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OFFICE OF NAVAL RESEARCH
Grant No. N00014-91-J-1655
R&T Code 4132058---02

TECHNICAL REPORT NO. 19

Liquid Crystalline Side-Chain Polysiloxanes with
4-Amino-4'-Stilbene-Carboxylic Ester Mesogens

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 12/9/93		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE Liquid Crystalline Side-Chain Polysiloxanes with 4-Amino-4'-Stilbene-Carboxylic Ester Mesogens				5. FUNDING NUMBERS Grant No. N00014-91-J-1655	
6. AUTHOR(S) Marietta O. Bautista, Warren T. Ford, R.S. Duran and Matthias Naumann					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) R. S. Duran Department of Chemistry University of Florida Gainesville, Florida 32611				8. PERFORMING ORGANIZATION REPORT NUMBER 19	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Dr. Kenneth J. Wynne Code 1113PO, Office of the Chief of Naval Research 800 North Quincy Street Arlington, VA 22217-5000 (703) 696-4409				10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION / AVAILABILITY STATEMENT				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) The liquid crystalline phases of polysiloxanes have been characterized by DSC, optical microscopy, and powder X-ray diffraction. The polysiloxanes form monolayers at the air/water interface with molecular areas of 30 - 35 Å ² , and the films do not collapse at pressures of about 40 mN/m. The monolayers of CPS-1 and -2 showed good stability on water compared to those of HPS-1 and -2 as measured by isobaric surface area changes as a function of time. Moreover, there was little hysteresis between isotherms obtained by compression and subsequent decompression below 40 mN/m for CPS-1 and -2.					
14. SUBJECT TERMS				15. NUMBER OF PAGES	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	
20. LIMITATION OF ABSTRACT					

LIQUID CRYSTALLINE SIDE-CHAIN POLYSILOXANES WITH 4-AMINO-4'-STILBENE-CARBOXYLIC ESTER MESOGENS

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INTRODUCTION

Side-chain liquid crystalline polymers (SCLCPs), especially siloxanes, are potentially useful in electro-optical devices,¹ and are easily fabricated into thin films. SCLCPs with conjugated π electron donor-acceptor substituents at the ends of delocalized electron systems have large second order nonlinear optical (NLO) coefficients, $\chi^{(2)}$,² commonly measured by second harmonic generation (SHG), the doubling of the frequency of a laser beam. Since second order NLO polarizability requires noncentrosymmetric structure, poled glassy polymers, and acentric liquid-crystalline (LC) films are promising approaches to high-efficiency NLO materials.

In this paper, we report the preparation, characterization, and nematic behavior of liquid crystalline polysiloxanes having polarized mesogens in the side chains.

RESULTS AND DISCUSSION

Syntheses

Monomers, 1 and 2, were synthesized by transesterification of the benzo-methyl esters³ with ω -undecylenyl alcohol in the presence of (acac)₃Sn. Hydrosilylation of the monomers with either (hydromethyl)siloxane or a copolymer of 50% (hydromethyl)siloxane - 50% (dimethyl)siloxane in dry toluene was catalyzed by chloroplatinic acid isopropyl alcohol. An equivalent amount of triethylamine was added to catalyst solution to neutralize the HCl, which otherwise would poison the amino group of the monomers. Even after refluxing the mixtures for 48 hrs, a small residual 2160 cm⁻¹ band remained in the IR spectrum of the mixture, so 1-octene was added to try to consume remaining Si-H groups. The ²⁹Si NMR spectra of the final side-chain polysiloxanes showed no peak at -37 ppm for the Si-H groups. However, NMR spectra showed a small peak at 4.7 ppm for Si-H groups. HPS-1 showed about 9% while the other polymers have about 1% of unreacted Si-H groups present in the final structure. HPS-1 was insoluble in organic solvents at room temperature but soluble in hot toluene and chloroform. HPS-1 was purified by precipitation from toluene six times. CPS-1, HPS-2 and CPS-2 were soluble in organic solvents at room temperature and were purified by precipitation six or seven times from chloroform into ethanol. GPC analyses of the molecular weights based on polystyrene standards and residual monomer contents are reported on Table I. GPC analyses using polystyrene standards underestimate the molecular weights of SCLCPs because the hydrodynamic volume of a comb-like polymer is smaller than that of polystyrene of the same molecular weight.⁴

Table I. GPC Analyses of Side-Chain Polysiloxanes

Polymer	M _n	M _w	M _w /M _n	% monomer
PS-1	6,800	9,800	1.4	<1
PS-1	5,400	8,800	1.5	<1
PS-2	19,400	37,600	1.9	2
PS-2	7,200	10,500	1.5	5

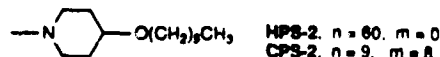
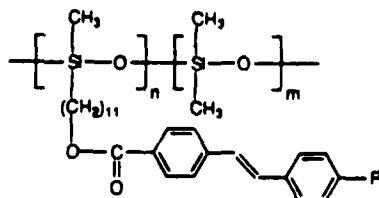
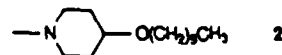
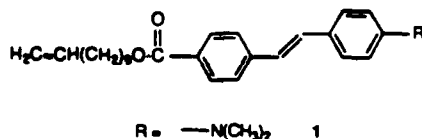


Fig. 1. Structures of monomers, homopolysiloxanes, and copolysiloxanes.

Phase Transitions

Phase transitions of the monomers and the polysiloxanes measured by DSC and microscopy are reported in Table II. The phase assignments are based on powder X-ray diffraction and polarizing optical microscopy. The isotropization temperatures of all of the polymers were obtained by microscopy. The heats of transition from the mesophase to the isotropic liquid phase were too small to observe in the DSC.

Table II. Phase Transition Temperatures of Monomers and Polysiloxanes

Sample	Phase transition temperature ^a , °C (ΔH , kcal mol ⁻¹)					
1		C	146	I		
CPS-1	G -35	C	146 (7.06)	S _A	183 ^b	I
HPS-1		C	167 (4.84)	N	215 ^b	I
2		C	109 (0.54)	S _B	172 (1.52)	S _A 183
CPS-2	G -43	C	112 (0.27)	S _B	182 (1.04)	S _A 220 ^b
HPS-2		C	110 (0.15)	S _B ^c	192 (1.0)	N 258 ^b

^a C = orthorhombic crystal or smectic E, G = glass, I = isotropic, S_A = smectic A, N = nematic, S_B = smectic B. ^b Transition temperatures were determined by microscopy. All other data is from DSC. ^c Possibly an ordered nematic.

There was no evidence of any glass transition for HPS-1 in the range -123 °C to 146 °C. This is likely due to the small volume fraction of the siloxane backbone, making the glass transition too weak to detect. With strong dipole-dipole interactions between the mesogenic side chains, and long flexible methylene spacer chains, the polymer behaves semicrystalline rather than glassy. Annealing of HPS-1, even just below the isotropization temperature, did not give a recognizable texture. Powder X-ray diffraction of HPS-1 at 195 °C showed a diffuse peak in the wide angle region and sharp peaks in the small angle region, characteristic of a nematic phase.

CPS-1 showed a weak, wide glass transition, -35 °C, and only one sphase. The X-ray pattern at 172 °C showed sharp peaks in the small angle region, indicative of smectic layers, and a diffuse peak at the wide angle region, characteristic of the S_A phase. Only a fine grained texture was observed by polarizing microscopy.

HPS-2 had both a high temperature nematic phase and an ordered phase initially assigned as S_B from the powder X-ray diffraction pattern at 171 °C. However, this phase showed no reflections in the small angle region, which meant the absence of layers. Possibly this mesophase is an ordered nematic with hexagonal structure. Friedzon and coworkers⁵ reported a similar X-ray pattern and suggested that it was due to a new phase, N_B, in which the mesogenic groups were packed in a hexagonal array but without translational order in the direction of their long axes. No microscopic texture was obtained for HPS-2.

In addition to a glass transition and a high temperature S_A phase, CPS-2 had a low temperature mesophase assigned a S_B structure, because powder X-ray diffraction pattern at 171 °C showed the typical sharp peaks in the small angle region denoting the presence of layers and a strong sharp peak in the wide angle region corresponding to 110 and 200 reflections. Microscopy of CPS-2 under crossed polarized light showed a typical fan-shaped texture for the S_A phase.

Each polysiloxane exhibited a low temperature crystalline phase notified by X-ray diffraction patterns and reported in Table II. Three sharp peaks in the wide angle region correspond to 110, 200 and 210 reflections, which are characteristic of an orthorhombic crystal. Sharp peaks in the small angle region mean the molecules are arranged in layers. These phases might be S_B, which also gives the three reflections in the wide angle region. To distinguish a smectic E phase from an orthorhombic crystal, one must use an oriented sample for X-ray diffraction studies.

Monolayers

Monolayers of the polysiloxanes were characterized by measurement of the film pressure, Π - mean molecular area, $\bar{A}^2$, isotherm. In this work, an molecular area is defined as area per mesogenic repeat unit of the polysiloxane. The room temperature isotherms in Fig. 2 were reproducible. The curves obtained for HPS-1 and CPS-1 were smooth, without any observable discontinuities, and showed no evidence of phase transformations. Upon extrapolation of the steeply sloping linear region to zero surface pressure, the intercept gives the area per molecule of a closely packed monolayer. The minimum stable areas per mesogenic polysiloxane repeat unit were -23 $\bar{A}^2$ and -34 $\bar{A}^2$ for HPS-1 and CPS-1, respectively. The isotherms for HPS-2 and CPS-2 showed evidence of "phase transitions" just above 30 $\bar{A}^2$ to about 50 $\bar{A}^2$. HPS-2 and CPS-2 gave the same mean molecular area per repeat unit, ~ 30 $\bar{A}^2$. Because side-chain polysiloxane films exhibited high viscosities, it was necessary to use a Langmuir balance, rather than a Wilhelmy plate, to measure the surface pressure. The films can be compressed to about 40 mN/m with no apparent collapse. The copolysiloxanes showed less hysteresis than the homopolysiloxanes upon compression and subsequent expansion of the monolayers. Further compression-expansion runs showed a much improved hysteresis behavior for CPS-1 and CPS-2. Fig. 3 shows the observed surface area of HPS-2 and CPS-2 at 15 mN/m as a function of time. Similar stable monolayer behavior was observed at 15 mN/m for the other polysiloxanes. There was a bigger decrease of the mean molecular area of HPS-1 during the first 30 minutes than observed with CPS-1. The same trend was observed with HPS-2 compared to CPS-2. The reasons of mean molecular area during the first 30 minutes were much different with the dimethylaminostilbene polysiloxanes, HPS-1 and CPS-1, than with the hexyloxypiperidinostilbene polysiloxanes, HPS-2 and CPS-2, due to the greater movement of the side-chain mesogen containing the flexible hexylpiperidino group.

Preliminary deposition experiments were performed on hydrophobic, octadecyltrichlorosilane-treated quartz slides at room temperature. There was no deposition of the monolayers of the polysiloxanes onto a hydrophilic substrate. LB monolayers of CPS-1 were obtained with a transfer ratio of 0.8 during the first dip and a decreasing transfer ratio on succeeding dips. Monolayers of CPS-2 also showed deposition, although the transfer ratio of the first dip was only 0.5. S-1 and HPS-2 did not deposit onto the hydrophobic substrate.

Acknowledgement. This research was supported in part by the Office of Naval Research. We thank Angie Thibodeaux for instruction on the monolayer experiments.

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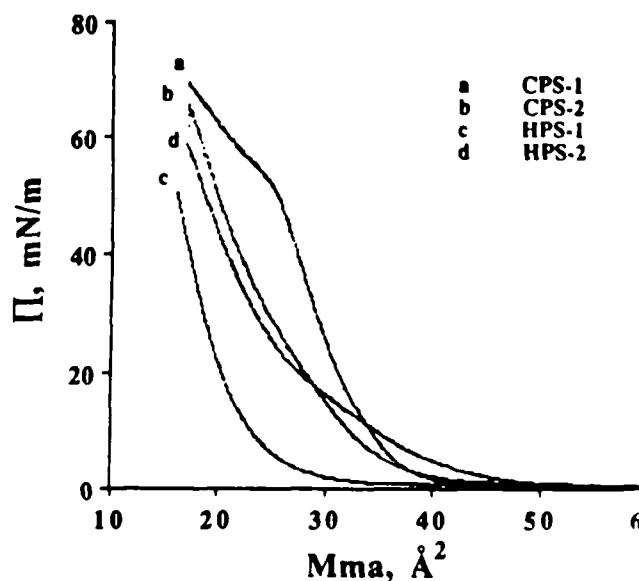


Fig. 2. Surface pressure - area isotherms of polysiloxanes. Each compression took about 1 hr.

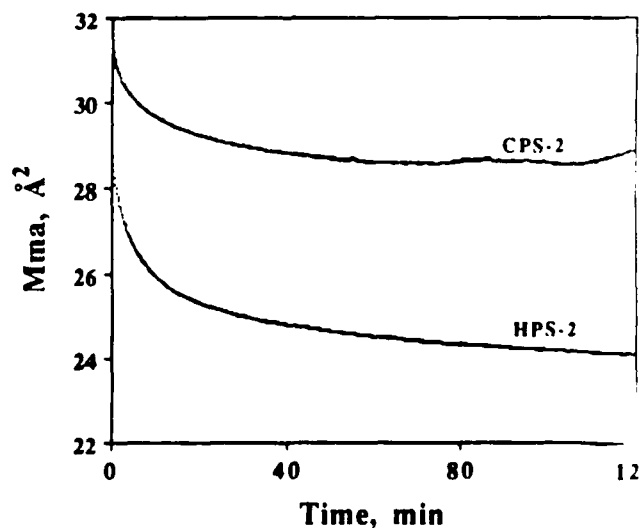


Fig. 3. Molecular area as a function of time at constant film pressure of 15 mN/m and room temperature.

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