor. These materials displayed enantiotropic liquid crystalline phases which were mainly nematic structure. The triethyleneglycoxy spacer group displayed melting temperatures that were sufficiently high to induce decomposition in the complexes formed with 3RP system and sublimation in the AZOP complexes. These difficulties were not observed in the lower melting 4 and 5 NBAs. There was an obvious increase in the clearing temperature as the mesogen length (from both the hydrogen bond donor and acceptor species, going from two ring pyridyls to three) increased. The inclusion of an azobased bispyridyl spacer *decreased* the transition temperatures as compared to the alkenyl species. One supposition for this is a slightly lower electron density on the pyridyl nitrogen from the azo group in a para position when compared with the system with an alkene in the same position. Increasing the length of the flexible ethyleneglycoxy spacer groups between the hydrogen bond donors decreased the clearing temperatures of the hydrogen bonded systems. This follows what is commonly accepted in liquid crystalline knowledge—more flexibility between the mesogenic units promotes a lower melting temperature, which would in turn lead to a lower clearing temperature for the assembled molecules. Bis-(4-mercaptopyridine) methane (a nonmesogen promoting pyridyl species) was used in the formation of supramolecular polymers. These systems displayed a strong tendency for fiber formation—short-lived, long fibers were pulled from the melt of the polymer. Optical micrographs of these fibers displayed a uniform, hollow nonbirefringent strand.

Naphthoic acid derivatives allow for the formation of supramolecular complexes. The fused rings of the naphthalene structure provide an extended, rigid structure capable of creating mesogenic units. These species are also capable of forming remarkably stable nonmesogenic materials when complexes with a bisfunctionalized mercaptopyridine hydrogen bond acceptor. The

naphthoic acid species provide achievable transition temperatures for the formation of associative chain structures.

The authors thank Dr. David Lewis and James Phillips for their help and guidance in this work.

References

1. Gray, G.; Jones, B. *J Chem Soc* 1953, 4197.
2. Kato, T. *Supramol Sci* 1996, 3(1–3), 53.
3. Hwang, I.; Lee, S.; Chang, J. *J Polym Sci Part A: Polym Chem* 2003, 41, 1881.
4. Kang, S.; Samulski, E.; Kang, P.; Choo, J. *Liq Cryst* 2000, 27, 377.
5. Bladon, P.; Griffin, A. *Macromolecules* 1993, 26, 6604.
6. Parra, M.; Hildago, P.; Barberá, J.; Alderete, J. *Liq Cryst* 2005, 32, 573.
7. Felekis, T.; Tsiourvas, D.; Tziveleka, L.; Paleos, C. *Liq Cryst* 2005, 32, 39.
8. Griffin, A.; Havens, S. *J Polym Sci Part B: Polym Phys* 1981, 19, 951.
9. Kleppinger, R.; Lillya, C.; Yang, C. *J Am Chem Soc* 1997, 119, 4097.
10. Choi, E.-J.; Ahn, J.-C.; Chien, L.-C.; Lee, C.-K.; Zin, W.-C.; Kim, D.-C.; Shin, S.-T. *Macromolecules* 2004, 37, 71.
11. Xu, B.; Swager, T. *J Am Chem Soc* 1995, 117, 5011.
12. Kato, T.; Frechet, J. *J Am Chem Soc* 1989, 111, 8533.
13. Tschierske, C. *Annu Rep Prog Chem Sect C* 2001, 97, 191.
14. Kumar, U.; Kato, T.; Frechet, J. *J Am Chem Soc* 1992, 114, 6630.
15. Kihara, H.; Kato, T.; Uryu, T.; Frechet, J. *Chem Mater* 1996, 8, 961.
16. Bladon, P.; Griffin, A. *Macromolecules* 1993, 26, 6604.
17. He, C.; Lee, C.; Griffin, A.; Bouteiller, L.; Lacourde, N.; Boileau, S.; Fouquey, C.; Lehn, J. *Mol Cryst Liq Cryst* 1999, 332, 251.
18. Nishikawa, E.; Samulski, E. *Liq Cryst* 2000, 27, 1457.
19. Kang, Y.; Kim, H.; Zin, W. *Liq Cryst* 2001, 28, 709.
20. Alexander, C.; Jariwala, C.; Lee, C.; Griffin, A. *Macromol Symp* 1994, 77, 283.
21. He, C.; Donald, A.; Griffin, A.; Waigh, T.; Windle, A. *J Polym Sci Part B: Polym Phys* 1998, 36, 1617.
22. Rogness, D.; Riedel, P.; Sommer, J.; Reed, D.; Wiegel, K. *Liq Cryst* 2006, 33, 567.
23. Collings, P.; Hird, M. *Introduction to Liquid Crystals*; Taylor and Francis: London, 1998.
24. Bhowmik, P.; Atkins, E.; Lenz, R.; Han, H. *Macromolecules* 1996, 29, 1910.
25. Lin, H.; Ko, C.; Guo, K.; Cheng, T. *Liq Cryst* 1999, 26, 613.
26. Launay, J.; Tourrel-Pagis, M.; Lipsker, J.; Marvaud, V. *Inorg Chem* 1991, 30, 1033.
27. Lee, C.-M., Ph. D. Dissertation, University of Cambridge, 1994.
28. St. Pourcain, C.; Griffin, A. *Macromolecules* 1995, 28, 4116.