OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 12

Synthesis and Characterization of the Liquid Crystalline Side Chain Polymer 4'-Cyano-4-Pentyloxystilbene Polysiloxane

by

Girija Subramanian and R. K. Gilpin

Liquid Crystal Institute*
Kent State University
Kent, OH 44242

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

Prepared for Publication

in

Macromolecules

July 22, 1988

Unclassified
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. 12	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)
Synthesis and Characterization of the Liquid Crystalline Side Chain Polymer 4'-Cyano-4-Pentyloxystilbene Polysiloxane (Unclassified)

12 PERSONAL AUTHOR(S)
Girija Subramaniam and R. K, Gilpin

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Interim, Technical	FROM _____ TO 07/21/88	1988-July-21	30

16 SUPPLEMENTARY NOTATION
Prepared for publication in Macromolecules
Research carried out at Kent State University (subcontractor) (LCPRC Publication No.)

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

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

The liquid crystalline side chain polymer 4'-cyano-4-pentyloxystilbene polysiloxane has been synthesized via direct condensation polymerization of the dichlorosilane monomer. Likewise, the synthesis of the starting silane, 4'-cyano-4-4(5-dichloromethylsilyl)pentyloxystilbene as well as 4'-cyano-4-(5-chlorodimethylsilyl)pentyloxystilbene which was used to terminate the reaction is reported. The mesogenic properties of the polymer, the side chain liquid crystal precursor and the respective dichlorosilane monomer are discussed.

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/Joann Milliken	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

SYNTHESIS AND CHARACTERIZATION OF THE LIQUID CRYSTALLINE SIDE CHAIN POLYMER 4'-CYANO-4-PENTYLOXYSTILBENE POLYSILOXANE

Girija Subramaniam and R. K. Gilpin*

Department of Chemistry

Kent State University

Kent, Ohio 44242

*Author to whom correspondence should be addressed.

ABSTRACT

The liquid crystalline side chain polymer 4'-cyano-4-pentyloxystilbene polysiloxane has been synthesized via direct condensation polymerization of the dichlorosilane monomer. Likewise, the synthesis of the starting silane, 4'-cyano-4-4(5-dichloromethylsilyl)pentyloxystilbene as well as 4'-cyano-4-(5-chlorodimethylsilyl)pentyloxystilbene which was used to terminate the reaction is reported. The mesogenic properties of the polymer, the side chain liquid crystal precursor and the respective dichlorosilane monomer are discussed.

INTRODUCTION

The synthesis of liquid crystalline side chain polymers, especially polysiloxanes, has become an active research area because of the potential use of these materials in electrooptical devices[1-4]. Siloxane polymers enjoy a unique position due to their lower glass transition temperatures and flexibility.

Although polysiloxanes with various mesogenic side chain units (biphenyl[5,6], phenyl benzoates[7], and steroids[8]) have been synthesized and used as stationary phases in gas chromatography, only a few have had cyano functional groups[9-11]. Usually mesogens with a terminal cyano group are strongly polar nematic compounds with positive dielectric anisotropy and display a twisted nematic effect.

Attempts have been made to produce polymeric cyano analogs which can be used in display devices. To date, they have been prepared via polyhydrosilylation reaction of polyhydrogenmethylsiloxane (PHMS - commercially available) and appropriate vinylic mesogens using a wide variety of catalysts. The most commonly employed catalyst is chloroplatinic acid, H_2PtCl_6. Often problems are encountered in this conventional synthesis of polysiloxanes which include non-reproducibility, discoloration and cross linking of the resulting polymer.

Since the cause of these problems has been attributed to the use of platinum during the polymeric addition reaction[11], a way

of minimizing them is elimination of Pt during the polymerization. This can be accomplished by first preparing the silyl monomer from the vinylic mesogen followed by direct condensation.

The current paper describes the synthesis and characterization of a liquid crystalline side chain polysiloxane polymer which bears the fluorescent cyanostilbene pendant. The material is prepared via condensation of the dichlorosilane monomer.

EXPERIMENTAL SECTION

Materials and Techniques: Most chemicals were purchased from the Aldrich Chemical Company (Milwaukee, WI) and used as received. The starting silanes, which also were used as received, were from Petrarch (Levitttown, PA). The microscopic studies were made in triplicate at heating rates of either 2°C or 10°C/min. using a Leitz-Wetzler Ortholux polarizing instrument fitted with a modified Mettler FP-2 heating stage. Photographs were taken with a Leitz Microscopic 35mm camera using Kodak Ektachrome film (160 ASA). The DSC measurements were carried out on a Perkin-Elmer Model DSC-2 differential scanning calorimeter at a heating rate of 2.5°C/min. under nitrogen. The weight and number average molecular weight of the polymer were determined on a Waters liquid chromatograph equipped with a refractive index detector and GPC column. Polystyrene standards were used as calibration materials. ^{1}H and ^{13}C NMR spectra were recorded on a General Electric GN-300 spectrometer. Infrared spectra were recorded on IBM model IR/32 FTIR spectrometer.

Synthesis: 4-Pentenoxybenzaldehyde, 1. A mixture of p-hydroxybenzaldehyde (24.2g, 0.2mol), 5-bromo-1-pentene (25g, 0.17mol), acetone (200 mL) and anhydrous potassium carbonate (35.5g, 0.25mol) were refluxed for 24 h. while mechanically stirring. The reaction mixture was poured into water, the acetone removed and the aqueous layer was extracted with ether (60 mL, 4x). The ether layer was washed with aqueous potassium

hydroxide (2M, 50 mL, 4x), water (50 mL, 4x) and saturated brine (50 mL, 2x), and then dried using anhydrous sodium sulfate. Removal of the ether gave a yellow oil which was purified by distillation at reduced pressure, bp 135-140°C/0.35mm (yield 80.6%). IR (Neat): 1690, 1600, 1500, 1260, 1160, 920, 830, 655, 615, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ:9.86 (s, 1H, -CHO), 7.80-6.96 (AA' BB', 4H, Aromatic), 5.85, 5.08-5.01 (m, 3H, -vinyl), 4.02 (t, 2H $-OCH_2$), 2.23, 1.90 (m, 4H, $-CH_2CH_2$). ^{13}C NMR ($CDCl_3$) δ:190.60, 164.13, 137.40, 131.93, 129.86, 115.49, 114.73, 67.48, 30.00, 28.20.

4'-Cyano-4-pentenoxystilbene, 2. Ethanolic solutions of 1 (32.5g, 0.17 mol) and lithium ethoxide (0.2M, 855 mL) were added to a stirred solution of 4-cyanobenzyltriphenylphosphonium chloride (75g, 0.18 mol) and absolute ethanol (200 mL). The solution was stirred for three days at RT. Subsequently, water (795 mL) was added and the precipitate which formed was filtered, washed with absolute ethanol and dried. The product was purified by recrystallization from a mixture of toluene and petroleum ether. A yield of 20% was obtained, mp (cp) 123-125°C; IR (Diffused Reflectance) (solid): 2200, 1600, 1500, 1450, 1160, 1100, 975, 925, 830, 650, 585, 550, 475 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ: 7.57-7.41 (m, 6H, Aromatic), 7.14-7.09 (d, 1H, -CH=), 6.9-6.86 (m, 3H, Aromatic), 5.85-5.80, 5.08-4.98 (m, ABX, Vinyl), 3.96 (t, 2H, $-OCH_2$), 2.24, 1.87 (m, 4H, $-CH_2CH_2-$); ^{13}C NMR ($CDCl_3$) δ: 159.40, 142.08, 137.54, 132.25, 131.84, 128.77, 128.13, 126.38, 124.23, 119.01, 115.15, 114.71, 109.81, 67.13, 29.94, 28.24.

4'-Cyano-4-(5-dichloromethylsilyl)pentyloxystilbene 3: A mixture of 2 (1.45g, 0.005mol), chloroplatinic acid (THF solution 0.122M, 3 drops) toluene (5 mL) and dichloromethylsilane (0.52 mL, 0.005 M) was heated at 40-50°C for 16 h. The reaction mixture was cooled and the resulting solid was redissolved in boiling toluene, filtered (under N_2), concentrated and allowed to crystallize. A pale yellow solid was obtained at a yield of 90%; ^1H NMR ($CDCl_3$) δ: 7.63-7.45 (m, 6H, aromatic), 7.19-7.13 (d, 1H, -CH=), 6.97-6.89 (m, 3H, aromatic), 3.99 (m, 2H, $-OCH_2$), 1.83 (m, 2H, $-CH_2$), 1.6 (m, 4H, $-CH_2CH_2$), 1.17 (m, 2H, $-CH_2$), 0.79 (3H, $-CH_3$); ^{13}C NMR ($CDCl_3$) δ: 159.59, 142.25, 132.39, 132.01, 129.01, 128.23, 126.52, 124.48, 119.04, 114.87, 110.07, 67.79, 28.90, 28.73, 22.24, 21.53, 5.18.

4'-cyano-4-(5-chlorodimethylsilyl)-pentyloxystilbene, 4. It was prepared via the same procedure as 3 with a yield of 77%. ^1H NMR ($CDCl_3$) δ: 7.52-.35 (m, 6H, aromatic), 7.1-7.04 (d, 1H, -CH=) 6.87-6.81 (m, 3H, aromatic), 3.9 (t, 2H, $-OCH_2$), 1.73 (m, 2H, $-CH_2$), 1.45 (m, 4H, $-CH_2CH_2$), 0.78 (m, 2H, $-CH_2$), 0.35(s, 6H, $SiCH_3$); ^{13}C NMR ($CDCl_3$) δ:159.49, 142.11, 132.27, 131.66, 128.73, 128.15, 126.40, 124.22, 119.03, 116.70, 109.80, 67.78, 29.19, 28.14, 22.11, 18.78, 1.56.

Polysiloxane, 5. Water (0.5 mL) was slowly added to a stirred solution of THF (8 mL) which contained 3 (0.8g, 0.0019 mol). An immediate exothermic reaction was noted. After 15 min. pyridine (0.4 mL) was added and the mixture refluxed for 22 h. followed by the addition of 4'-cyano-4-(5-chloro-dimethylsilyl)-

pentyloxystilbene, 4 (0.5g, 5% by wt.). The mixture was refluxed for another 5 h. The resulting polymer was precipitated by the addition of methanol and was purified from chloroform by addition of methanol. This latter process was carried out three times. A yield of 75% was obtained for the cream colored polymer.

RESULTS AND DISCUSSION

Synthesis: The 4'-cyano 4-pentyloxy stilbene polysiloxane polymer was prepared by the four-step synthesis shown in Scheme 1. All steps, except the Wittig reaction proceeded with yields of 75-90%. However, in the latter case, only 20% of the mesogenic trans-stilbene could be isolated. The final polymer after purification was granular and cream colored. Its weight average and number average molecular weights were 5.5589×10^3 and 3.1716×10^3 respectively. The polydispersity ratio was 1.7527.

The molecular weight of the polysiloxane obtained via direct condensation is similar to that obtained by traditional polyhydrosilylation reactions[12-15]. Although a relatively low molecular weight polymer was produced (M_n -3200), higher degrees of polymerization should be achievable with increased reaction times.

An important advantage of direct polymerization over polyhydrosilylation procedures is that the method assures the presence of consecutive mesogenic pendants over the polymer's entire length. In carrying out the latter method NMR is often used to monitor the progress of hydrosilylation. The inherent limitation of this technique is detection of the Si-H resonance which is approximately 20 mole percent[16]. Hence, the absence of the Si-H peak in NMR spectrum does not guarantee complete addition. The direct condensation method does not suffer from this disadvantage. Additional problems of cross linking (by the

hydrosilylation cyano function) and discoloration (usually shades of grey and black) were not encountered via direct polymerization. Even though H_2PtCl_6 is used as a catalyst, it is used in a step (third step - monohydrosilylation) where purification is more easily accomplished.

Mesogenic Properties: The mesogenic properties of the precursors, (2 and 3) and the polymer, (5), were studied by polarized microscopy and differential scanning colorimetry.

Microscopy: The vinylic stilbene, 2 showed three transitions on heating: a crystal to crystal change at ~ 70°C, a crystal to nematic change at 94.5°C and a nematic to isotropic change at 124.8°C. The second transition was reproducible both on heating and cooling whereas supercooling occurred for the nematic to crystal change. The nematic nature of the mesophase was confirmed by a characteristic marble-Schlieren texture and by nematic droplets which formed near the isotropic temperature. A representative photomicrograph is reproduced in Figure 1.

The dichloro-monomer, (3) also exhibited mesogenic properties. Crystal to (unidentified) smectic and smectic to homeotropic transitions were observed at 119.4°C and 191.4°C respectively. A homeotropic texture formed readily on heating suggesting that 3 probably reacted with the glass slide forming a surface aligned monolayer with an average perpendicular orientation. Since 3 is also hydrolytically unstable, it is likely that a small amount of reaction occurred during the microscopic examination which resulted in the formation of low

molecular weight oligomers. On cooling, the formation of batonnets (Figure 2A) occurred followed by gradual coalescence into tiny broken fans (Figure 2B). The viscosity and the texture obtained on cooling confirmed that 3 had smectogenic properties.

The polysiloxane polymer underwent a smectic transition at 115°C with a texture similar to that of 3 at 119.4°C. With further heating, more fluidity was observed. At approximately 161°C focal conic fans formed, which changed to a homeotropic texture (i.e., confirmed by conoscopic observations) with light and dark gray shades at 170.8°C. On cooling formation of batonnets occurred (Figure 3A) which coalesced to form well-developed focal conic fans against a gray background (Figure 3B). Further cooling resulted in the growth of tiny fans from the remainder of the dark pseudoisotropic phase (Figure 3C). This texture persisted even after cooling to -7°C.

Differential Scanning Calorimetry: The DSC data of the vinylic precursor, 2, and the monomer, 3, are presented in Table 1. The results for 2 agreed with that obtained by microscopy. The crystal to crystal transition, although barely observable by microscopy, was seen clearly by DSC. Crystal to nematic and nematic to isotropic changes were observed at 93.7°C and 125.1°C respectively.

The DSC scan of the monomer, 3, showed only one major transition at 116.2°C. The second transition observed by microscopy was not detected. No other transitions were seen even up to a temperature of 252°C. The magnitude of ΔH indicates a

first order transition. The enthalpy value of 2.86 cal/gm is consistent with reported values for Smectic A mesophases[17]. The cooling scan showed only a poorly defined exotherm at 68.7°C.

The temperatures and heats of transition of the polysiloxane, 5, are summarized in Table II. Data from three heating and cooling cycles are given. The first cycle data were obtained from purified material directly precipitated from the solution. The second cycle data were obtained after an annealing period of a month and the third cycle data collected immediately following the second cycle. The final temperature for the first heating cycle was 192°C whereas the second and third cycles were heated to 252°C. The lower limit was 27°C for all experiments. The scan rate was 2.5°C/min. for all heating and cooling scans except for the third cooling scan (40°C/min. rate of cooling).

The DSC scans of the polymer showed a reproducible transition at approximately 111°C irrespective of the thermal history (Figures 4A, B and C). The second heating scan also showed the onset of a second broad transition between 167°C and 187°C which was not detected in the first and third scans. A sharp endotherm at 226°C was also seen in the second scan. These latter transitions were not visible in the third scan.

The enthalpy of the first transition varied between scans. The highest value was obtained on the annealed sample (second scan) indicative of a more ordered crystalline polymer. The lower value of the third scan may reflect an insufficient amount of annealing time between scans for the polymer chains to relax.

All cooling scans show only one major transition. However, the shape of the peak from the first scan reflects two closely occurring phase changes (Fig. 4A, cooling scan) - smectic mesophase formation immediately followed by crystallization. The higher ΔH value also is consistent with this possibility. Lower ΔH values from the second and third scans probably are due to partial crystallization. Supercooling was observed in the third scan due to the extremely rapid rate of cooling used. Similarity in the thermal behavior of the monomer and the polymer suggests that the siloxane backbone does not dramatically influence packing of the pendant groups within for the polymer studied.

REFERENCES

1. Ringsdorf, H.; Zentel R. Makromol. Chem., 1982, 183, 1245.

2. Shibaev, V. P.; Talrose,R. V.; Kostromin, S. G.; Plate, N. A.; Kresse, H.; Sauer, K.; Demus, D. Makromol. Chem. Rapid Commun. 1981, 2, 305.

3. Finkelmann, H.; Ringsdorf, H; Naegle,D. Makromol. Chem.,1979, 180, 803.

4. Finkelmann, H; Kiechle, U; Rehage, G. Mol. Cryst. Liq. Cryst., 1983, 94, 343.

5. Finkelmann, H., Apfel, M. A.; Janini, G. M.; Laub, R. J.; Luhmann, B. H.; Price, A.; Roberts, W. L.; Shaw, T. J.; Smith, C. A. Anal. Chem. 1984, 57, 651.

6. Bradshaw, J. S.; Schregenberger, C; Karen, H.; Chang, C.; Markides, K. E.; Lee, M. L. J. Chromatogr. 1986, 358, 95.

7. Nishioka, M.; Jones, B. A.; Tarbet, B. J.; Bradshaw, J. S.; Lee, M. L. J. Chromatogr. 1986, 357, 79.

8. Adams, N. W.; Bradshaw, J. S.; Bayona, J. M., Markides, K.E., Lee, M. L. Mol. Cryst. Liq. Cryst. 1987. 147, 43.

9. Shibaev, V. P.; Kostromin, S. G.; Plate, N. A. Eur. Polym. J. 1982, 18, 651.

10. Grammell, P. A.; Gray, G. W.; Lacey, D. Mol. Cryst. Liq. Cryst. 1985, 122, 205.

11. Gray, G. W.; Lacey, D.; Nester, G.; White, M. S. Makromol. Chem. Rapid. Commun. 1986, 7, 71.

12. Markides, K. E.; Nishioka, M.; Tarbet, B. J.; Bradshaw J. S.; Lee, M. L. Anal. Chem. 1985, 57, 1296.

13. Finkelmann, H.; Rehage, G. Makromol. Chem. Rapid Commun. 1980, 1, 31.

14. Hahn, B.; Percec, V. Macromolecules, 1987, 20, 2962.

15. Hsu, C. S.; Percec,V. J. Polym. Sci. 1987, Part A, 25, 2909.

16. Janini, G. M.; Laub, R. J.; Pluyter, G. L., Shaw, T. J. Mol. Cryst. Liq. Cryst., 1987, 153, 479.

17. Gray, G.W.; Goodby, J. W. Smetic Liquid Crystals, Textures and Structures. Leonard Hill, Glasgow & London, 1984, p. 21.

TABLE I: DSC DATA FOR THE PRECURSORS, 2 AND 3

Compound	C-C*	C-N,S	N,S-I
2	73.4# (2.57)	93.6 (16.3)	125.1 (0.32)
3	-	116.2 (2.86)	-

* C denotes crystal phase; N denotes nematic phase; S denotes smectic phase; I denotes isotropic phase.

‡ Temperatures in °C. & the values in parentheses are ΔH in cal/gm.

TABLE II: THERMAL TRANSITIONS AND THERMODYNAMIC PARAMETERS OF POLYMER 5

No.	T_1*	ΔH#	ΔS&	T_2	ΔH	ΔS
			Heating Scans			
1	111.1	4.54	0.012	-	-	-
2	111.3	5.74	0.015	226.0	0.56	0.001
3	110.6	3.60	0.009	-	-	-
			Cooling Scans			
1	92.1	-6.01	0.016	-	-	-
2	88.8	-4.70	0.013	-	-	-
3	63.5	-2.66	0.008	-	-	-

* Temperature in °C; # H in Cal/gm; & ΔS in Cal/deg. gm.

LIST OF FIGURES

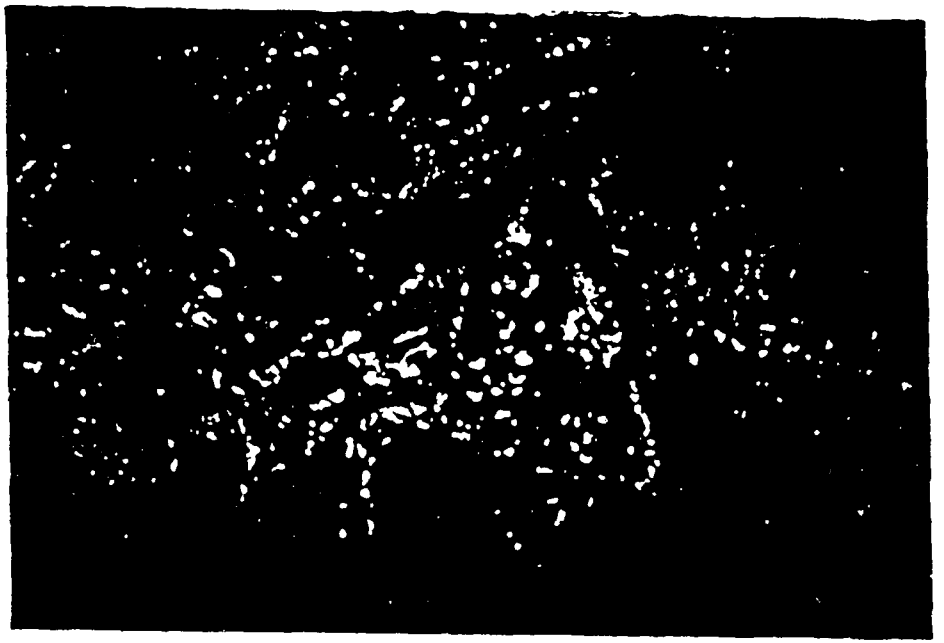
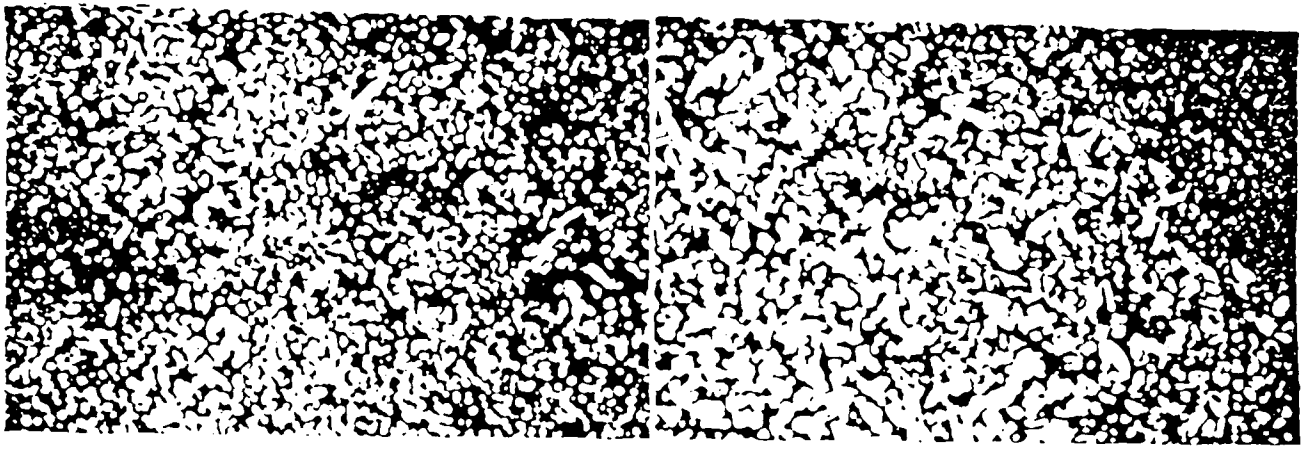
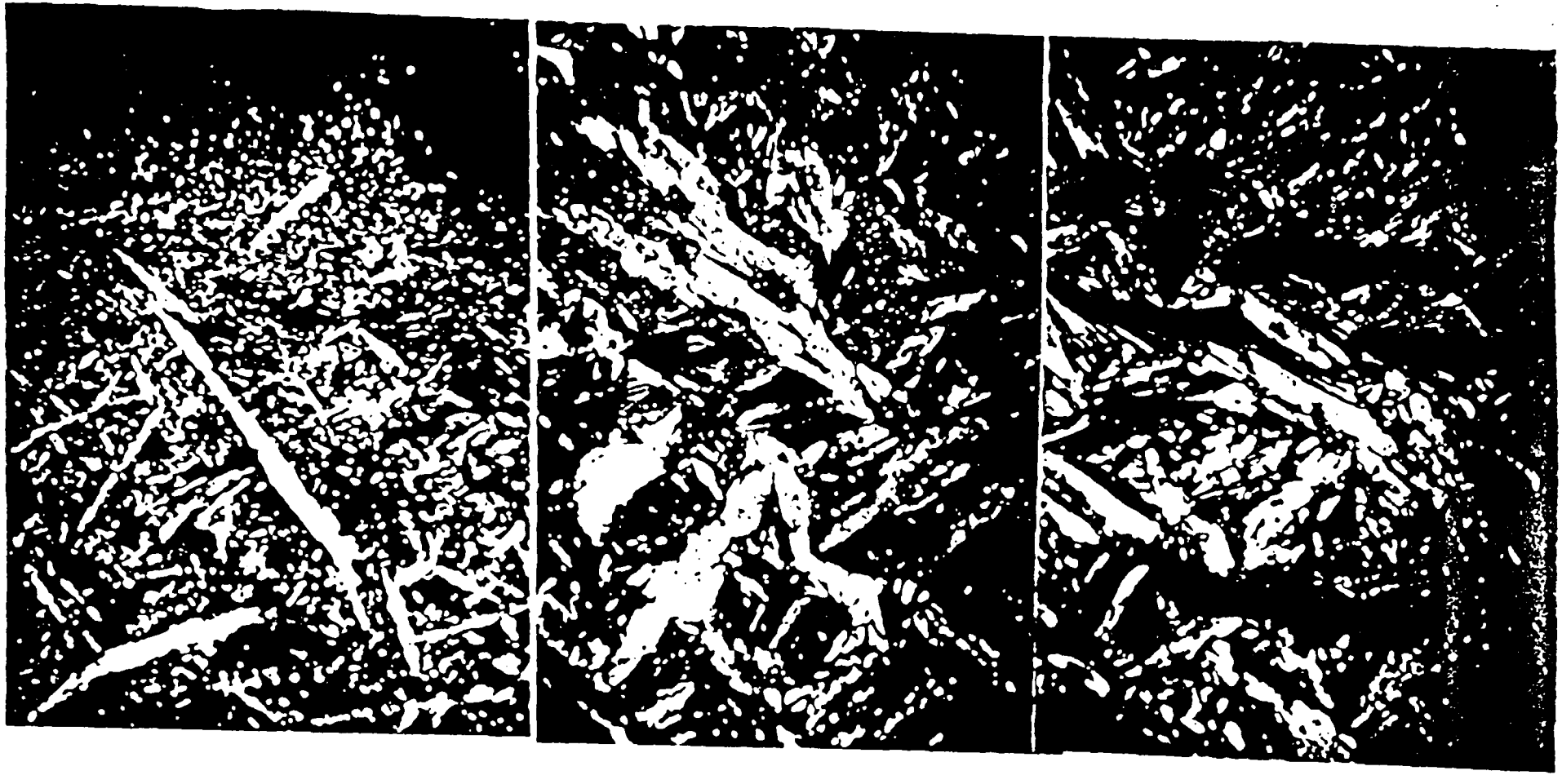


Figure 1. Typical optical polarization micrograph of 4'-cyano-4-pentenoxystilbene - Nematic marble texture.



(A) (B)

Figure 2. Optical polarization micrograph of 4'-cyano-4-(5-dichloromethyl-silyl)pentyloxystilbene; (A) Batonnets formation; (B) Broben fan texture of S_A mesophase.

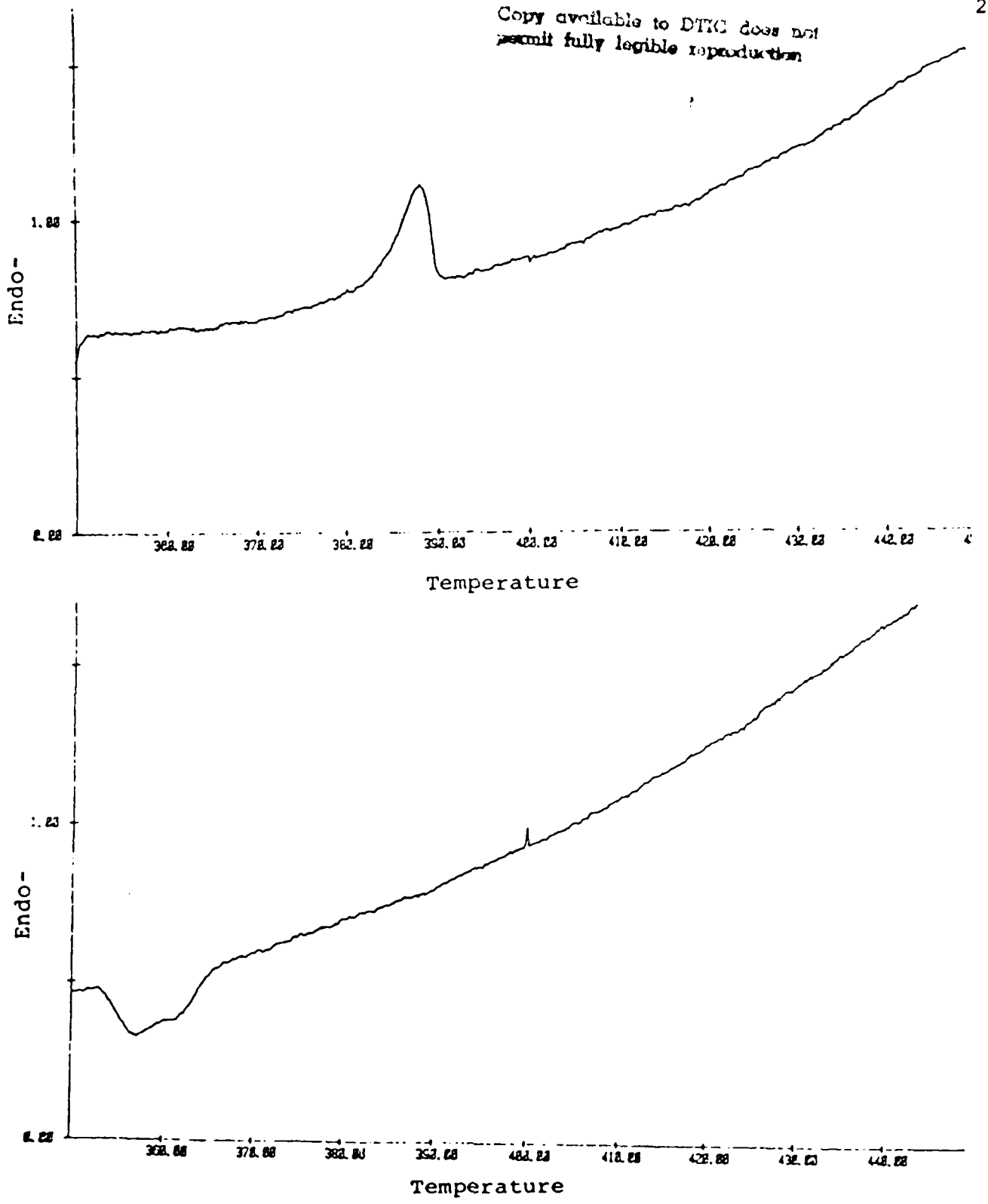


(A) (B) (C)

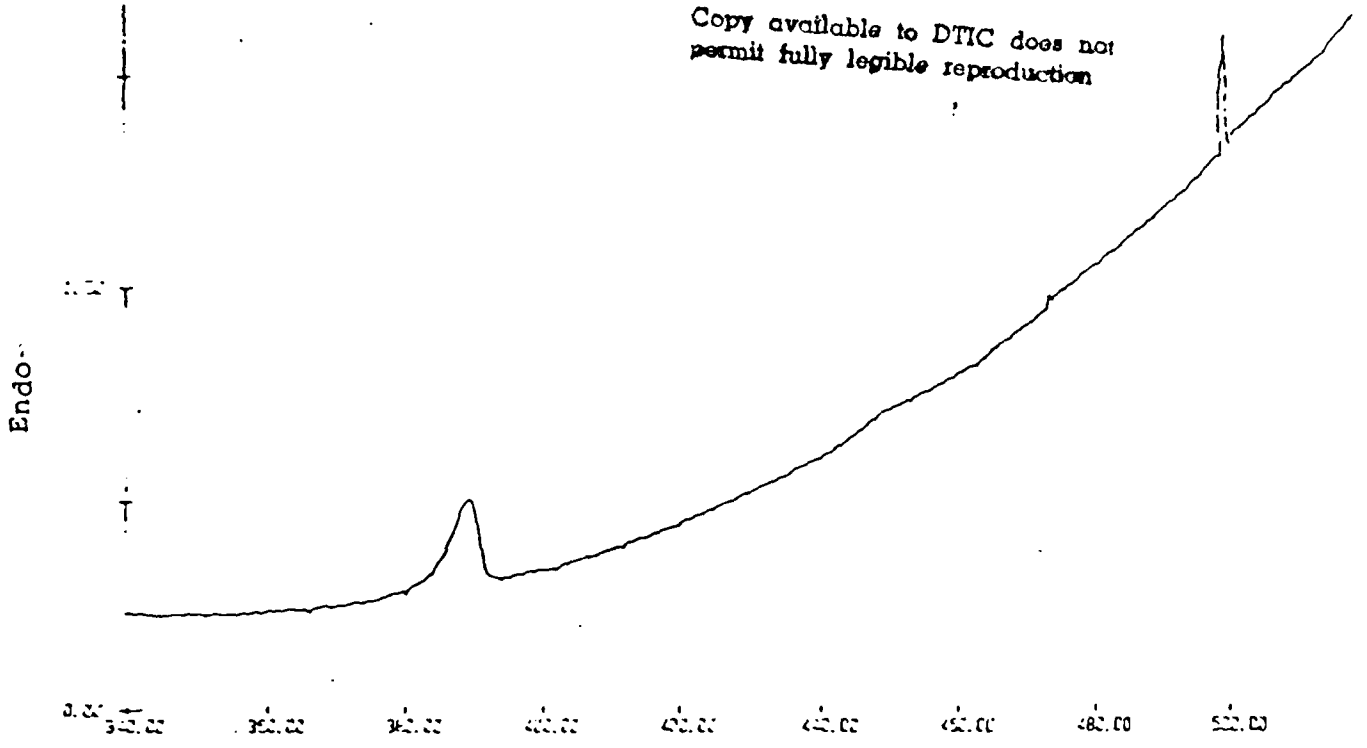
Figure 3. Optical polarization micrograph of polysiloxane; (A) Batonnets formation; (B) Fan texture of S_A developing, showing biphasic regions; (C) Fully developed fan texture.

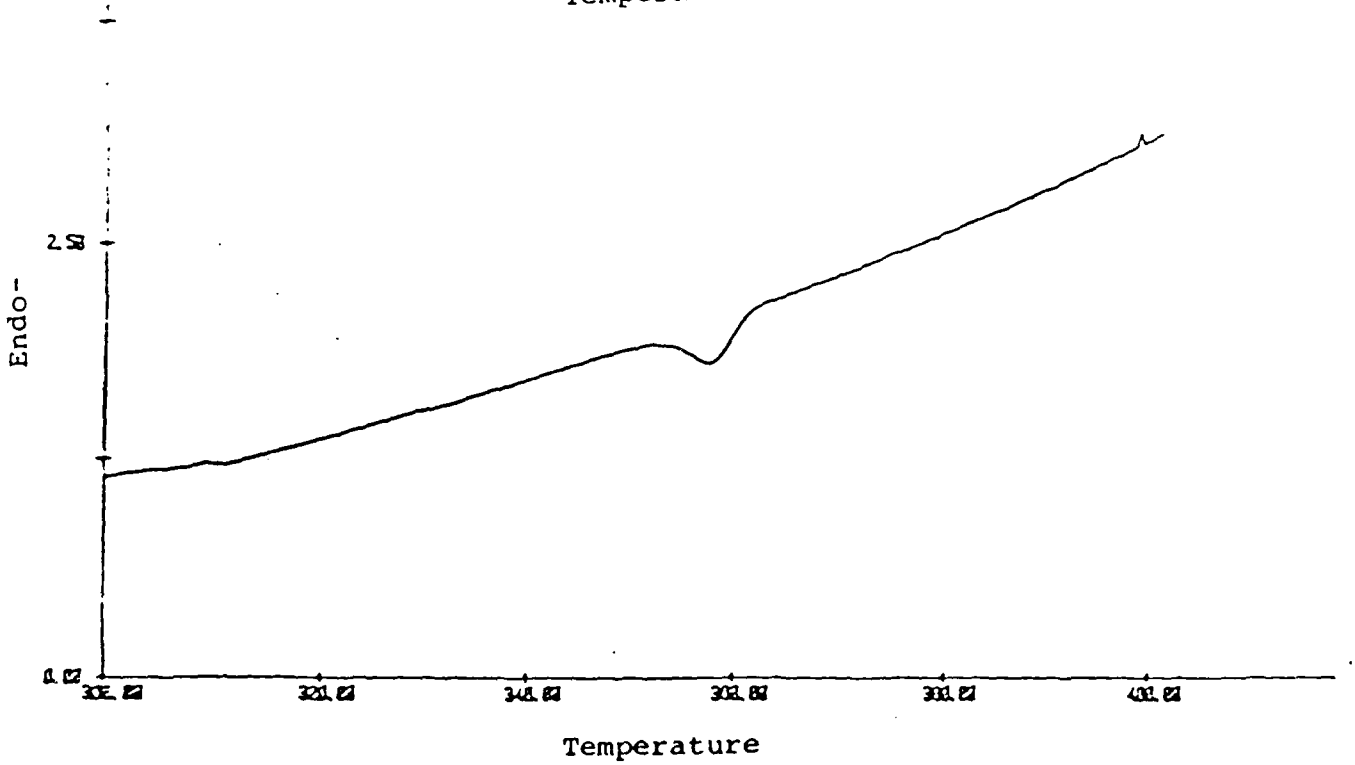
Fig. 4. DSC Scans of Polysiloxane, 4

Upper curves - Heating Scans
Lower curves - Cooling Scans

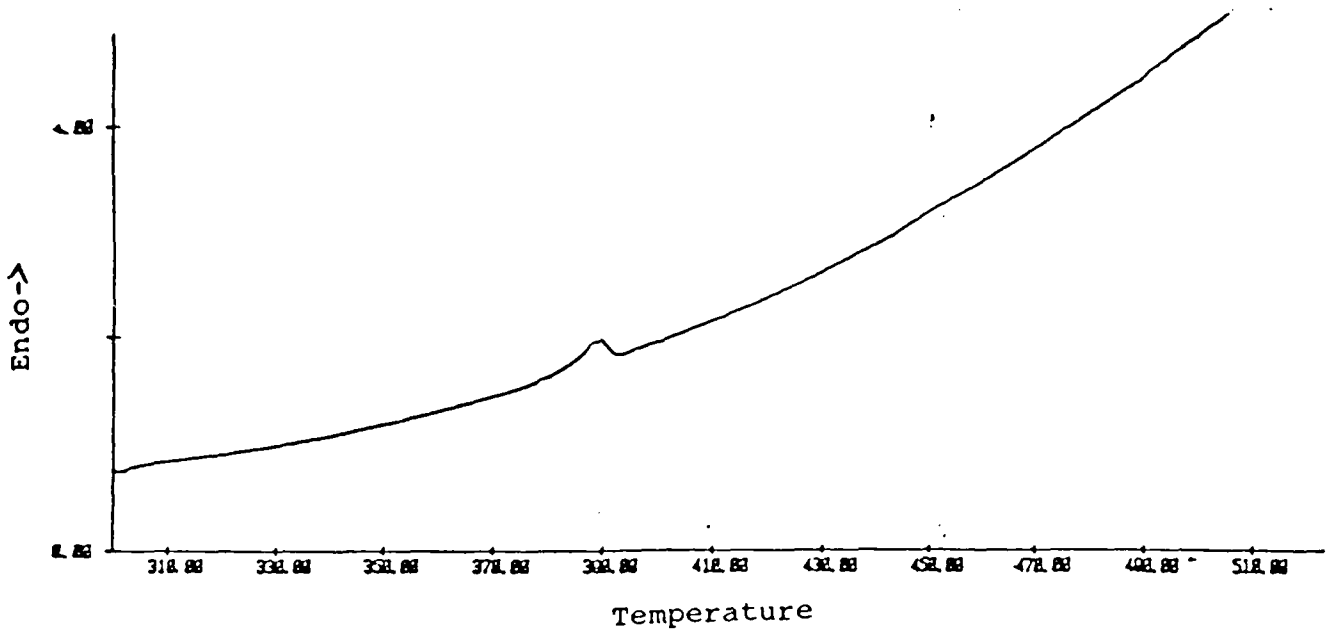


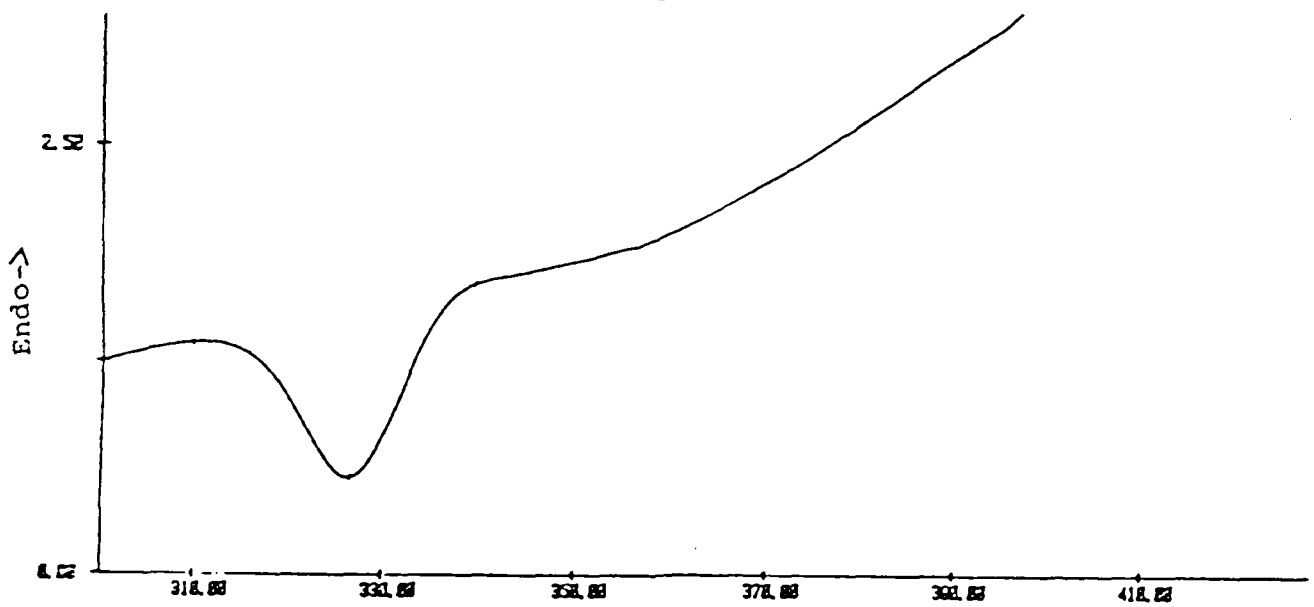
A. First Cycle





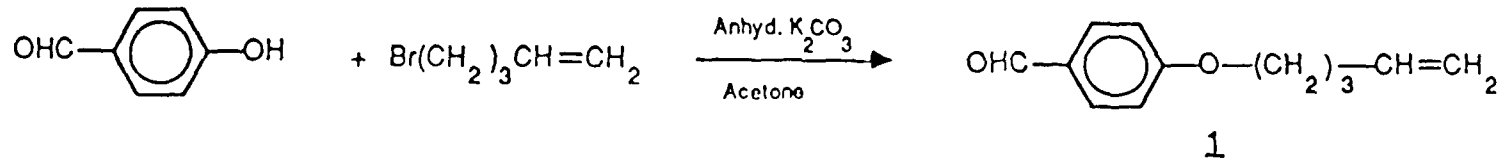
B. Second Cycle



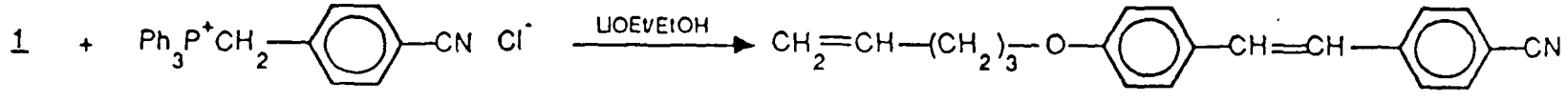


C. Third Cycle

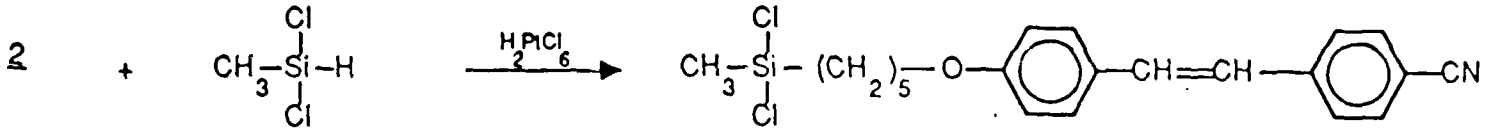
Scheme I



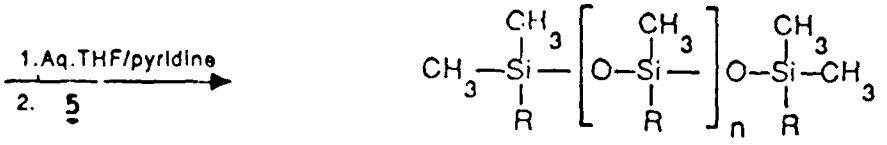
1



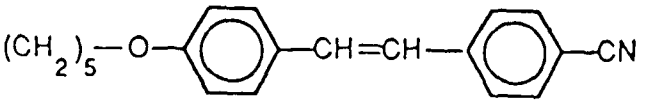
2



3



4

R = 

ACKNOWLEDGEMENT

Support from DARPA-ONR contract N0014-86-0772 is acknowledged.

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