Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Polymethine Dye Synthesis and Its Leuco Property Investigation

Young-A Son [a], Byung-Soon Kim [a], Myung-Sik Choi [b] & Sung-Hoon Kim [b]

[a] BK21 FTIT, Department of Organic Materials and Textile System Engineering, Chungnam National University, Daegeon, South Korea

[b] Department of Textile System Engineering, Kyungpook National University, Daegu, South Korea

Version of record first published: 22 Sep 2010

To cite this article: Young-A Son, Byung-Soon Kim, Myung-Sik Choi & Sung-Hoon Kim (2007): Polymethine Dye Synthesis and Its Leuco Property Investigation, Molecular Crystals and Liquid Crystals, 472:1, 225/[615]-230/[620]

To link to this article: http://dx.doi.org/10.1080/15421400701547524

Mol. Cryst. Liq. Cryst., Vol. 472, pp. 225/[615]–230/[620], 2007

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400701547524

Taylor & Francis
Taylor & Francis Group

Polymethine Dye Synthesis and Its Leuco Property Investigation

Young-A Son
Byung-Soon Kim
BK21 FTIT, Department of Organic Materials and Textile System Engineering, Chungnam National University, Daegeon, South Korea

Myung-Sik Choi
Sung-Hoon Kim
Department of Textile System Engineering, Kyungpook National University, Daegu, South Korea

Polymethine dyes have been synthesized using bis-dimethylaminophenylethylene compound. These dyes can be converted to the colorless leuco form by the treatment with alkali. Interestingly, these leuco dyes showed reversible color formation properties with following acid addition. The feasibility of the use as thermo-chromic indicator was investigated using bisphenol A and 1-hexadecanol.

Keywords: leuco; polymethine dye; reversible; thermo chromic-indicator

INTRODUCTION

Methine dyes [1–5] have attracted much attention because of their potential application in organic coloring materials. Based on bis-dimethylaminophenylethylene moiety, interesting polymethine dyes were synthesized with 4-diphenylaminobenzaldehyde and N-ethylcarbazole-3-corboxylaldehyde [6]. In addition, these methine dyes can be converted to the corresponding colorless leuco structure which can be used to the reversible color formation system. Leuco dyes could play a great role to the color occurring reaction in so many new high-technology applications [4]. In this context, the research of

Address correspondence to Sung-Hoon Kim, Department of Textile System Engineering, Kyungpook National University, Daegu 702-701, South Korea. E-mail: shokim@knu.ac.kr

synthesis and application for new methine compound has become greatly important for many color formation systems.

Another important experimental attempt for color formation system was considered to investigate the feasibility of the use as thermochromic indicator. Acidic bisphenol A compound and 1-hexadecanol were mixed to leuco form of the methine dyes. Leuco form of the methine dyes developed its absorption color in the presence of acidic bisphenol A compound. Reversible color and colorless form of the methine dyes were repeated and controlled by the melting behavior of 1-hexadecanol. In other words, this color formation reaction can be controlled above and below melting point of the higher alcohol.

In this context, this article herein concerns an investigation of the reversible color formation reactions as a thermochromic-indicator purpose which caused by leuco structure properties.

EXPERIMENTAL

Visible spectra were recorded by Shimadzu UV 2100 spectrophotometer. Colorimetric data of colored and colorless compounds were determined using a Datacolor SF 600 plus spectrophotometer interfaced to a PC. Measurements were taken with the specular component of the light excluded and the UV component included, using illuminant D_{65} and 10° standard observer.

Materials

4,4′-vinylidenebis(*N*,*N*-dimethylaniline) and 4-diphenylaminobenzaldehyde were purchased from Aldrich. *N*-ethylcarbazole-3-carboxylaldehyde was purchased from TCI. All other chemicals including methanol and sodium hydroxide were laboratory grade reagents.

Synthesis of Methine Dyes

The methine dyes were prepared from the method described in previous work [6]. 4,4′-vinylidenebis(*N*,*N*-dimethylaniline) having active methylene groups within the molecule reacted with two aldehyde compounds, namely 4-diphenylaminobenzaldehyde and *N*-ethylcarbazole-3-carboxylaldehyde.

Leuco Form and Its Thermo Color Formation System

Leuco forms were prepared to examine the reversible thermo color formation system [4]. These methine dyes were reversibly converted by

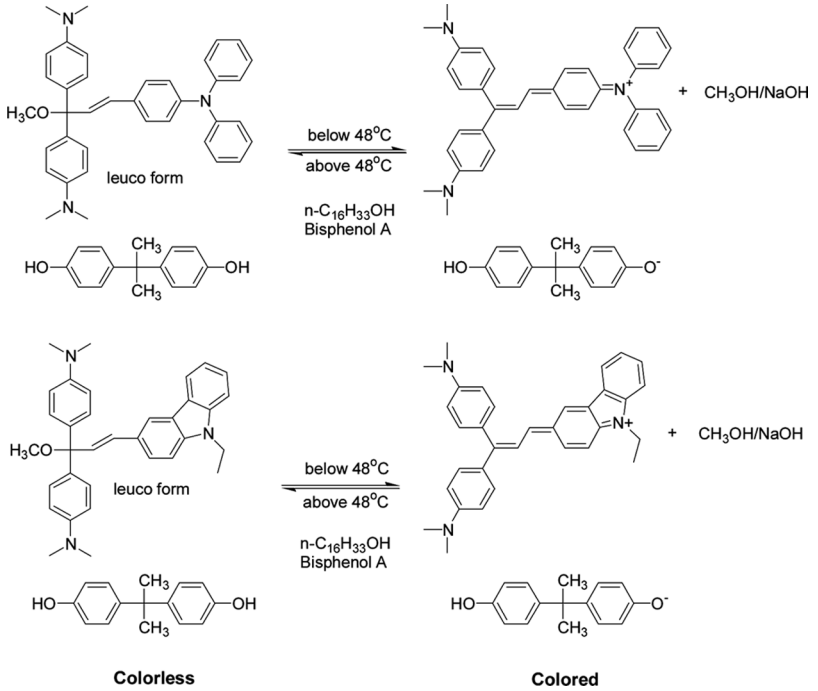

FIGURE 1 Scheme of the reversible thermo color formation system.

alkali addition [6]. To determine color formation reaction using the prepared methine dyes, these dyes were applied to the concept of thermo-color formation system. A molten mixture of the methine dyes (1 part) and 4,4′-isopropylidenediphenol (bisphenol A) (5 part) was prepared. In the presence of 1-haxadecanol (94 part), this prepared mixture displayed colorless and colored forms above and below temperature of 48°C i.e., the melting point of 1-hexadecanol [4] (Fig. 1).

RESULTS AND DISCUSSION

The leuco form of the prepared methine dyes was converted by treatment using methanol with NaOH. As the term of leuco indicates, it can be considered the reversibly reduced form of dye. In addition, this leuco dye is considered to the colorless form of a dye which may be produced by a nonreductive process such as pH, heat and light effect. In this context, Figures 2 and 3 show that the absorption spectra of the colored form which converted from leuco dyes by addition of

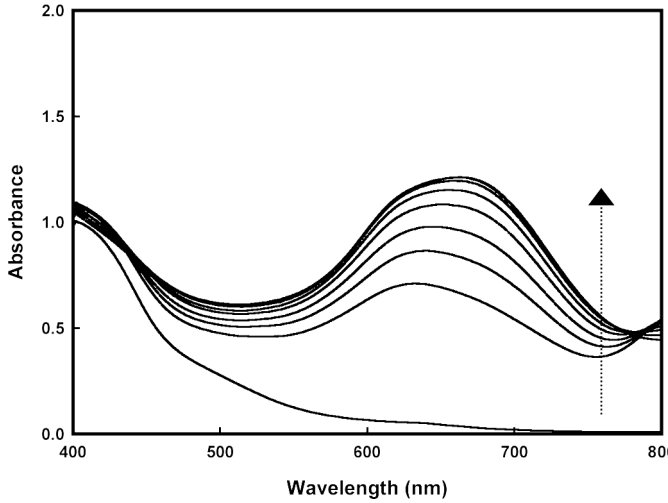

FIGURE 2 Color formation with acid addition (HCl) to leuco form of the methine dye 1.

0.05 N HCl in ethyl acetate. It is clear that the absorption of colored form gradually increased with increasing HCl amount. This rapid formation of an intense absorption band in visible range is important from the viewpoint of leuco dye chemistry.

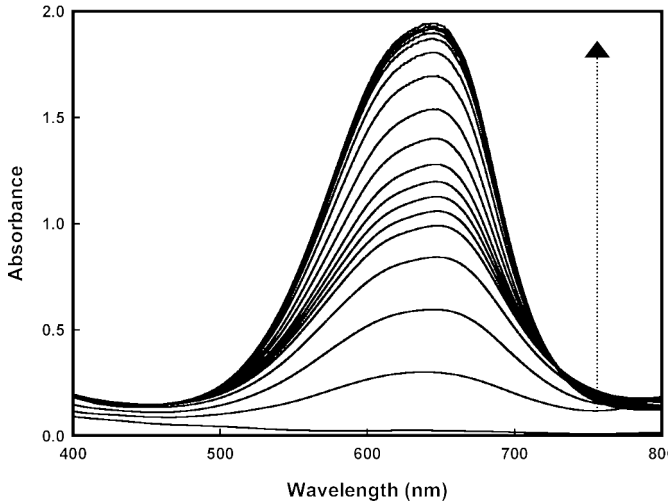

FIGURE 3 Color formation with acid addition (HCl) to leuco form of the methine dye 2.

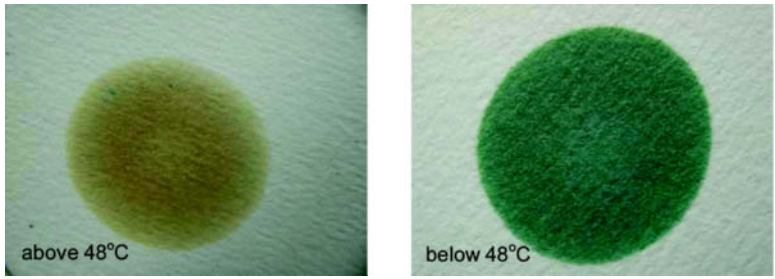

FIGURE 4 Photographic images of the reversible color formation reaction (methine dye 1).

Considering above interesting color formation reaction of the two methine compounds caused by acid addition, another approach was applied to the reversible color occurring systems using heat treatment. It is interesting concept that the prepared colorless or nearly colorless compounds react with acidic compound to provide extension of the conjugated double bond system, enabling color formation. This color formation reaction induced by heat can be generated as reversible reaction system. In this context, thermochromic color properties using the methine dyes were investigated.

For this purpose, it is designed that when solid organic compound such as bisphenol A are used as the acidic compound, higher alcohols such as 1-haxadecanol may control the reversible color-formation reaction. Figure 4 shows the image of color formation reaction caused by heat treatment. The molten mixtures using methine dye 1, bisphenol A and 1-hexadecanol developed the colored and colorless leuco forms with melting point of 1-hexadecanol.

This chromism behavior induced by heat was attributed to the effect of acidic compound (bisphenol A) in the medium. Table 1 also represents the colorimetric data of the colored form and the colorless leuco form of the methine dye 1. Colored form treated with acidic bisphenol A at below 48°C showed higher color strength value (K/S value) compared to the colorless form of the leuco compound. Below the

TABLE 1 Colorimetric data of the Reversible Color Formation (Methine Dye 1)

	L^*	a^*	b^*	C^*	h	K/S(680 nm)
colorless	71.8	−16.1	12.6	20.4	142.0	0.65
colored	50.0	−28.5	5.26	29.0	169.6	7.56

melting point of 1-hexadecanol the affinity of the methine dye with bisphenol A is stronger than that of 1-haxadecanol with bisphenol A, which cause the color formation reaction. In other words, above the melting point of 1-hexadecanol it functions as an inhibitor of the color forming reaction. Thus, this remarkable property can be used as a thermochromic indicator compound in general area of imaging and copying.

CONCLUSIONS

Polymethine dyes based on bis-dimethylaminophenylethylene moiety were synthesized and absorption properties were examined. In addition, their corresponding reversible color formation reactions were determined using dye leuco form conversion. The molten mixtures using methine dye 1, bisphenol A and 1-hexadecanol developed the colored and colorless leuco forms with melting point of 1-hexadecanol. Thus, these dyes could be appropriate to apply towards the thermo-color formation system.

REFERENCES

[1] Waring, D. R. & Hallas, G. (1990). *The Chemistry and Application of Dyes*, Plenum press: New York.
[2] Gregory, P. (1991). *High-Technology Applications of Organic Colorants*, Plenum press: New York.
[3] Gregory, P. (1990). *Dyes and Pigments*, *13*, 251.
[4] Muthyals, R. (1997). *Chemisty and Applications of Leuco Dyes*, Plenum press: New York.
[5] Chatterjee, S., Davis, P. D., Gottshalk, P., Kurz, M. E., Sauerwein, B., Yand, X., & Schuster, G. B. (1990). *J. Am. Chem. Soc*., *112*, 6329.
[6] Son, Y. A. & Kim, S. H. (2007). *Dyes and Pigments*, *72*, 403.