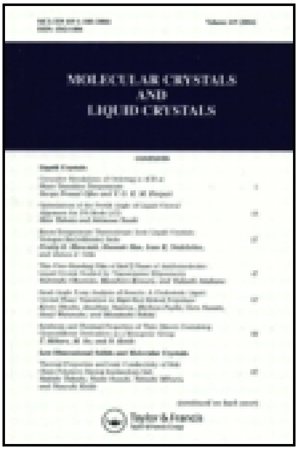


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

New Liquid-Crystal Polymer with 1,3-Oxathiane Ring

Yuichiro Haramoto [a] & Hiroyoshi Kamogawa [a]
[a] Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu, 400, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Yuichiro Haramoto & Hiroyoshi Kamogawa (1994): New Liquid-Crystal Polymer with 1,3-Oxathiane Ring, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 250:1, 15-19

To link to this article: http://dx.doi.org/10.1080/10587259408028188

Mol. Cryst. Liq. Cryst., 1994, Vol. 250, pp. 15–19
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

New Liquid-Crystal Polymer with 1,3-Oxathiane Ring

YUICHIRO HARAMOTO and HIROYOSHI KAMOGAWA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400, Japan

(Received June 11, 1993)

New polymerizable liquid crystal materials: 4-(5-alkyl-1,3-oxathian-2-yl)-phenylacrylate (**9**) and 4-(5-alkyl-1,3-oxathian-2-yl)-phenyl methacrylates (**9'**) have been synthesized and converted into respective polymers. Polymer **9'** having the 1,3-oxathiane ring in their principal structure show a shlieren texture of nematic liquid crystal phase (G 81 N 140 I), therefore this is a new type of liquid crystal polymer having 1,3-oxathiane ring in their principal structure.

Keywords: 1,3-oxathiane, liquid-crystal polymer

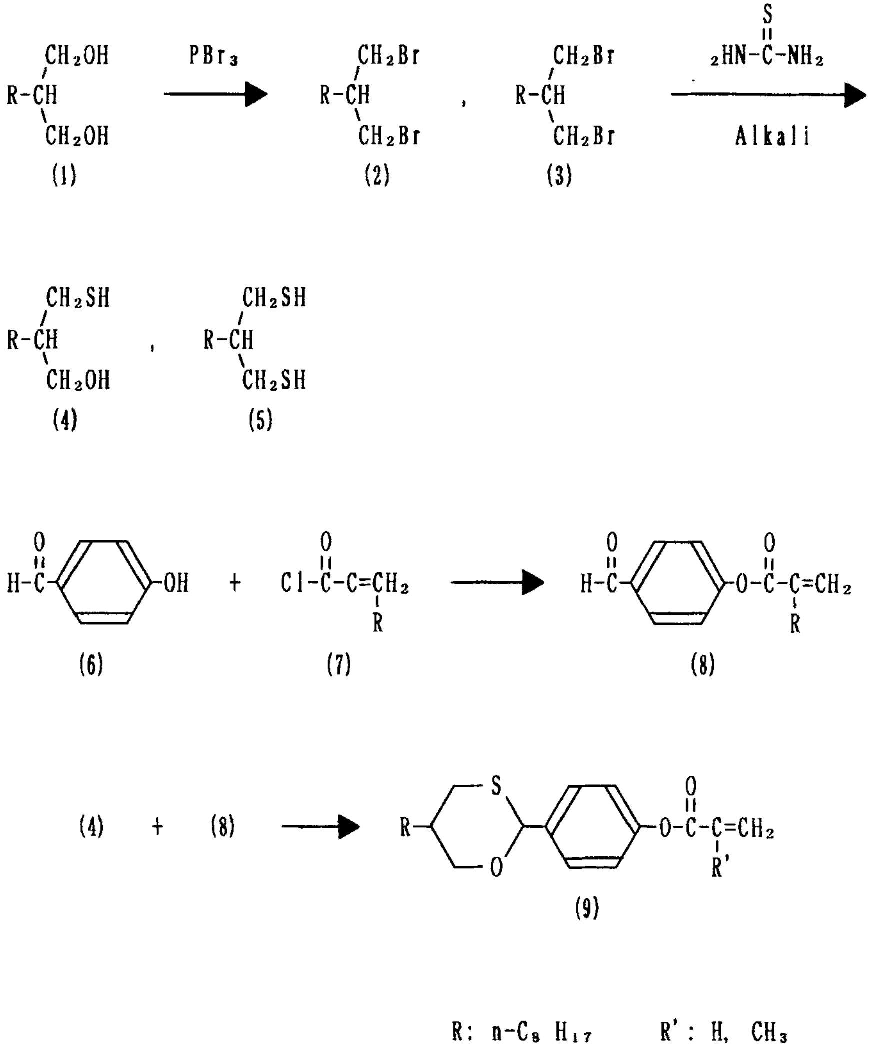
INTRODUCTION

In the last fifteen years, 2,5-disubstituted-1,3-dithianes, 1,3-oxathianes, and 1,3-dioxanes have been reported as new types of liquid crystal materials.[1-25] From several years ago, liquid crystal polymers have been noticed as functional materials and various liquid crystal polymers were synthesized. However, oxathiane type liquid crystal polymers are not reported. Accordingly, we have synthesized 1,3-oxathiane type new liquid crystal monomers with polymerizable double bond and the corresponding 1,3-dioxane type monomers and polymerized them. In this communication we report the syntheses and mesomorphic behaviors of new 1,3-oxathiane type monomers and polymers.

RESULTS AND DISCUSSION

4-(5-Alkyl-1,3-oxathian-2-yl)phenyl acrylate and 4-(5-alkyl-1,3-oxathian-2-yl)phenyl methacrylate were synthesized by the following route.

Though, in the bromination step both mono- and di-bromide were produced, separation of them did not carried out in this step. So that, in the syntheses of mercaptane, a mixture of compounds (**2**) and (**3**) was used. Compounds (**4**) was separated by the column chromatography, it eluted with ether solvent (Wakogel C-300). In the syntheses of monomers (**9**), SH group may react with double bond. But in this case, the main reaction was formation of the 1,3-oxathiane ring, and

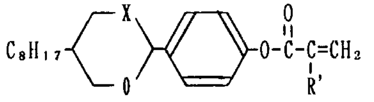


SCHEME 1

(**9**) was obtained in 30–40% yields. These yields are comparable to those for general 1,3-oxathiane syntheses. Therefore, in this case we did not need to use another reaction pass way. Synthesized monomers (**9**), (**9′**) contain trans and cis isomers, respectively. Therefore, these monomers were purified by the column chromatography and subsequent several time recrystallizations (hexane:ether = 5:1). In the ^{1}H-NMR data of monomers (**9**) and (**9′**), the C-2 proton signals for the 1,3-oxathiane ring for the trans and cis isomers appeared at δ = 5.75, 5.80, respectively. Therefore, the removal of cis isomer by purification can be checked by the disappearance of the cis isomer's peak.

TABLE I

Transition temperatures for monomers **9**, **9′**, **10**, and **10′** and the corresponding polymers



(9, 9', 10, 10')

Compound	X	R'	Phase transition temperatures (°C)[a] (Monomer)	(Polymer)	Mn	Mw[b]
9	S	H	$\begin{tikzcd} C \arrow[rr, "45"] & & I \arrow[dl, shift left, "41"] \\ & N \arrow[ul, "37"] \arrow[ur, shift left] & \end{tikzcd}$	$G \xrightarrow{38} C \xrightarrow{154} I$	7900	18600
9'	S	CH_3	$C \underset{36}{\overset{77}{\rightleftarrows}} I$	$G \xrightarrow{81} N \xrightarrow{140} I$	21900	96000
10	O	H	$\begin{tikzcd} C \arrow[rr, "53"] & & I \arrow[dl, shift left, "48"] \\ & SmA \arrow[ul, "32"] \arrow[ur, shift left] & \end{tikzcd}$	$G \xrightarrow{35} N \xrightarrow{140} I$	8200	16900
10'	O	CH_3	$\begin{tikzcd} C \arrow[rr, "70"] & & I \arrow[dl, shift left, "65"] \\ & SmB \arrow[ul, "46"] \arrow[ur, shift left] & \end{tikzcd}$	$G \xrightarrow{79} N \xrightarrow{164} I$	33000	85000

a) : C: Crystal, N: Nematic, Sm: Smectic, I: Isotropic, G: Glass,
I: Isotropic.

b) : Mn: number average molecular weight.
Mw: weight average molecular weight.

Side chain polymers were prepared by the free radical polymerization of monomers (**9**, **9'**), respectively. The number and weight average molecular weights (Mn and Mw) were determined using a Toso high speed GPC system HLC 8020. These values indicated the production of polymers (Table I).

Measurement of transition temperatures and assignment of the mesophases were carried out by means of a micro melting point apparatus equipped with polarizers and a Mettler DSC 20 system. Phase identification was made by comparing the observed textures with those in the literature.[26,27] Phase transition temperatures for compounds (**9**) and (**9'**) and the corresponding 1,3-dioxane compounds are given in Table I.

Polymer **9'** having 1,3-oxathiane ring in their principal structure show a schlieren texture of nematic liquid crystal phase. Therefore this is the first liquid crystal polymer with 1,3-oxathiane ring.

Though monomer **9** exhibits nematic liquid crystal phase the corresponding **9'** did not exhibit any liquid crystal phases. The difference between **9** and **9'** lies in R'. As monomer **9'** has a methyl group as a branch, the molecular width of **9'** must be wider than that of monomer **9**. This seems to be a main reason for the result written above.

Though monomers **10** and **10'** exhibited smectic phases, the corresponding **9** and **9'** did not exhibit any smectic phases. For appearance of a smectic phase, interaction among long alkyl chains must be necessary. Therefore the molecular width near a long alkyl chain is important. In monomers **9** and **9'**, 1,3-oxathiane ring exists near a long alkyl chain. As the 1,3-oxathiane ring having a larger sulfur atom causes wider molecular width, long alkyl chains can not interact sufficiently. This seems to be the reason why in **9** and **9'** a smectic phase did not appear.

Though polymer **9'** exhibited a nematic liquid crystal phase, polymer **9** did not exhibit any liquid crystal phases. This result is against that for the corresponding monomer. It is difficult to explain this result. But we can suppose that in polymer **9'** one group of mesogens which belong to one polymer chain can interact with other group of mesogens which belong to other polymer chain. And polymer **9'** can possess many spots like this.

The transition temperature of liquid crystal phase to isotropic for polymer **9'** is lower than the corresponding **10'**. This result is consistent with the results in monomer. That is, in monomer the transition temperatures of liquid crystal phase to isotropic for 1,3-oxathiane compounds are lower than those of the corresponding 1,3-dioxanes.

Acknowledgment

The authors wish to express their gratitude to Dr. Ujiie for extensive support for the measurement of liquid crystal properties.

References

1. D. Demus and H. Zaschke, (to V. E. W. Kombinat Microelectronik), Japan Pat. Appl. No. 54-160916, Dec. (1979).

2. H. Kamogawa, T. Hirose and M. Nanasawa, *Bull. Chem. Soc. Jpn.*, **56**, 3517 (1983).
3. Y. Haramoto and H. Kamogawa, *J. Chem. Soc., Chem. Commun.*, **75**, (1983).
4. Y. Haramoto, A. Nobe and H. Kamogawa, *Bull Chem. Soc. Jpn.*, **57**, 1966 (1984).
5. Y. Haramoto, K. Akazawa and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **57**, 3173 (1984).
6. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 477 (1985).
7. Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **79**, (1985).
8. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **58**, 1821 (1985).
9. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 101, (1985).
10. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **131**, 201, (1985).
11. Y. Haramoto, M. Sano and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 1337 (1986).
12. Y. Haramoto, Y. Tomita and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **59**, 3877 (1986).
13. Y. Haramoto and H. Kamogawa, *Chem. Lett.*, **755**, (1987).
14. Y. Haramoto and H. Kamogawa, *Rev. In Inorg. Chem.*, **9**, 65 (1987).
15. Y. Haramoto, K. Kawashima and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **61**, 431 (1988).
16. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst. Lett.*, **5**, 117 (1988).
17. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **173**, 89 (1989).
18. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **63**, 156 (1990).
19. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **182B**, 195 (1990).
20. Y. Haramoto and H. Kamogawa, *Bull. Chem. Soc. Jpn.*, **63**, 3063 (1990).
21. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **201**, 161 (1991).
22. Y. Haramoto, T. Hinata and H. Kamogawa, *Liq. Cryst.*, **11**, 335, (1992).
23. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **226**, 115 (1993).
24. Y. Haramoto, M. Meki and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, **231**, 175 (1993).
25. Y. Haramoto and H. Kamogawa, *Mol. Cryst. Liq. Cryst.*, in press.
26. D. Demus and L. Richter, "Textures of Liquid Crystals," Verlag Chemie, Weinheim, New York (1978).
27. G. W. Gray and J. W. Goodby, "Smectic Liquid Crystals Textures and Structures," Heyden & Son Inc., Philadelphia (1984).