(4)

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 28

Thermotropic Liquid Crystals with Nitrocinnamylidene Unit

by

J. L. Hong and S. J. Huang

Liquid Crystalline Polymer Research Center
University of Connecticut
Storrs, CT 06268

Prepared for Presentation

at

The 1988 Fall Meeting of
The Materials Research Society
Boston, MA, Nov. 28 - Dec. 2, 1988

October 14, 1988

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: Unclassified	1b RESTRICTIVE MARKINGS: None
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION/AVAILABILITY OF REPORT: Approved for Public Release, Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): Technical Report No. 28	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: University of Connecticut; 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION: Office of Naval Research
6c ADDRESS (City, State, and ZIP Code): Storrs, CT 06268	7b ADDRESS (City, State, and ZIP Code): 800 North Quincy Avenue Arlington, VA 22217
8a NAME OF FUNDING/SPONSORING ORGANIZATION; 8b OFFICE SYMBOL (If applicable): ONR/DARPA	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: N00014-86-K-0772
8c ADDRESS (City, State, and ZIP Code): 800 North Quincy Avenue Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO; PROJECT NO; TASK NO; WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)
"Thermotropic Liquid Crystals with Nitrocinnamylidene Unit" (Unclassified)

12 PERSONAL AUTHOR(S)
J. L. Hong and S. J. Huang

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim Technical	FROM _____ TO 10/13/88	1988/10/13	15

16 SUPPLEMENTARY NOTATION
Prepared for presentation at the 1988 Fall Meeting of the Materials Research Society, Boston, MA, November 28th - December 2nd, 1988 (LCPRC Publication No. LCPRC88-19)

17 COSATI CODES		
FIELD	GROUP	SUB GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
Liquid Crystalline Polymers
non-linear optical properties

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Highly polarizable organic molecules in an ordered morphology are sought after for their non-linear optical properties. Among the polymeric systems that have received a lot of attention are poly(diacetylenes) and poly(methacrylates) with liquid crystalline side chains. Although many poly(diacetylenes) have been studied there is none with the side group in strong interaction with the conjugated polymer chains. We reason that poly(diacetylenes) with strongly polarizable side chains attached directly to the conjugated chains should have very interesting optical properties. Furthermore if the monomers are liquid crystalline poly(diacetylenes) with very high order should be obtainable via polymerization in crystalline and/or liquid crystalline states. For ferroelectrical optical displays, on the other hand, polarizable chiral smectic C liquid crystals are desirable. Our approach to these areas started with the design and synthesis of a polarizable mesogen 3-aryl propylenylidene anilines. (A(u))

(Cont. on reverse)

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION: Unclassified
22a NAME OF RESPONSIBLE INDIVIDUAL: Dr. Kenneth J. Wynne	22b TELEPHONE (Include Area Code): (202) 696-4410; 22c OFFICE SYMBOL: ONR

DD FORM 1473, 84 MAR 83 APR edition may be used until exhausted. All other editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE
Unclassified

Thermotropic Liquid Crystals with Nitrocinnamylidene Unit

J. L. Hong and S. J. Huang
Institute of Materials Science
University of Connecticut
Storrs, CT 06268

Introduction

Low molar mass liquid crystals of schiff base (-CH=N-) type have been long time recognized and studied[1]. However, liquid crystals containing conjugated Schiff base (-(CH=CH)n-CH=N-) are still not explored extensively. Back in 1929, D. Vorlander first introduced molecules of conjugated Schiff base (-(CH=CH)n-CH=N, n= 1 and 2) type[2], which were synthesized by reacting either 5-phenyl-1-pentadiene or 7-phenyl-1-heptatriene with different p-substituted anilines. The resulting molecules are either non-liquid crystals or monotropic materials. A plausible reason may be due to the absence of suitable tails at both ends. In order to further explore this topic, we report here the first example of liquid crystals containing 4-nitrocinnamylidene (4-O_2N-Ph-CH=CH-CH=N-) unit.

Monomeric liquid crystas (MLCs), can be readily functionalized and coupled to form oligomers of liquid crystals. Also, flexible-center dimer, dimeric liquid crystals (DCLs), can be prepared by coupling two mesogenic cores with aliphatic spacer chain[3]. It was previously argued that the central flexible spacer has profound effect on the final mesomorphic properties of DCLs and can distinguish them from MCLs. It is therefore interesting to study the effect of spacer on DCLs and compare the difference between DCLs and MCLs. In this study, MCLs and DCLs were synthesized and carefully examined.

Also, DCLs with four different spacers were prepared in order to investigate the function of spacers.

Results and discussion:

Syntheses of monomers ((1) and (4)) and dimers ((7), (10), (14), (15) and (16)) are depicted in Scheme 1 and 2, details are given in experimentals section. Figure 1 showed DSC thermograms of MCLs ((1) and (4)) and DCLs ((7) and (10)). A summary result was given in Table 1.

Cinnamylidene-P-octyloxyaniline was synthesized primarily by reacting cinnamaldehyde with p-octyloxyaniline and exhibits no mesomorphic property. Apparently, terminal nitro group is essential for the construction of liquid crystal. As seen from Table 1, DCLs (7) and (10) possess higher melting and cleaning points than MCLs (1) and (4). The density of nitro groups in either MCLs or DCLs are approximately the same. Whatever, both ends of DCLs are fixed due to the intermolecular interaction of terminal mesogenic units; this contributes to the higher transitions of DCLs than MCLs'. Also, monomer (4) has the higher enthalpy change of melting process than monomer(1) (29.2 compared with 26.78 Cal/g). Simply depicted from chemical structure, monomer (4) with terminal -OH has extra intermolecular hydrogen bonding compared to monomer (1). This hydrogen bonding may be the cause of higher enthalpy and also Tm of monomer (4) to (1). X-ray diffraction may be used to further verify this point.

Flexible spacers play important role of the final properties of DCLs'. Previously, Griffin's study on diester dimers[4] showed that the flexibility of the central spacers is deterious to mesogenic behavior because of the large amount of nonlinear geometies the molecule can adopt if the center is

flexible. Dimer (10), with central triethylene glycol as spacer, will interfere the packing of the terminal nitrocinnamylidene group to a higher degree as compared with dimer (7), where less flexible octanedioxy group was used as central spacer. This effect was revealed by the apparently lower Tm and Tc of dimer (10) than dimer (7). In addition, the solubilities of dimer (7) and (10) differ dramatically as shown in Table 2. The deterious effect of triethylene glycol may well enhance the solubility of the corrsponding dimer (10).

Another interesting point will be the effect of the central spacers' length on the products' transition temperatures. As seen from Table 1, compound (15), with tetraethylene glycol as central spacer, possesses lower T_m and T_c as compared with those of compound (14), which has shorter triethylene glycol spacer. Increasing central spacer's length by one ethylene glycol unit results in material with 35 - 37°C lowered thermal transition temperatures. Whatever, further attempt to disclosethe relationship between central spacers' length and mesomorphism tured out to be ambiguous. Compound (16) with its longest spacer, pentaethylene glycol, possesses a very narrow mesogenic range. This, of course, may be due to the presence of large quantities of impurities. Further purification is needed for compound (16),

Recently, microscopy and X-ray were used to identify the the textures of monomers and dimers, which all these monomers and dimers turned to be nematic above their melting points. In order to evaluate the effect of tails in monomeric system, two other monomers with longer tails (O_2N-Ph-CH=CH-CH=N-Ph-O-$(CH_2)_n$-CH_3; n = 11, (17); n = 15, (18)) were synthesized. Compound (17) and (18) appears to be smectic above their melting points (for (17), T_m = 64°C and Tc = 118°C; (18), T_m = 94°C and T_c = 144°C according to microscopy).

Apparently, tails with longer length will enhance the packing in the jkliquid crystalline state of the corresponding substrates. The low melting point and broad liquid crystalline state of compound (17) make it interesting to further explore this system.

Table 1. Summary data from DSC thermograms

	Tm (°C) (H, Cal/g)	Tc (°C) (H, Cal/g)
(1)	108	135
	(26.78)	(0.27)
(4)	124	156
	(29.20)	(0.47)
(7)	192	238(Dec.)
	(27.25)	---
(14)	151	181
	(26.52)	---
(15)	114	146
	---	---
(16)	114 ---> 117 (?)	

Table 2. Solubility test of MCLs (7) and (10) at room temperature.

	NMP	DMSO	Acetone	Chloroform	CF_3CO_2H
(7)	N	N	N	N	S
(10)	S	S	N	S	S

N : not soluble S : soluble

Experimental:

Purification and Handlings of Laboratory Materials

4-Octyloxyanilinine (99%; Aldrich) and 4-fluronitrobenzene(99%; Aldrich) were vacuum distilled and stored in refrigerator. THF was distilled from CaH_2 and stored under Argon. 4-Nitrocinnamylidene (98%; Aldrich), 4-nitrophenol (99%: Aldrich), Hydrazine hydrate (hydrazine content 55%; Aldrich) and palladium on activated carbon (palladium content 5%; Aldrich) were used without further purification.

Synthesis

(4-Nitrocinnamylidene)-P-aminooctyloxybenzene (1): 4-Nitrocinnamylidene (0.995mmole) and 4-octyloxyaniline (0.995mmole) were heated at reflux for 2 hrs with 20mL of ethanol under argon atmosphere. Reaction vessel was cooled to room temperature. The yellow product was filtered and recrystallized with ethanol (0.220g; 60%). IR spectrum (KBr pellet); $cm^{-}1$: 1620, 1600, 1515. ^1H-NMR ($CDCl_3$); δ: 7.3-8.4(m, aromatic H's in -Ph-NO_2 and CH's in -CH=N-, 5), 6.6-7.3(m, aromatic H's in -Ph-O- and CH's in -CH=CH-, 6), 0.6-2.2(m,-$(CH_2)_6$-CH_3. 15).

4-(6'-Hydroxyhexyloxy)nitrobenzene (2): Suspension of hexanediol (127mmole) and K_2CO_3 (1.8g) in 160 mL of DMAc was slowly heated to 160°C under argon atmosphere. Fluronitrobenzene (12.7mmole) in 30 mL of DMAc was slowly added through dropping funnel. Stir for 2 hrs before precipitated from distilled water. The crude yellow product was redissolved in chloroform and dried with $MgSO_4$. Final product (m.p. 69-71°C) was obtained by removal of chloroform

followed by recrystallization with toluene. IR spectrum (KBr pellet); cm^{-1}: 3600-3200, 1610, 1600, 1510, 1350, 1260. ^{1}H-NMR ($CDCl_3$); δ: 6.8-7.4(m, aromatic H's ortho to -NO_2, 2), 6.6-7.2(m, aromatic H's meta to -NO_2, 2), 4.5-5.0(b, -OH, 1), 3.8-4.4(t, CH_2's in -Ph-O-CH_2-, 2), 3.4-4.0(t, CH_2's in -CH_2-OH, 2), 1.2-2.3(m, CH_2's in -O-CH_2-$(CH_2)_4$-CH_2-OH, 8).

4-(6'-Hydroxyhexyloxy)aniline (3): 4-(6'-Hydroxyhexyloxy)nitrobenzene (41.8mmole) and palladium on activated carbon (0.4g) were suspended in 100 mL of anhydrous ethanol under argon. Hydrazine hydrate (125.4mmole; 3.5 times) was slowly added through dropping funnel. Reaction vessel was slowly heated to reflux (heating rate 10°C/hr) for overnight. Filter through celite and ceramic filtration funnel before precipitating with distilled water. The crude product was recrystallized with toluene under argon (m.p. ; 80%). IR spectrum (KBr pellet); cm^{-1}: 3100-3450, 1510, 1240. ^{1}H-NMR(DMSO-d6); δ: 6.4(aromatic H's,4), 3.8-4.3(b, -OH and -NH_2, 3), 3.5-3.8(t, CH_2's in -Ph-O-CH_2-, 2), 3.1-3.5(t, CH_2's in -CH_2-OH), 0.7-2.0(b, CH_2's in -CH_2-$(CH_2)_4$-CH_2-, 8).

(4-Nitrocinnamylidene)-p-(6'-hydroxyhexyloxy)aniline (4): Synthesis was followed the procedure as described for monomer (1). Final product was recrystallized with toluene. IR spectrum (KBr pellet); cm^{-1}: 3160-3600, 1610, 1600, 1575, 1515, 1505, 1340, 1250. ^{1}H-NMR ($CDCl_3$); δ: 7.4-8.4(m, aromatic H's in -Ph-NO_2 and CH's in -CH=N-,5), 6.6-7.4(m, aromatic H's in =N-Ph-O- and CH's in -CH=CH-, 6), 3.7-4.2(t, CH_2'S in -Ph-O-CH_2-, 2), 3.5-3.7(t, CH_2's in -CH_2-OH, 2), 1.0-2.1(M, CH_2's in -CH_2-$(CH_2)_4$-CH_2-, 8).

Dinitro compound (5), (8), (9) and (10) and their reduced diamino compounds (6), (11), (12) and (13): Diamino compounds were obtained from the reduction of their dinitro analogues. All of these procedures were described from recent literatural report[4].

Dimer (7), (14), (15) and (16): Dimers were synthesized from the condensation of 4-nitrocinnamaldehyde and corresponding diamino compounds, (6), (11), (12) and (13). General procedure is refluxing two equivalents of 4-nitrocinnamaldehyde with one quivalent of diamino compounds in appropriate solvents for 4 hours. Except in the case of dimer (7), where THF was used as reaction solvent, ethanol was employed as solvent for the syntheses of dimer (14), (15) and (16). Dimer (7) was purified by recrystallized with NMP for three times. Dimer (14), (15) and (16) was recrystallized with ethanol.

REFERENCE

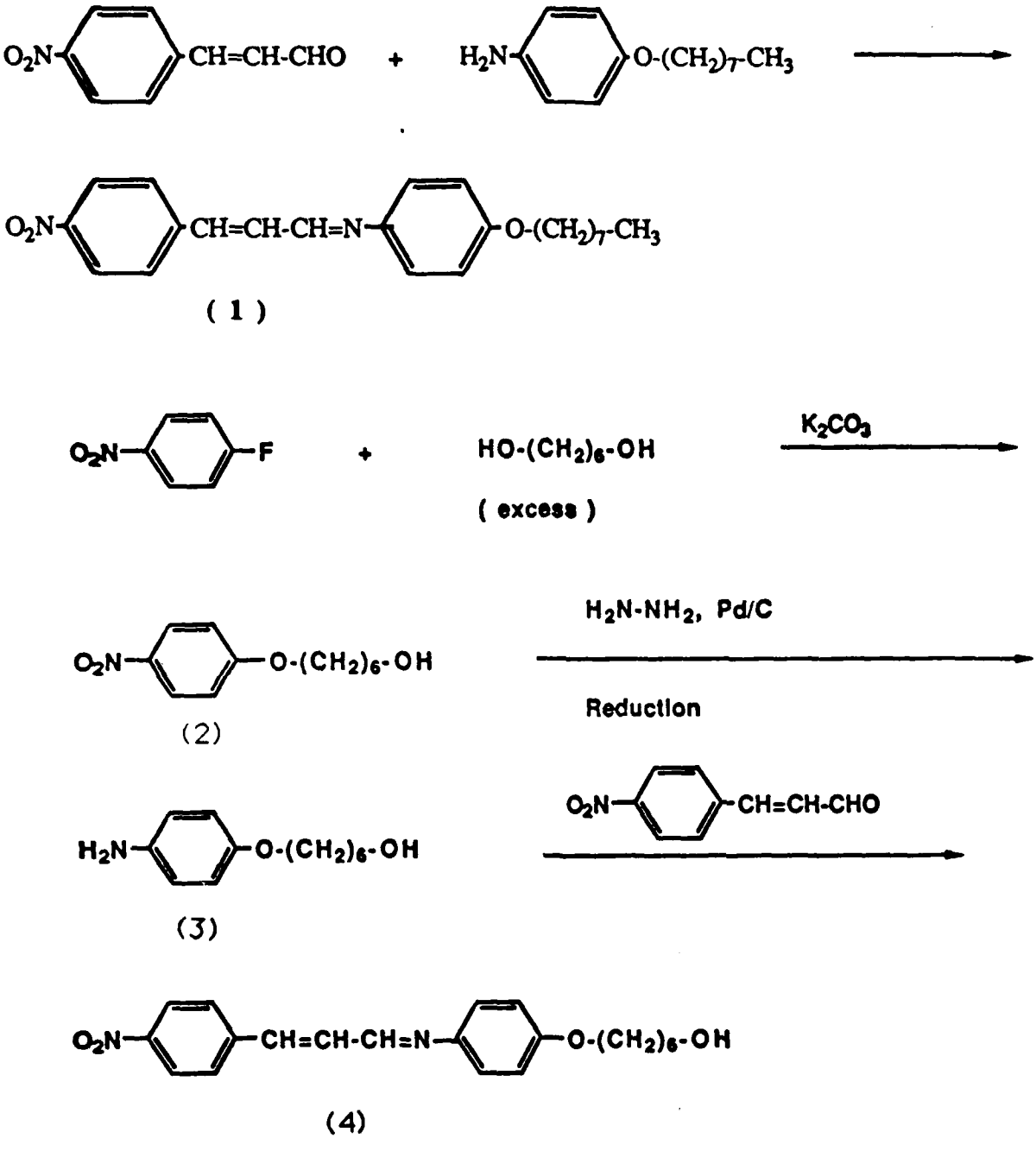
(1) Gray, G. W. in "Advances in Liquid Crystals", 2, pp 1 - 72, Eds. Brown, G. H., Academic Press Inc., New York, N. Y. 10003.

(2) Vorlander, D. and Daehn, E. Ber. 1929, 62B, 541.

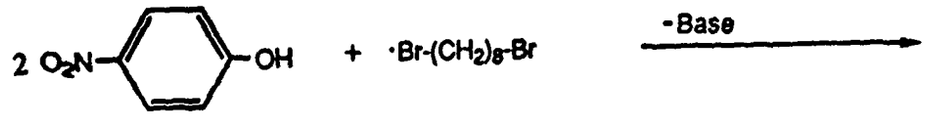
(3) Griffin, A. C. and Samulski, E. T. J. Am. Chem. Soc. 1985, 107, 2975.

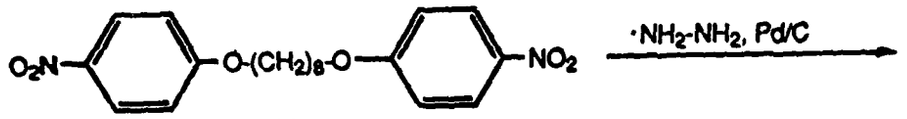
(4) Groffin, A. C. and Britt, T. R. J. Am. Chem. Soc. 1981, 103, 4957.

Scheme 1 Synthesis scheme of monomeric liquid crystals (MCL's).

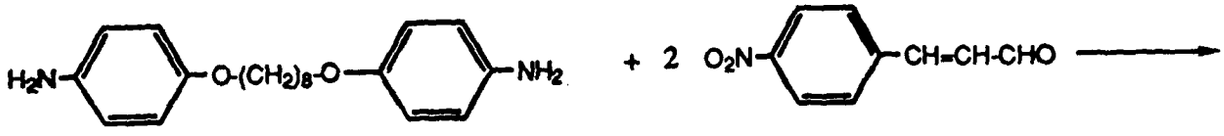


Scheme 2. Synthesis scheme of dimeric liquid crystais (DCL's()

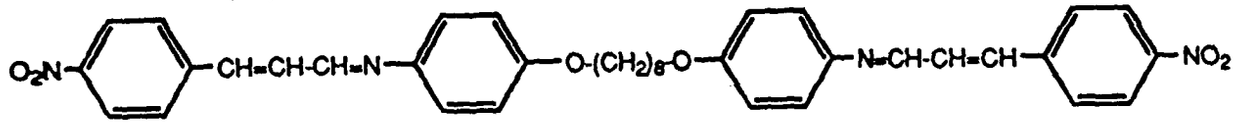




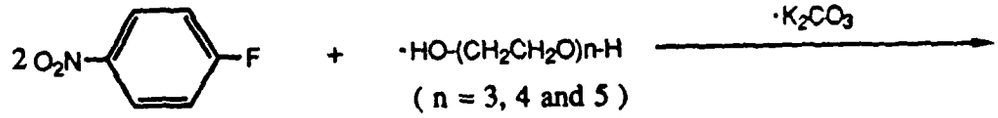
(5)

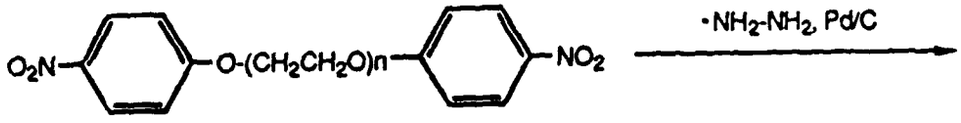


(6)

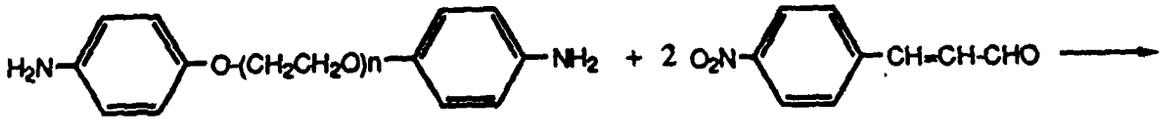


(7)

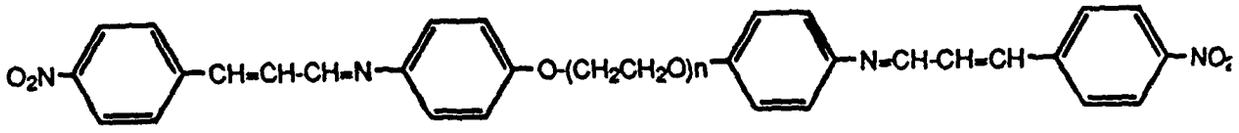




(n = 3, (8); 4, (9); 5, (10))

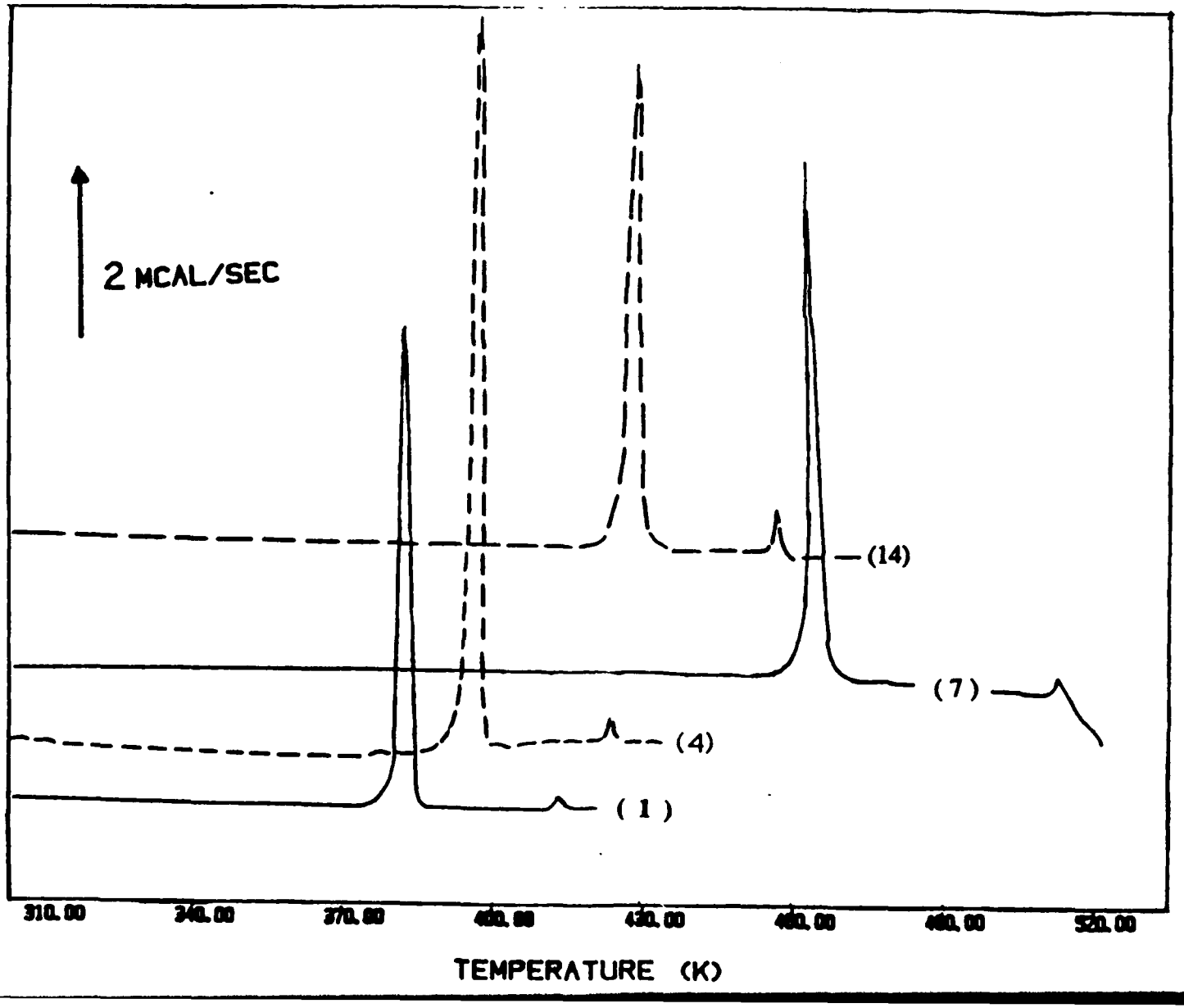


(n = 3, (11); 4, (12); 5, (13))



(n = 3, (14); 4, (15); 5, (16))

Fig. 1 DSC thermograms of compounds (1), (4), (7) and (14).



DL/1113/87/2

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	No. Copies
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2
Dr. Bernard Douda Naval Weapons Support Center Code 50C Crane, Indiana 47522-5050	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code L52 Port Hueneme, California 93401	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1
Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1