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

Synthesis and Properties of Highly Fluorescent Liquid Crystals Containing Benzoxazole Moiety

Sehoon Kim [a] & Soo Young Park [a]

[a] Department of Fiber and Polymer Science, Seoul National University, Seoul, 151-742, Korea

Version of record first published: 24 Sep 2006

To cite this article: Sehoon Kim & Soo Young Park (1999): Synthesis and Properties of Highly Fluorescent Liquid Crystals Containing Benzoxazole Moiety, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 337:1, 405-408

To link to this article: http://dx.doi.org/10.1080/10587259908023463

Mol. Cryst. and Liq. Cryst., 1999, Vol. 337, pp. 405-408
Reprints available directly from the publisher
Photocopying permitted by license only

Synthesis and Properties of Highly Fluorescent Liquid Crystals Containing Benzoxazole Moiety

SEHOON KIM and SOO YOUNG PARK

Department of Fiber and Polymer Science, Seoul National University, Seoul, 151–742, Korea

Highly fluorescent anisotropic molecules (**M1~M5**) containing benzoxazole moiety were synthesized. Four of them exhibited various liquid crystalline phases. Polarized emission was identified from the nematic phase of **M2**. The liquid crystalline and photoluminescent (PL) properties of these materials are discussed.

Keywords: benzoxazole; liquid crystals; photoluminescence; polarized emission

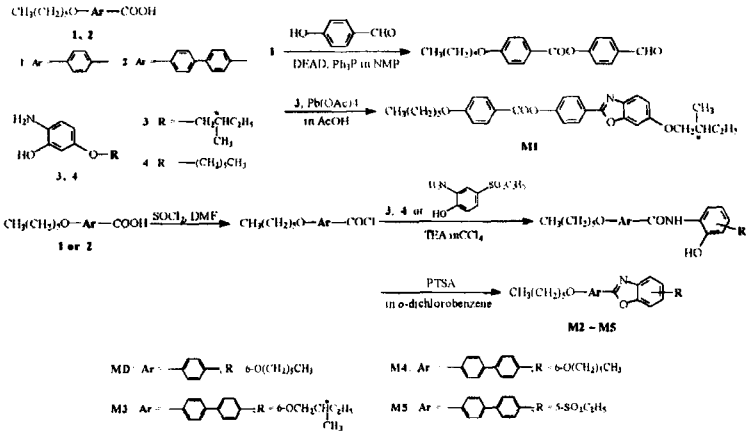
INTRODUCTION

2-Arylbenzoxazole derivatives are characterized by the anisotropic molecular shape as well as the efficient π electron conjugation. Anisotropic molecular shape is responsible for the liquid crystallinity of these materials as was reported by Pavluchenko and coworkers.[1] On the other hand, fully conjugated heteroaromatic structure of 2-arylbenzoxazole was separately exploited as a fluorescent material or laser dyes.[2] Therefore, we came to consider that fluorescent liquid crystals which shows polarized emission could be synthesized by the appropriate molecular design of 2-arylbenzoxazoles. In this work, we report the synthesis and properties of highly fluorescent liquid crystals containing 2-phenylbenzoxazole unit as a mesogenic core.

EXPERIMENTAL

All the 2-phenylbenzoxazole compounds (**M1~M5**) were prepared by the reaction of *o*-aminophenol derivatives with benzaldehyde or benzoic acid derivatives, as depicted in

SCHEME 1. Compounds **1**~**5** were synthesized by the methods described in our previous work.[3] 2-Amino-4-(ethylsulfonyl)phenol was obtained from Aldrich Chem. Co. Ring formation reaction for **M1** was carried out according to our earlier report.[3]



SCHEME 1 Synthesis of fluorescent liquid crystals.

M2~**M5** were prepared by dehydrative cyclization of *o*-(acylamino)phenols according to the literature method.[4] The structures of compounds **M1**~**M5** were fully identified by the elemental analysis (LECO CHNS-932) and ^{1}H NMR spectra (Jeol JNM-LA300, 300 MHz, in $CDCl_3$). Thermal analysis was performed on Perkin-Elmer DSC7 at rate of 10℃/min. Microscopic observations were carried out with Leica DMLP equipped with hot stage controlled by Eurotherm temperature controller. Absorption spectra in $CHCl_3$ were determined using a Shimadzu UV-210PC. Photoluminescence spectra in $CHCl_3$ were recorded using two monochromators and photomultiplier tube (Spectra Pro-150, Spectra Pro-300I, PD438, Acton Research Co.). Absolute PL quantum efficiencies were obtained using integrating sphere (Newport 819-IS-4). Polarized emission spectra were recorded from the **M2** filled sandwich cell (5 μm spacer) where the alignment of liquid crystal was achieved by rubbed polyimide layer (AL-1051, Japen Synthetic rubber, Co.). The cell was placed at an angle of 45° to both the excitation source and detector, and the polarizer was placed between detector and sample.

RESULTS AND DISCUSSION

Chemical structures of M1~M5 were fully identified by ^{1}H NMR and elemental analysis. As an example, that of **M5** is shown below.

5-Ethylsulfonyl-2-(4`-hexyloxybiphenyl-4-yl)benzoxazole (**M5**): overall yield through amide formation and ring enclosure is 45%; ^{1}H NM R ($CDCl_3$, ppm) 0.92-1.85 (m, 14H), 3.19 (quartet, *J*=7.32 Hz, 2H), 4.02 (t, *J*=6.39 Hz, 2H), 7.02 (d, *J*=8.61 Hz, 2H), 7.62 (d, *J*=8.61 Hz, 2H), 7.76 (d, *J*=8.43 Hz, 2H and 1H overlapped), 7.94 (dd, *J*=2.2, 8.61 Hz, 1H), 8.31 (d, *J*=8.43 Hz, 2H), 8.33 (d, *J*=2.2 Hz, 1H); Elem. anal. calcd. for $C_{27}H_{29}NO_4S$: C 69.95, H 6.31, N 3.02, S 6.92. Found: C 70.19, H 5.26, N 3.02, S 7.

All the compounds exhibited blue emission and four of them (M1~M4) are liquid crystalline. Liquid crystalline and optical properties are summarized in TABLE I. **M1** showed many transitions due to ester linkage and chiral tail. Especially, isotropic liquid crystalline phase (possibly TGB phase), which was dark and exhibited no texture between the crossed polarizers, occurred monotropically in cooling below cholesteric phase. The photoluminescent efficiency of **M1** was low due to the presence of aromatic ester group. **M2** with simple 2-phenylbenzoxazole mesogen exhibited nematic phase monotropically in cooling. It also shows recrystallization from crystalline phase in heating. Among **M3~M5** which possess same mesogen containing biphenyl, **M3** and **M4** showed almost the same optical properties. **M3** had unstable cholesteric phase, probably resulting from the bulky chiral center near the bent structure of benzoxazole. It was also

TABLE I The liquid crystalline and optical properties

	Transition temperature (°C) 2nd heating / Cooling	λmax abs. (nm)	λmax fl. (nm)	η_{PL}
M1	K 82 K 114 N* 133 I I 128 N* 95 II. 79 K 75 K 70 K	339	381	0.16
M2	K 28 (exotherm) K 48 I 41 N 22 K 12 K	323	373 388	0.56
M3	K 106 N* 112 I I 102 N* 86 K	358	400	0.59
M4	K 99 K 103 A 169 N 176 I I 170 N 165 A 75 K 65 K	336	401	-
M5	K 193 I	366	409	0.90

I: isotropic, K: crystalline, N: nematic, N*: cholesteric, II.: isotropic liquid crystalline (see text), A: unidentified phase, λmax abs., λmax fl.: peak of absorption and photoluminescence in chloroform, η_{PL}: absolute photoluminescence quantum efficiency in chloroform.

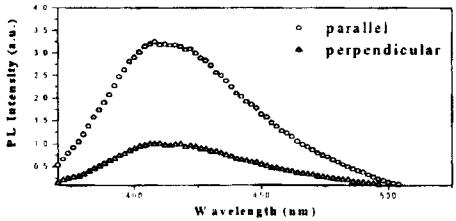


FIGURE 1 Polarized photoluminescence spectra of M2 in the aligned nematic phase, excited with unpolarized light of 323 nm.

deduced from that M4 having achiral tail exhibited more stabilized liquid crystalline phases. M5 was not liquid crystalline, but highly fluorescent (η_{PL}=0.90) with slight red shift due to the electron withdrawing ability of sulfone group. The exact natures of LC phases are to be investigated by X-ray diffractometry. FIGURE 1 shows the fluorescence emission of M2 in aligned nematic phase, excited with unpolarized light. Emission anisotropy is clearly seen, and the intensity of emission polarized parallel to the rubbing direction is about three times larger than that polarized perpendicularly.

CONCLUSION

Compounds for fluorescent liquid crystal containing benzoxazole moiety were synthesized successfully. All of them exhibited blue photoluminescence and four of them were liquid crystalline. Polarized emission was identified from the nematic phase of M2.

Acknowledgements

This research was supported by CRM-KOSEF (1998). We are grateful to Prof. Jang-Ju Kim in Dept. of Materials Science and Engineering, K-JIST, for photoluminescence measurements.

References

[1] A. Pavluchenko, N. Smirnova, V. Titov, E. Kovshev, and K. Djumaev, *Mol. Cryst. Liq. Cryst.*, **37,** 35 (1976).

[2] J. Kauffman and G. Bajwa, *J. Heterocyclic Chem.*, **30,** 1613 (1993).

[3] S. Kim, J. Sohn, and S. Y. Park, "Synthesis and phase behavior of chiral liquid crystalline monomers and side-chain polymers containing 2-phenylbenzoxazole in mesogenic unit", submitted to *Bull. Kor. Chem. Soc.*

[4] Jpn. Kokai Tokkyo Koho JP 03 232, 868.