

AD-A103 732

LIQUID CRYSTALLINE POLYMERS CONTAINING
HETEROCYCLOALKANE MESOGENS BIPHASI. (U) CASE WESTERN
RESERVE UNIV CLEVELAND OH DEPT OF MACROMOLECULAR
C S HSU ET AL. 1987 TR-8 N00014-86-K-0204 F/G 7/6

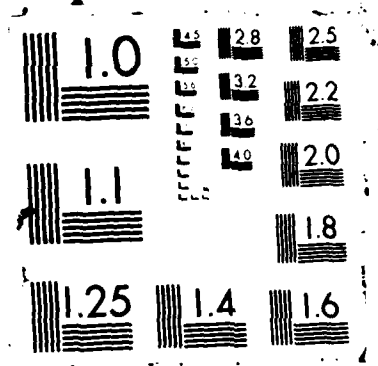
1/1

UNCLASSIFIED

NL



END
9-87
DTIC



AD-A183 732

OFFICE OF NAVAL RESEARCH

Contract N00014-86-K-0284

R&T Code 413c024---01

Technical Report No. 8

DTIC
ELECTE
AUG 05 1987
S D
C/D

Liquid crystalline polymers containing heterocycloalkane mesogens,
Biphasic side-chain liquid crystalline polysiloxanes containing
trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups

By

Chain S. Hsu and Virgil Percec
Department of Macromolecular Science
Case Western Reserve University
Cleveland, OH 44106-2699

Published in

Makromolekulare Chemie, Rapid Communications
Volume 8, 1987

Reproduction in whole or in part is permitted for
any purpose of the United States Government.

This document has been approved for public release and sale;
its distribution is unlimited.

87 8 4 060

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION Unclassified		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION / AVAILABILITY OF REPORT Available for publication Distribution unlimited	
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) Technical Report No. 8		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION Case Western Reserve University	6b. OFFICE SYMBOL (if applicable) 4B56b	7a. NAME OF MONITORING ORGANIZATION ONR	
6c. ADDRESS (City, State, and ZIP Code) 2040 Adelbert Road Cleveland, OH 44106		7b. ADDRESS (City, State, and ZIP Code) Office of Naval Research Arlington, VA 22217	
8a. NAME OF FUNDING / SPONSORING ORGANIZATION ONR	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code) Office of Naval Research 800 N. Quincy Arlington, VA 22217		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. N00014-86	PROJECT NO. K-0284
		TASK NO. 413c024--0	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Liquid Crystalline Polymers Containing Heterocycloalkane Mesogens, Biphasic Side-chain Liquid Crystalline Polysiloxanes Containing trans-5-n-undecanyl-2-(4-cyanophenyl)-1,3-			
12. PERSONAL AUTHOR(S) C. S. Hsu and V. Percec		dioxane side groups	
13a. TYPE OF REPORT Preprint	13b. TIME COVERED FROM _____ TO _____	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION Macromolekulare Chemie, Rapid Communications, Vol. 8, 1987			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
		Side-chain thermotropic liquid crystalline polymers	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) See attached.			
20. DISTRIBUTION / AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

ABSTRACT



Polysiloxanes and copolysiloxanes containing the trans 5-(n-undecanyl)-2-(4-cyanophenyl)-1,3-dioxane side group as mesogen were synthesized. Their phase behavior was studied by differential scanning calorimetry and optical polarization microscopy. Homopolymers containing the mesogen and a copolymer containing 33% of the mesogen showed smectic mesomorphism. The copolymers containing the mesogen showed two well defined T_g and thus present strong evidence for a phase separated morphology.



Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Availability for Special
A-1	



MAKROMOL CHEM
Rapid Commun.
MS No. 178/26

Makromol. Chem., Rapid Commun. **3** (1982)

Liquid crystalline polymers containing heterocycloalkane mesogens, ³
| Biphasic side-chain liquid crystalline polysiloxanes ^a
| containing
trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups

Handwritten notes:
Fig. 1
calculations

Chain S. Hsu,  Virgil Percec*

Department of Macromolecular Science,
Case Western Reserve University,
Cleveland, Ohio 44106, USA

date of receipt: January 5, 1982

^a Part 2: cf. 14)

INTRODUCTION

Systematic investigations on the synthesis and characterization of thermotropic side-chain liquid crystalline polymers (LCP) became possible only after Finkelmann and Ringsdorf (1, 2) proposed that a flexible spacer has to be inserted between the main chain and the mesogens to decouple the motions of the polymer main chain and of the side groups in the liquid state. ^{-crystalline/} 1

Subsequent experiments performed by Ringsdorf et al revealed that parts of the spacer take part in the anisotropic orientation of the mesogens (3), and that for spacers containing up to six methylene units, no complete decoupling exists, indicating a dynamic coupling of the main- and side-chain motions via the spacer (4).

Therefore, the most accurate picture of a side-chain LCP may be regarded as two semi-independent thermodynamic subsystems (i.e., main-chain plasticized by part of the spacer, and mesogenic unit stabilized by part of the spacer) interacting through a part of the flexible spacer (5, 6).

It is interesting to mention that Ringsdorf et al (7) and Finkelmann et al (8) have shown that the miscibility rules developed by Sackmann and Demus (9) do not apply to the nematic phases of some side-chain LCP. According to Krigbaum (10), this may indicate that these polymeric nematic phases have a micro- 2 3

phase structure, with clusters of nematogenic side groups embedded in a continuous phase formed by the polymeric backbones. A system like this would have to present independent relaxation of the main-chain and side-groups, and therefore exhibit two glass transition temperatures. Comb-like polymers exhibiting two glass transition temperatures were already reported by Cowie et al (11, 12).

It is the goal of this communication to present our results on the first examples of side-chain LCP exhibiting two glass transition temperatures. The

particular case described here refers to polysiloxanes and copolysiloxanes containing trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups. These LCP are biphasic systems, and therefore can be regarded as polymers resembling the behavior of phase separated graft copolymers.

EXPERIMENTAL PART

A. Materials

Poly(methylhydrosiloxane)s ($\bar{M}_n=4500-5000$ and $\bar{M}_n=2270$) and poly[(30-35%)-or (15-18%)-hydrogenmethyl-(65-70%)-or (82-85%)-dimethylsiloxane] ($\bar{M}_n=2000-2100$) were obtained from Petrarch Systems Inc., and were used as received. 4-Cyanobenzaldehyde and the other reagents (Aldrich) were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon.

B. Techniques

Experimental techniques used in the characterization of intermediary compounds and of polymers are identical to those previously reported (13).

C. Synthesis of Monomers and Polymers

The syntheses of 5-(11-undecylenyl)-2-(4-cyanophenyl)-1,3-dioxane and of the polysiloxanes are outlined in Scheme 1.

Diethyl-2-(11-undecylenyl)malonate

Cleanly cut Na (3.45g, 0.15 mole) was added in portions to absolute ethanol (150 ml). After the sodium was completely dissolved, diethyl malonate (24 g, 0.15 mole) was added to the reaction mixture and the solution was stirred for 1 hr. 11-Chloro-1-undecene (28.3 g, 0.15 mole) was then added to the reaction mixture. After 16 hrs of stirring at room temperature, the ethanol was evaporated on a rotavapor. The residue was dissolved in ethyl ether, washed several times with water, dried over anhydrous Na_2SO_4 , and ethyl ether was removed on a rotavapor. The

product was distilled at 155-158°C/10-12 mmHg, to yield 39g (83%). 200 MHz $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 1.13 to 2.08 (m, 24 H, $-(\text{CH}_2)_9$ and $\text{CH}_3\text{CH}_2\text{O-}$), 3.30 (t, 1H, $-\text{HC}$ $\begin{matrix} \text{CO-} \\ \diagup \\ \text{CO-} \end{matrix}$), 4.20 (m, 4H, $-\text{CH}_2\text{O}$), 4.94 (m, 2H, $\text{CH}_2=$), 5.80 (m, 1H, $=\text{CH-}$).

2-(11-Undecylenyl)-1,3-propanediol

A solution of diethyl 2-(undecylenyl)malonate (39 g, 0.125 mole) in 50 ml of dried ethyl ether was added dropwise to a suspension of LiAlH_4 (4.75 g, 0.125 mole) in 250 ml of dried ethyl ether. After the addition was complete, the reaction mixture was stirred at 40°C for 20 hrs, cooled to room temperature, and excess LiAlH_4 was reacted with ethyl acetate. The resulting solution was treated with dilute hydrochloric acid and extracted with ethyl ether. The organic phase was washed with 2% aqueous solution of NaHCO_3 , water, and dried over anhydrous Na_2SO_4 . The crude product obtained after the solvent was evaporated was recrystallized from ethyl ether at 0°C to yield 27 g (94%). mp=58-59°C.

200 MHz $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 1.06 to 2.16 (m, 18 H, $-(\text{CH}_2)_9$), 3.30 to 3.81 (m, 5H, $-\text{CH}$ $\begin{matrix} \text{CH}_2\text{O} \\ \diagup \\ \text{CH}_2\text{O} \end{matrix}$), 4.94 (m, 2H, $\text{CH}_2=$), 5.80 (m, 1H, $=\text{CH-}$).

Trans-5-(11-undecylenyl)-2-(4-cyanophenyl)-1,3-dioxane

2-(11-Undecylenyl)-1,3-propanediol (5.0 g, 0.0218 mole), 4-cyanobenzaldehyde (2.86 g, 0.022 mole) and p-toluenesulfonic acid (200 mg) were dissolved in 200 ml of dried benzene. The reaction mixture was refluxed until 0.4 ml of water were collected on a Dean-Stark trap. After cooling to room temperature, the solution was washed with 2% aqueous solution of NaHCO_3 , water, dried over anhydrous Na_2SO_4 , and the solvent was evaporated on a rotavapor. The obtained solid was recrystallized several times from n-hexane at 0°C to yield 5.5 g (73%) of trans compound. mp=65°C (DSC). 200 MHz $^1\text{H-NMR}$ (CDCl_3 , TMS, δ , ppm): 1.11 to 2.16 (m, 19 H, $-(\text{CH}_2)_9$ - CH $\begin{matrix} \text{C} \\ \diagup \\ \text{C} \end{matrix}$), 3.54 and 4.23 (m, 4H, two $-\text{CH}_2\text{O}$), 4.94 (m, 2H,

$\text{CH}_2=$), 5.41 (s, 1H, $\text{Ph}-\underset{\text{O}}{\overset{\text{O}}{\text{C}}}\text{CH}$), 5.80 (m, $=\text{CH}-$), 7.61 (q, 4 aromatic protons).

Synthesis of Polymers and Copolymers

Polysiloxanes and copolysiloxanes were synthesized by hydrosilation of the corresponding olefin with poly(hydrogenmethylsiloxane), poly[(30-35%)-hydrogenmethyl-(65-70%)dimethylsiloxane] and poly[(15-18%)-hydrogenmethyl-(82-85%)dimethylsiloxane] using dicyclopentadienyl platinum (II) chloride (14) as catalyst in toluene. A detailed procedure for complete hydrosilation free of side reactions is given as follows. The olefinic derivative (1.0g, 10 mole% excess versus the Si-H groups present in polysiloxane) was dissolved in 100 ml of sodium dried freshly distilled toluene together with the proper amount of poly(hydrogenmethylsiloxane) or a copolymer containing hydrogenmethylsiloxane and dimethylsiloxane units. The reaction mixture was heated to 110°C under nitrogen, and 100 μl of dicyclopentadienyl platinum (II) chloride catalyst were then injected with a syringe as solution in methylene chloride (1mg/ml). The reaction mixture was refluxed (110°C) under nitrogen until both IR and 200 MHz ^1H -NMR analyses showed that the hydrosilation reaction was complete. The white (powder) or colorless (liquid) polymers were separated by precipitation in methanol, and purified by several reprecipitations from chloroform solutions into methanol. When the resulting polymers were insoluble in hexane (both homopolymers) a final purification was done by precipitation from chloroform solution into hexane. Then the polymers were dried under vacuum at constant weight. We recommend only teflon tape and teflon gaskets to be used in the assemblage of the hydrosilation equipment. Rubber septa can poison the catalyst, while traces of silicon grease or oil can contaminate the resulting polymer and therefore should be completely avoided. Silicon grease can be used only when the final purification of the polymer can be done by successive precipitations into hexane (good solvent for polydimethylsiloxane).

RESULTS AND DISCUSSION

Cowie et al (11, 12) have reported biphasic comb-like polymers based on poly(di-n-alkyl itaconate)s exhibiting two glass transition temperatures. Only the polymers containing diheptyl to diundecyl pendant groups presented phase separation. Polymers containing shorter alkyl groups than heptyl do not undergo phase separation, while those containing longer alkyl groups than undecyl give rise to side chain crystallization. The two glass transition temperatures observed in these polymers indicate that the side chains relax in a cooperative way and independently of the main chain, and therefore undergo a separate glass transition process. These polymers behave like a two-phase system (i.e., by analogy with phase separated block or graft copolymers) with the side chains acting independently of the backbone. Comb-like polymers containing only one alkyl group per structural unit do not exhibit two glass transition temperatures. This might suggest that the side chains have to represent the major part of the macromolecule (more than 60 weight %) in order to give rise to a phase separated system. When side chain crystallization occurs, it prevents the location of the side-chains glass transition temperature. It could be that the miscibility of the side-chains and backbone can also prevent phase separation.

The polysiloxane backbone is a good candidate for the preparation of phase separated systems because of its immiscibility with many other polymers and organic compounds. To prepare LC polysiloxanes containing a high weight percent of side groups with longer spacers than seven methylene units is not a trivial experiment since most of these LCP give rise to side-chain crystallization (15,16).

Recently, we have shown that trans 2,5-disubstituted-1,3-dioxane mesogens can be attached as side-chains to polymer backbones through up to eleven methylenic units without side-chain crystallization to occur (14, 17). This behavior seems to be the result of multiple conformational isomers of the 2,5-disubstituted-1,3-dioxanes.

Scheme 1 illustrates the synthesis of polysiloxanes and copolysiloxanes containing trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane side groups. Heating and cooling differential scanning calorimetric traces of the homopolymers with different molecular weights and of the copolymer no.6 from Table I are presented in Fig. 1, only for the high temperature range. The copolymer no.7 from Table I does not exhibit liquid crystalline properties. As expected, the isotropization temperature for the LCP is both molecular weight and composition dependent. Within this range of molecular weights the glass transition temperature of the homopolymers is not molecular weight dependent. It decreases for the LC copolymer, but not to the expected theoretical value calculated according to Fox equation (18) ($1/T_g = W_1/T_{g1} + W_2/T_{g2}$, where T_g is the value of the copolymer, $T_{g1} = -10^\circ\text{C}$, $W_1 = 0.73$ are the LCP's T_g , and the weight fraction of its structural units in copolymer; $T_{g2} = -125.5^\circ\text{C}$ (19), $W_2 = 0.27$ are the T_g of the polydimethylsiloxane with $\bar{M}_n = 2260$, and the weight fraction of its structural units in copolymer), i.e., $T_g = -55.6^\circ\text{C}$. This result already suggests that the copolymer presents a two phase morphology.

Figure 2 presents four representative DSC traces for the low temperature range of the copolymers containing mesogenic units no.6 and 7 from Table I (curves A and B), poly(hydrogenmethyl-co-dimethylsiloxane) no.2 from Table I (curve C) and a polydimethylsiloxane homopolymer (DP=80) no.1 from Table I (curve D). The polydimethylsiloxane (curve D) presents the expected T_g , followed by crystallization and two melting transitions (19). Both poly(hydrogenmethyl-co-dimethylsiloxane) (curve C, Fig. 2 and Table I, no.2 and 3) samples used as starting materials for the synthesis of LC copolymers exhibit a single glass transition temperature. The DSC thermograms of both copolymers containing mesogenic units present two well defined glass transition temperatures. The heat capacity change of the low T_g is proportional to the weight fraction of the polymer backbone, while the heat capacity change of the high T_g is proportional to the weight fraction of the mesogenic groups. Therefore,

Tg1 from Table I is due to the independent motion of the polymer backbone, while Tg2 from the same table is due to the cooperative but independent motion of the side-groups.

In our opinion, these results represent a strong evidence for a well defined phase separated morphology. This demonstrates that the mobility of the LC domains is completely independent of the mobility of the backbone domains although they are interconnected.

Table I summarizes all the phase transitions of the LCP and LC copolymers, poly(hydrogenmethyl-co-dimethylsiloxane)s and of a polydimethylsiloxane. Since the weight fraction of the polymer backbone in the LCP no.4 and 5 represents only 0.18 from the overall polymer, it is difficult to clearly assign a Tg1 for the two homopolymers only based on DSC experiments. Therefore, at the present time we will refrain from making additional comments on these two LCP.

A close inspection of the low temperature transitions reported in Table I reveals that the transitions of the LCP's backbone and of the pure polydimethylsiloxane are within the same range of temperatures, suggesting that at least the last methylenic unit of the spacer is part of the polymer backbone. The enthalpy and entropy changes reported in Table I were calculated assuming that the mole repeat unit contains the mesogenic unit and ten methylenic units. Under these circumstances, the degree of order of the mesogenic units, seems to be higher in the copolymer than in the homopolymer.

It is certain that the mesomorphic behavior of the LCP should be strongly affected by the weight ratio of the domains, domain size, interfacial miscibility, and all the other particularities which dictate the overall properties of the phase separated polymeric systems.

Both optical polarization microscopy (focal-conic fan texture) and X-ray diffraction data support a smectic-A liquid crystalline mesophase for all three LCP. When the texture of the LC copolymer is sheared, it reveals both isotropic and anisotropic domains. Additional support for a biphasic morphology was obtained by dielectric relaxation measurements which are going to be published soon.

These results are raising a number of fundamental questions concerning the behavior of biphasic versus monophasic side-chain liquid crystalline polymers.

ACKNOWLEDGEMENTS

Financial support of this work by the Office of Naval Research is gratefully acknowledged.

REFERENCES

- 7 1. H. Finkelmann, H. Ringsdorf and J. H. Wendorff, Makromol. Chem., 179, 273(1978)
2. H. Finkelmann, M. Happ, M. Portugal and H. Ringsdorf, Makromol. Chem., 179, 2541(1978)
3. C. Boeffel, B. Hisgen, U. Pischorn, H. Ringsdorf and H. W. Spiess, Isr. J. Chem., 23, 388(1983)
4. K. H. Wassmer, E. Ohmes, M. Portugal, H. Ringsdorf and G. Kothe, J. Am. Chem. Soc., 107, 1511 (1985)
5. M. Engel, B. Hisgen, R. Keller, W. Kreuder, B. Reck, H. Ringsdorf, H. W. Schmidt and P. Tschirner, Pure Appl. Chem., 57, 1009(1985)
6. F. Cser, in "Liquid Crystals and Ordered Fluids", Vol. 4, A. C. Griffin and J. F. Johnson Eds., Plenum Press, New York, 1984, p. 945
7. H. Ringsdorf, H. W. Schmidt and A. Schneller, Makromol. Chem., Rapid Commun., 3, 745(1982)
8. C. Casagrande, M. Veyssie and H. Finkelmann, J. Phys., (Paris) Letters, 43, L-671(1982)
- 7 9. H. Sackmann and D. Demus, Mol. Cryst. Liq. Cryst., 21, 239(1973)
10. W. R. Krigbaum, J. Appl. Polym. Sci.: Appl. Polym. Symp., 41, 105(1985)
11. J. M. G. Cowie, Z. Hag and I. J. McEwen, J. Polym. Sci. Polym. Lett. Ed., 17, 771(1979)
12. J. M. G. Cowie, Z. Hag, I. J. McEwen and J. Velickovic, Polymer, 22, 327(1981)
13. J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Part A: Polym. Chem., 24, 1363(1986)
14. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, J. Polym. Sci. Part A: Polym. Chem., in press
15. H. Finkelmann and G. Rehage, Adv. Polym. Sci., 60/61, 99(1984)
16. V. P. Shibaev and N. A. Plate, Adv. Polym. Sci., 60/61, 173(1984)

References, continued

17. C. S. Hsu, J. M. Rodriguez-Parada and V. Percec, Makromol. Chem., in press
18. T. G. Fox, Bull. Am. Phys. Soc., 1, 123(1956)
19. S. J. Clarson, K. Dodgson and J. A. Semlien, Polymer, 26, 930(1985)

Figures and Schemes Captions

Scheme 1: Synthesis of Polysiloxanes and Copolysiloxanes Containing trans 5-n-undecanyl-2-(4-cyanophenyl)-1,3-dioxane Side Groups

Figure 1: DSC thermograms (20°C/min) of: A) homopolymer No. ⁴2 from Table I, heating scan; B) cooling scan; C) homopolymer No. ³3 from Table I, heating scan; D) cooling scan; E) copolymer No. ⁶4 from Table I, heating scan; F) cooling scan

Figure 2: DSC thermograms (20°C/min) of: A) copolymer no. 6 from Table I, heating scan; B) copolymer no.7 from Table I, heating scan; C) copolymer no. 2 from Table I, heating scan; D) polydimethylsiloxane no. 1 from Table I, heating scan.

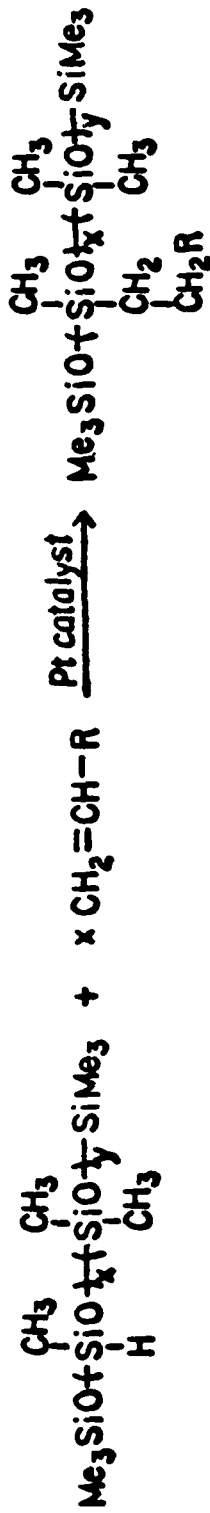
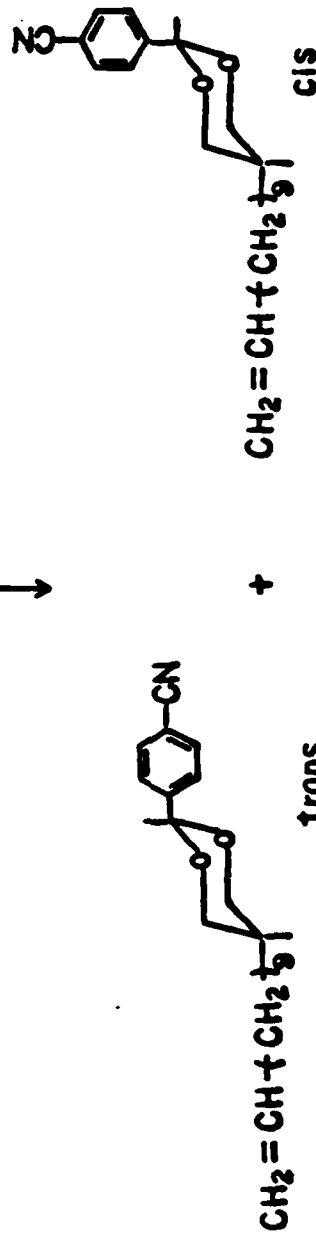
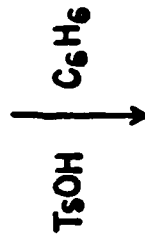
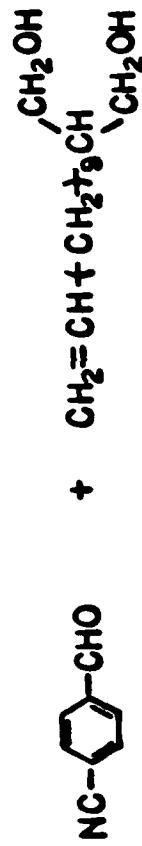
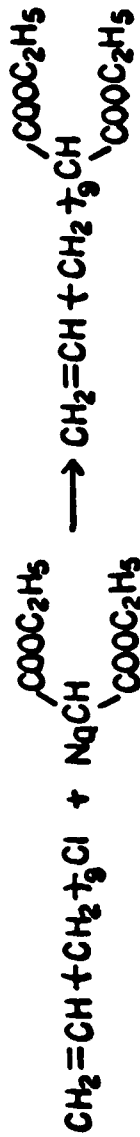
TABLE I: THERMAL TRANSITIONS AND THERMODYNAMIC PARAMETERS OF POLYSILOXANES

POLYMERS	THERMAL TRANSITIONS, (°C) AND THERMODYNAMIC PARAMETERS, $\Delta H(\text{KCAL/MRU}^*), \Delta S(\text{CAL/MRU}^* \cdot \text{K})$												
	HEATING					COOLING							
No.	X	Y**	Tg1	Tc	Tm1	Tm2	Tg2	Ti	ΔH_I	ΔS_I	Ti	ΔH_I	ΔS_I
1	0	80	-123	-79	-40	-26	--	--	--	--	--	--	--
2***	10	20	-126	--	--	--	--	--	--	--	--	--	--
3***	5	25	-127	--	--	--	--	--	--	--	--	--	--
4	80	0	--	--	--	--	-10	149	0.57	1.35	140	0.56	1.36
5	38	0	--	--	--	--	-10	135	0.52	1.27	128	0.54	1.35
6	10	20	-100	--	--	--	-39	66	0.67	1.98	64	0.67	1.99
7	5	25	-105	--	--	--	-58	--	--	--	--	--	--

* MRU = MOLE OF REPEAT UNITS, CONSISTING OF MESOGENIC UNIT AND TEN METHYLENIC UNITS.

** X AND Y ACCORDING TO SCHEME I.

*** POLY(X-HYDROGENMETHYL-Y-DIMETHYLSILOXANE)



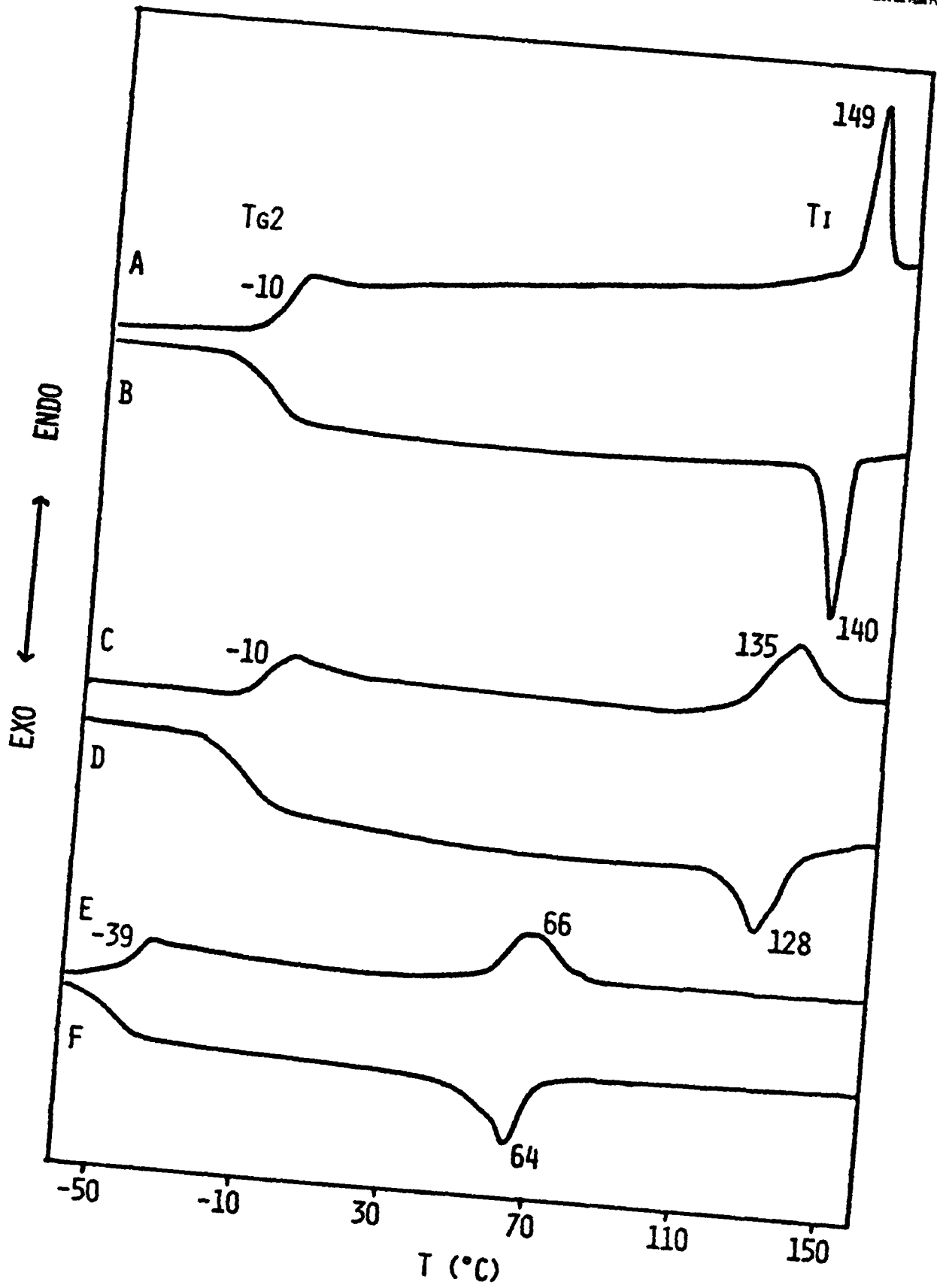
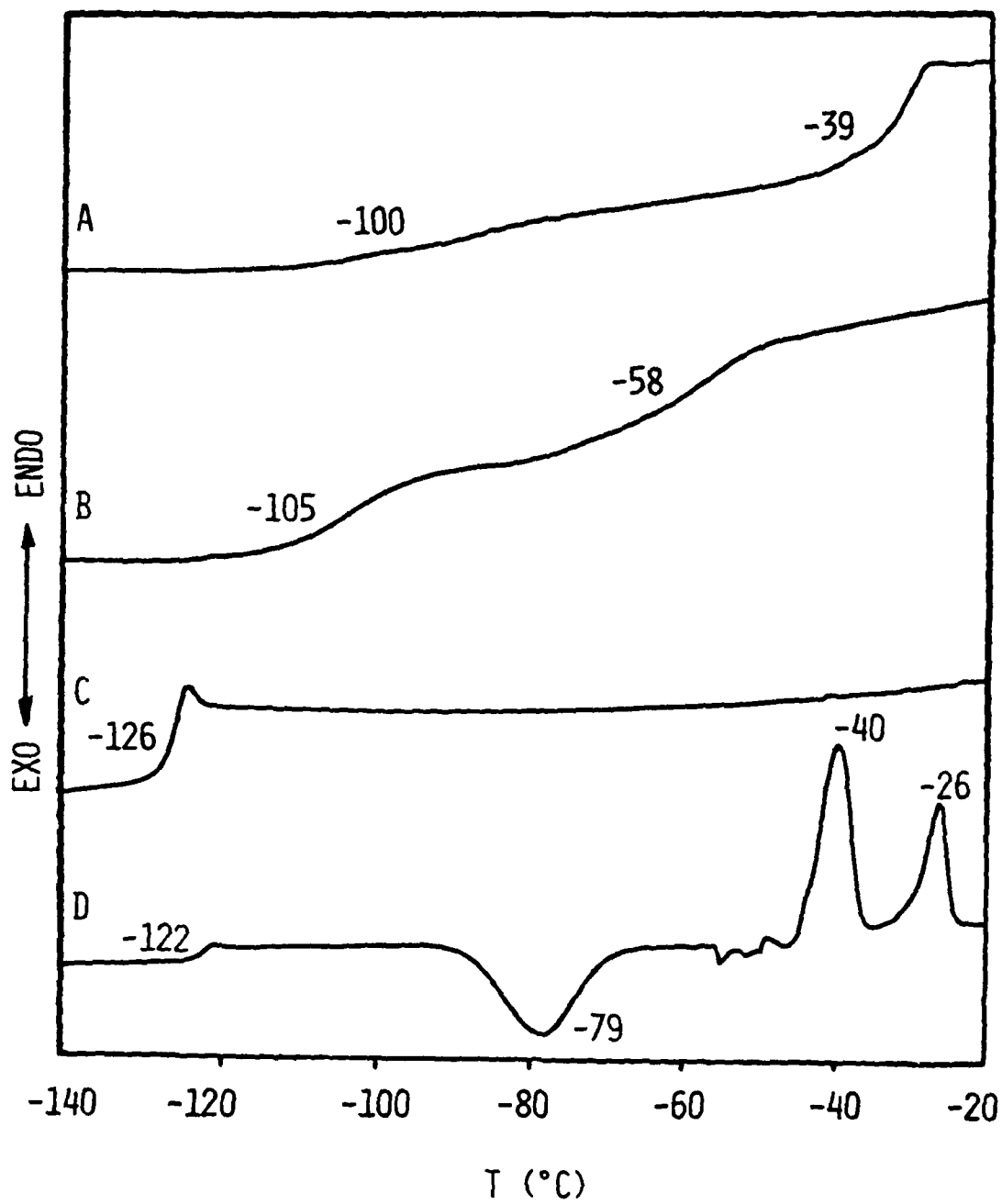


Fig. 1



END

9-87

DTIC