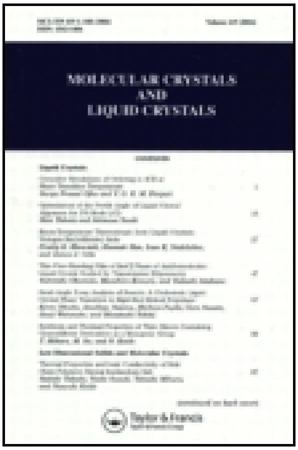


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Viscosity, Thermal and Ultraviolet Stability of Liquid Crystalline Isothiocyanato Compounds and Their Mixtures

Z. Stolarz [a] , R. Dąbrowski [a] , K. Kenig [a] , J. Parka [a] , Z. Raszewski [a] , J. Kędzierski [a] & J. Zmija [a]
[a] Military Technical Academy, 01-489, Warsaw, Poland

Version of record first published: 22 Sep 2006.

To cite this article: Z. Stolarz , R. Dąbrowski , K. Kenig , J. Parka , Z. Raszewski , J. Kędzierski & J. Zmija (1990): Viscosity, Thermal and Ultraviolet Stability of Liquid Crystalline Isothiocyanato Compounds and Their Mixtures, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 13-18

To link to this article: http://dx.doi.org/10.1080/00268949008031796

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 13–18
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

VISCOSITY,THERMAL AND ULTRAVIOLET STABILITY OF LIQUID CRYSTALLINE ISOTHIOCYANATO COMPOUNDS AND THEIR MIXTURES

ZOFIA STOLARZ, ROMAN DĄBROWSKI, KRYSTYNA KENIG,
JANUSZ PARKA, ZBIGNIEW RASZEWSKI, JERZY KĘDZIERSKI,
JÓZEF ŻMIJA

Military Technical Academy, 01-489 Warsaw, Poland

Abstract The thermal stability of 4-(isothiocyanatophenyl)-1-(4-trans-alkyl)cyclohexane (CHBT) purified by treating with different sorbents and doped with polar and non-polar compounds was tested.The doping effect of various compounds on the bulk viscosity, optical and dielectric anisotropy and clearing point of CHBT mixtures was studied.The most advantageous components for obtaining these mixtures have been chosen.

INTRODUCTION

Among polar compounds cyano derivatives have gained practical importance. The isothiocyanates did not attract greater interest until we found that 4-(4-isothiocyanatophenyl)-1-(4-trans-alkyl)cyclohexanes (CHBT)[1] are nematics exhibiting better some physico-chemical properties than 4-(4-cyanophenyl)-1-(4-trans-alkyl)cyclohexanes (PCH).[2] This manifestes istself especially in the lower viscosity and lower elastic constant ratio k_{33}/k_{11}.[3]
The aim of the present work was to test the chemical and thermal stability of the components of CHBT mixtures for obtaining mixtures exhibiting low viscosity and high electric resistance.

THERMAL AND ULTRAVIOLET STABILITY

The resistance of the 6CHBT d=0.7 cm liquid crystal layer was measured at 25°C with the use of 1V direct current by means of a B7-30 electrometr before and after treatment for 1 h at 150°C in a sealed ampoule. The 6CHBT compound was selected for the tests because it is: (a) liquid at room temperature, what facilitates the measurement of resistance, (b) a compound most difficult to purify and hence the obtained results are least advantageous and therefore most reliable. 6CHBT was tested as obtained from the synthesis according to the procedure described in ref.(1), and additionally purified by filtration through an alumina layer (MN-Aluminium oxide neutral, through Silicagel 60,(Merck), active carbon (obtained from high purity organic polymers), or shaking with the sorbents and filtration were applied; 0.5 g of sorbent was used per 5 g of liquid crystal. The obtained results are given in Table I.

The treatment with the sorbents leads to the increase of the specific resistivity of the compound by more than one order of magnitude and after the thermal test it is characterized by a resistance higher than or equal to $5 \cdot 10^{10}$ ohm cm and therefore meets the exacting requirements of Japanese companies. The compound treated simultaneously with the three above mentioned adsorbents and subsequently heated at 150°C assumes an only slightly yellowish colour, whereas the untreated compound turnes yellowish-brown.

The ultraviolet stability test consisted in irradiation with an UV Enuta VP-60 lamp of 5000 lx for 50 h at room temperature. Visually 6CHBT remains unchanged also after irradiation of the sample not treated with the

TABLE I Influence of purification methods on the thermal stability of 4-(4-isothiocyanato)-1-(4-trans-hexylcyclohexane (6CHBT) and its mixtures

Purification procedure	Resistivity (ohm cm) at 25°C	
	before heating	after heating
I. Distillation and crystallization	$1\cdot10^{11}$	$2.5\cdot10^{9}$
II. After filtration through the layer		
a- silicagel	$1.8\cdot10^{11}$	$4.5\cdot10^{9}$
b- active carbon	$1.2\cdot10^{11}$	$4.0\cdot10^{9}$
c- Al_2O_3	$2.1\cdot10^{11}$	$6.5\cdot10^{9}$
III. 24 h contact with the suspension		
a- Al_2O_3	$3.3\cdot10^{11}$	$1.4\cdot10^{10}$
b- Al_2O_3, silicagel and active carbon	$1.6\cdot10^{12}$	$5\cdot10^{10}$
IV. Mixture 70% 6CHBT and 30 wt% $C_5H_{11}C_6H_{10}COOC_6H_{11}OCH_3$		
a- without treatment	$1.3\cdot10^{11}$	$1\cdot10^{10}$
b- filtration through Al_2O_3	$3.0\cdot10^{11}$	
c- silicagel, active carbon and Al_2O_3 after 24 h treatment	$4\cdot10^{12}$	$1.2\cdot10^{11}$
V. Mixture 70 wt% CHBT and 30 wt% $C_4H_9C_6H_{10}C_6H_4CH_2CH_2C_6H_{10}C_6H_4NCS$		
a- without treatment	$4\cdot10^{11}$	
b- silicagel, active carbon and Al_2O_3 after 24 h treatment	$3\cdot10^{12}$	$6\cdot10^{10}$
VI. Mixture 70 wt% CHBT and 30 wt% $C_2H_5C_6H_4COOC_6H_4CN$		
a- without treatment	$1.4\cdot10^{10}$	

sorbent, and its resistance decreases from 10^{11} to $5{\cdot}10^{10}$ ohm·cm only.

Addition to 6CHBT of a low-polar compound, such as 4-methoxyphenyl 4-trans-pentylcyclohexanecarboxylate, yields mixtures with raised resistance; on the other hand addition of polar compounds such as 4-cyanophenyl benzoate gives a mixture of lower resistivity. Addition of other isothiocyanates does not affect the resistance of 6CHBT after thermal treatment.

The decrease of resistance of mixtures of cyano and isothiocyano compounds is on the one hand due to the increase of their polarity caused by the dissociation of the cyano compound dimers, and on the other it cannot be excluded that the compounds react with each other or that the impurities contained in them interact. After heating 6CHBT with cyano compounds (3OCB, 3PCH, 5-alkyl-2-cyanophenylpyrimidine) the presence of small amounts of new compounds was detected by tlc which are not formed when 6CHBT is heated under the same conditions alone or with water.

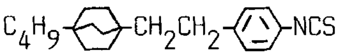
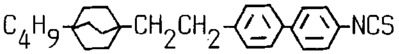
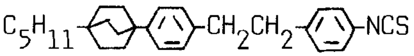
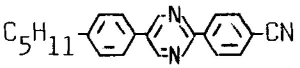
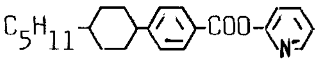
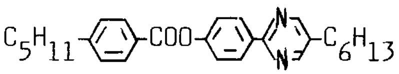
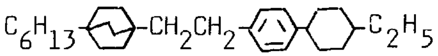
COMPONENTS FOR PREPARING THE MIXTURE

The ternary mixture A composed of the three CHBT components

$C_3H_7C_6H_{10}C_6H_4NCS$	37.6 wt%
$C_6H_{13}C_6H_{10}C_6H_4NCS$	44.9 wt%
$C_8H_{17}C_6H_{10}C_6H_4NCS$	17.5 wt%

was selected as the base mixture. Various compounds in quntities of 10 or 30% were added to mixture A and the viscosity, optical and dielectric anisotropy and the clearing point were measured. The results are summarized in

TABLE II Influence of compounds B (10 wt%) on viscosity, birefrigence (Δn), dielectric anisotropy and clearing point (T_{N-I}) of the base mixture A

No	Mixture	20°C (mPa s)	Δn 20°C	$\Delta\varepsilon$ 20°C	T_{N-I} (°C)	Solubility
	A	10.9	0.17	7.9	41.5	
	A and B					
1.	$C_4H_9C_6H_4C_6H_4NCS$	11.2	0.18	8.1	36.5	++
2.	$C_4H_9C_6H_4C_6H_4CH_2CH_2C_6H_4NCS$	11.1	0.18	8.0	49.0	++
3.	$C_4H_9C_6H_{10}C_6H_4CH_2CH_2C_6H_4NCS$	11.6	0.18	8.4	50.0	-
4.	$C_5H_{11}C_6H_{10}CH_2CH_2C_6H_4C_6H_4NCS$	10.8	0.19	8.6	60.0	-
5.	$C_4H_9C_6H_{10}C_6H_4CH_2CH_2C_6H_4NCS$	11.6	0.18	8.3	48.5	+
6.	$C_4H_9C_6H_{10}C_6H_4CH_2CH_2C_6H_{10}C_6H_4$- -NCS	11.6	0.18	8.9	65.0	++
7.		11.8	0.17	8.8	47.5	++
8.		11.5	0.19	8.3	66.0	-
9.		11.6	0.18	9.5	52.5	-
10.	$C_2H_5C_6H_4COOC_6H_4CN$	12.3	0.16	9.4	34.5	+
11.	$C_5H_{11}-C_6H_4C_6H_4C_6H_4CN$	12.7	0.19	10.0	60.0	-
12.		12.9	0.18	10.7	59.0	-
13.	$C_5H_{11}C_6H_{10}COOC_6H_4OCH_3$	11.4	0.16	6.5	43.5	++
14.		12.6	0.17	7.8	50.5	+
15.		13.8	0.18	8.1	52.5	++
16.		15.0	0.17	7.6	50.0	+
17.		12.3	0.16	5.5	52.5	++

- pure, + well, ++ very well

Table II. Among the polycyclic compounds, the ethane derivatives, (6,7) and (17) in Table II, exhibit the best solubility in mixture A and are the most suitable components for obtaining mixtures with high clearing points also because they increase the least the viscosity of mixture A. Compound (6) in Table II deserves particular attention, as when added to mixture A in an amount of 30% it gives a mixture whose clearing point is above 97°C and $\eta_{20^{\circ}}$=15.0 mPa•s.

Trinuclear cyano compounds show low solubility(less than 10 wt%) and strongly increase the viscosity.

The preffered components for obtaining mixtures with low optical anisotropy Δn are non-polar compounds such as (13) or (17). They exhibit very good solubility, are not liable to induction of smectic phases and give mixtures with Δn in the range of 0.16 to 0.1 (see Table III).

TABLE III Change of the properties of mixture A with concentration of the compound 13 at 20°C

(13) wt%	0	10	30	50	70
V_{10} (volt)	1.6	1.6	1.75	2.0	2.5
Δn	0.173	0.161	0.141	0.125	0.107
η (mPa·s)	10.9	11.4	12.0		
$T_{N\rightarrow I}$	41.5	43.5	46.5	47	57

REFERENCES

1. R. Dąbrowski, J. Dziaduszek and T. Szczuciński, Mol.Cryst.Liq.Cryst., 124, 241 (1985).
2. R. Eindenschink, D. Erdmann, J. Krause and L. Pohl, Angew.Chem., 89, 103 (1977).
3. M. Schadt, R. Buchecker, A. Villiger, F. Leenhouts and J. Fromm, IEEE Trans.Electron Dev., 33,1187(1986).