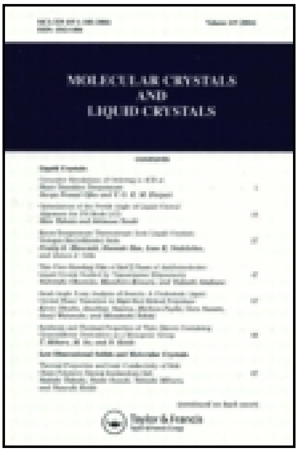

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermotropic and Lyotropic Copolymers of Bis(Dioxyphenyl) Silanes

D. J. Ray [a] , R. M. Laine [b] , T. R. Robinson [a] & C. Viney [c]

[a] Department of Materials Science and Engineering FB-10, University of Washington, Seattle, WA, 98195, USA

[b] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48109, USA

[c] Center for Bioengineering WD-12, University of Washington, Seattle, WA, 98195, USA

Version of record first published: 24 Sep 2006.

To cite this article: D. J. Ray , R. M. Laine , T. R. Robinson & C. Viney (1993): Thermotropic and Lyotropic Copolymers of Bis(Dioxyphenyl) Silanes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 225:1, 153-165

To link to this article: http://dx.doi.org/10.1080/10587259308036225

Mol. Cryst. Liq. Cryst., 1993, Vol. 225, pp. 153–165
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Printed in the United States of America

Thermotropic and Lyotropic Copolymers of Bis(Dioxyphenyl) Silanes

D. JEAN RAY,† RICHARD M. LAINE,†‡ TIMOTHY R. ROBINSON†

†Department of Materials Science and Engineering FB-10, University of Washington, Seattle, WA 98195, USA, ‡Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109, USA

and

CHRISTOPHER VINEY§

Center for Bioengineering WD-12, University of Washington, Seattle, WA 98195, USA

(Received June 3, 1992)

Novel inorganic polymers are synthesized from two-component and three-component solutions of bis(1,2-dioxyphenyl) silane, bis(4-*t*-butyl-1,2-dioxyphenyl) silane and 1,4-dihydroxybenzene (hydroquinone). Molecular modeling predicts that these polymers have extended, linear conformations. Thermotropic nematic liquid crystalline phases are identified by transmitted polarized light microscopy. Additionally, lyotropic nematic phases are formed by polymers dissolved in xylene. Further characterization by diffuse reflectance infrared fourier transform (DRIFT) spectroscopy and differential scanning calorimetry is described.

Keywords: nematic, organometallic, silicon, polymer, thermotropic, lyotropic

INTRODUCTION

Almost all of the compounds known to form liquid crystalline phases are organic, with C, O, N and occasionally S acting as chain-building atoms in the mesogenic segments. Relatively few types of liquid crystalline materials contain organometallic or inorganic moieties, though the list continues to grow:

(a) Both WO_3 and V_2O_5 form anisotropic (also known as "tactoidal") gels[1]; in the latter case, the long range molecular order has been specifically identified as nematic.[2]

(b) Some small molecule liquid crystalline compounds containing a central tetrahedrally-coordinated Si-atom have been identified: di-*iso*-butylsilanediol, in which molecules are hydrogen-bonded as dimers that form a discotic

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§To whom correspondence should be addressed.

arrangement,[3–5] and some tetrakis-siloxysilanes, that form thermotropic nematic and cholesteric phases.[6,7]

(c) Polysiloxane backbones[8] and polyphosphazene backbones (Reference 9, and citations therein) have been used in side-chain liquid crystalline polymers, where the side-chain mesogens are organic.
(d) Aromatic polyesters may be complexed with a metal center to yield smectic or other, unspecified, liquid crystalline phases.[10]
(e) Discotic mesophases may be formed by disk-like complexes that contain a central metal atom.[11–13] Lyotropic phases also form when such complexes are attached as pendant groups to a flexible organic backbone.[14]
(f) Lyotropic *main chain* polymers have been formed by extended chains consisting of acetylenes, phenyl groups, and palladium or nickel atoms.[15]
(g) Thermotropic nematic compounds containing square-planar coordinated Cu(II) atoms in the main chain have been synthesized.[16,17]
(h) Poly(di-*n*-alkyl silanes) thermotropically form columnar liquid crystalline phases.[18,19]

Only in cases (a), (g) and (h) do the inorganic components form a chain-building link in a *main chain thermotropic* polymer. In the present paper, we describe nematic phases formed by main chain random copolymers of biscatechol silane [i.e. bis(1,2-dioxyphenyl) silane] and bis(4-*t*-butyl-catechol) silane [i.e. bis(4-*t*-butyl-1,2-dioxyphenyl) silane]. In these compounds, the tetrahedrally coordinated Si-atoms are linked by pairs of 1,2-dioxyphenyl residues, some of which carry a 4-*t*-butyl group. We also describe the effect on nematic phase formation of replacing a minority of 1,2-dioxyphenyl residues with 1,4-dioxyphenyl groups, through reaction with hydroquinone.

There are several motives for seeking to incorporate a greater variety of elements in liquid crystalline polymers. In materials that are not conformationally rigid (including those discussed here), the formation of liquid crystalline phases depends on the stabilization of shape anisotropy by inter- and intramolecular forces. Our ability to model and predict this type of behavior is predicated on the careful characterization of as diverse a range of chemical compounds as possible. Also, exploration of organometallic and inorganic liquid crystalline polymers is expected to lead to new, processable materials that can be cross-linked for high temperature applications, and the presence of heteroelements in the polymer backbone will promote an extended variety of useful physical properties.

SYNTHESIS

Handling Procedures

Inert atmosphere procedures[20] were followed in all syntheses to avoid product hydrolysis to catechol and SiO_2. Schlenk glassware and a Vacuum Atmospheres (MO40-2) glovebox were used. All procedures were conducted under dry nitrogen.

Polymer Precursors

Catechol, 4-*t*-butyl-catechol and $SiCl_4$ were obtained from Aldrich Chemical Company. Preparation of biscatechol silane from $SiCl_4$ and catechol followed the Allcock synthesis[21] (Scheme I). The synthesis of bis(4-*t*-butyl-catechol) silane is analogous[22] (Scheme I). The ^1H NMR, ^{13}C NMR and IR spectra of these compounds are consistent with previously reported values.[22] Products were amorphous white powders.

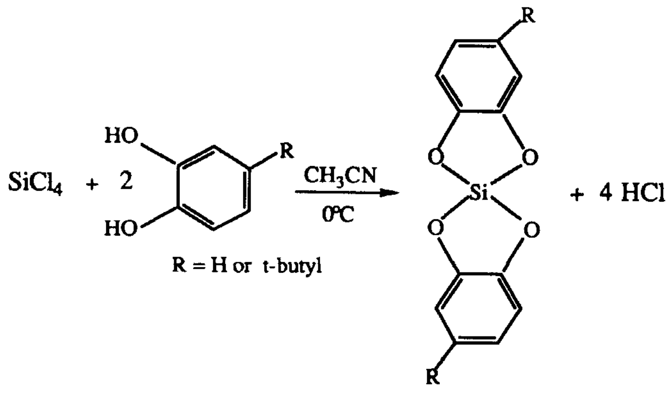
Analysis for residual chlorine in the synthesized compounds was by a microchemical chloride test, using $AgNO_3$.[23] The results were negative, showing that only biscatechol compounds (no dichloro monocatecholato silanes) were produced in the above syntheses.

Preparation of Copolymers

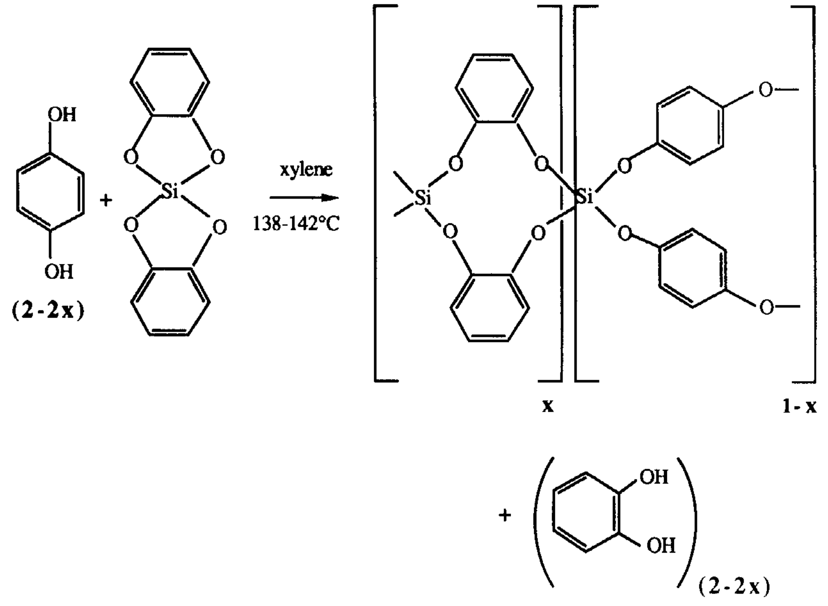
Biscatechol silane and bis(4-t-butyl-catechol) silane. Polymerization was performed in solution, to facilitate mixing. Biscatechol silane and bis(4-*t*-butyl-catechol) silane (0.1–0.3 gm each in the range 93:7 to 33:67 mole%) were weighed in the drybox and placed in suitable Schlenkware. 15–25 ml of dry chloroform (distilled from $MgSO_4$) or dry xylene (distilled from Na) was cannulated into the flask containing the dry reactants under N_2. The reaction mixture was cycled between vacuum and N_2 several times before refluxing under N_2. After refluxing for 90 hours, the solvent was removed by vacuum distillation. Copolymers were yellow to light brown glassy to resinous solids. In order to observe lyotropic liquid crystalline behavior with solvent, these solutions were vacuum distilled only to the point where a gummy or soft residue remained.

Biscatechol silane and hydroquinone. Hydroquinone was obtained from Aldrich Chemical Company. Synthesis was as above, (range 50:50 to 91:9 mole%). Hydroquinone provides 1,4-dioxyphenyl groups that partially or wholly replace 1,2-dioxyphenyl groups (Scheme II). Solids precipitated rapidly from xylene solution and more slowly (one hour) from chloroform. The resulting white solids are easily isolated by filtration and vacuum drying.

Bis(4-t-butyl-catechol) silane and hydroquinone. Synthesis was as above (reac-



SCHEME I



$$\mathrm{Si\,(1,2\ O\text{-}C_6H_4\text{-}O)_2 + (2\text{-}2x)\,(1,4\ HO\text{-}C_6H_4\text{-}OH)} \longrightarrow$$

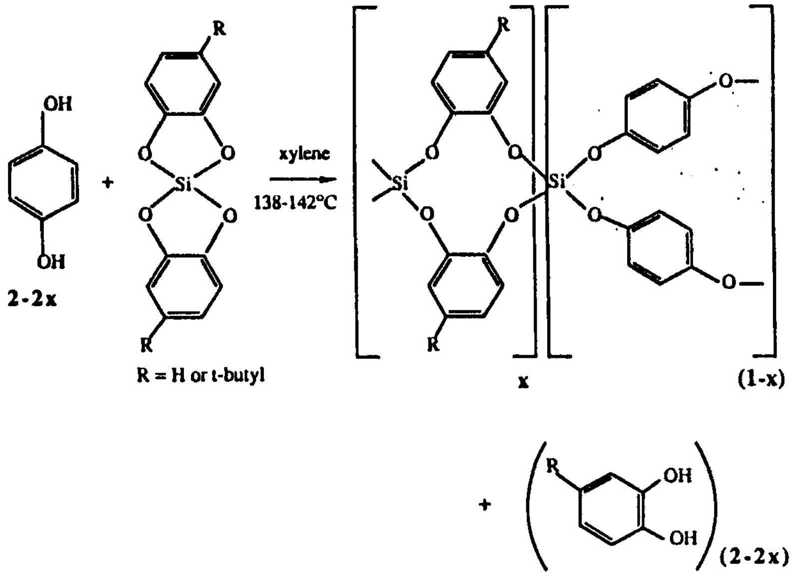
$$\mathrm{[Si\,(1,2\ O\text{-}C_6H_4\text{-}O)_2]_x\ [Si\,(1,4\ O\text{-}C_6H_4\text{-}O)_2]_{1\text{-}x} + (2\text{-}2x)\,(1,2\ HO\text{-}C_6H_4\text{-}OH)}$$

SCHEME II

tant concentrations 52:48 and 91:9 mole%). White solids were precipitated slowly from solution after 48 hours refluxing in xylene.

Biscatechol silane, bis(4-t-butyl-catechol) silane and hydroquinone. Synthesis was as above, with the initial monomer concentrations in the ranges 29–67 mole% biscatechol silane, 20–67 mole% bis(4-*t*-butyl-catechol) silane and 4–33 mole% hydroquinone. At initial hydroquinone concentrations exceeding 9 mole%, solids precipitated during the polymerization in xylene. The solution becomes cloudy, then solids are formed that may be fibrous and adhere to the sides of the container or the stir bar. At 67 mole% biscatechol silane, the reaction solution becomes cloudy within 30 min. of refluxing (138–142°C). The cloudy solution begins to generate precipitate immediately. In contrast, with 67 mole% bis(4-*t*-butyl-catechol) silane, approx. 48 hours of reflux are required before the appearance of a cloudy solution and subsequent gelation. This observation, i.e. that the reaction proceeds more rapidly for higher starting concentrations of biscatechol silane relative to bis(4-*t*-butyl-catechol) silane, is consistent with 4-*t*-butyl-catechol residues providing a greater degree of steric hindrance to attack by hydroquinone.

After refluxing for 72–90 hours, solids present (melting at high temperatures >500°C) were recovered by filtration under N_2 and liquids were evaporated under vacuum. Yellow to brownish polymers and also 1,2 dihydroxybenzene (catechol) were recovered from the liquid phase (Scheme III).



$$\mathrm{Si\,(1{,}2\ O\text{-}C_6H_4\text{-}O)_2 + Si\,[1{,}2\ O\text{-}C_6H_3(\mathit{t}\text{-}Bu)\text{-}O]_2 + (4\text{-}2x\text{-}2y)\,(1{,}4\ HO\text{-}C_6H_4\text{-}OH)}$$

$$\longrightarrow$$

$$\mathrm{[Si\,(1{,}2\ O\text{-}C_6H_4\text{-}O)_2]_x\,[Si\,[1{,}2\ O\text{-}C_6H_3(\mathit{t}\text{-}Bu)\text{-}O]_2]_y\,[\,Si\,(1{,}4\ O\text{-}C_6H_4\text{-}O)_2]_{2\text{-}x\text{-}y}}$$

$$\mathrm{+\ (4\text{-}2x\text{-}2y)\,(1{,}2\ HO\text{-}C_6H_4\text{-}OH}$$

SCHEME III

CHARACTERIZATION METHODS

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy were performed on a Varian XL 300 MHz spectrometer. Proton NMR spectra were obtained with the spectrometer operating at 300 MHz using a 4000 Hz sweep width, 1 sec. relaxation delay time, 82° pulse width, and 16K data points. Carbon NMR spectra were obtained with the spectrometer operating at 75 MHz using 16,000 Hz sweep rate, 0.5 sec. relaxation delay time, 60° pulse width, and 16 K data points. Samples were prepared in the drybox.

Diffuse reflectance infrared fourier transform (DRIFT) spectra were recorded on an IBM FTIR-44 spectrometer. Instrument resolution was 2.00 cm^{-1}, with 32 scans over the region 4000 cm^{-1} to 400 cm^{-1}. Sample pellets were prepared in the drybox by grinding the sample with KBr in an agate mortar and pestle, then pressing a pellet using a Spectra-Tech Econo-Press. The DRIFT sample chamber was purged with N_2 until CO_2 absorbances were no longer detected. The IR peak positions were identified using standard IBM FTIR 40 series software.

Models were built using Chem3D Plus software (version 3.0; Cambridge Sci-

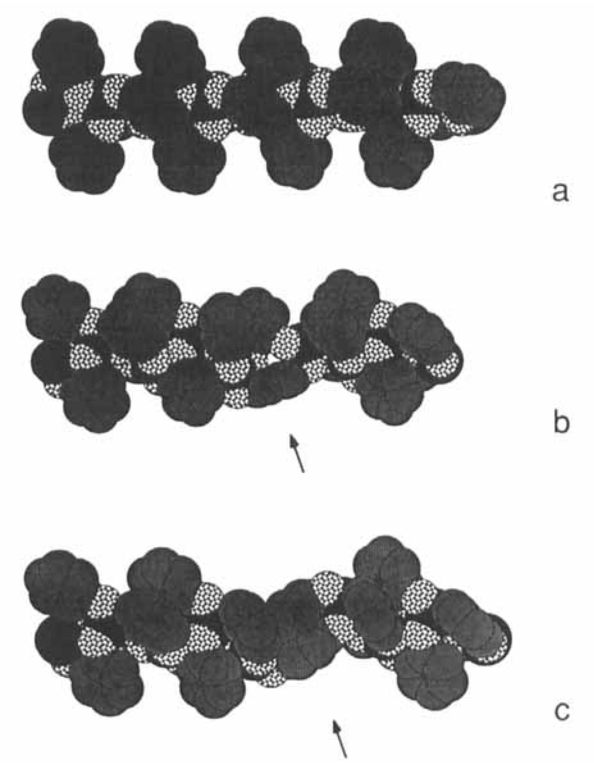


FIGURE 1 Conformation of molecules as predicted with Chem3D Plus software: (a) homopolymer of bis(1,2-dioxyphenyl) silane; (b) effect of replacing a single catechol residue with hydroquinone (arrow); (c) effect of substituting hydroquinone residues (arrow) for both catechol links between a pair of adjacent Si atoms.

entific Computing, Cambridge, MA) on a Macintosh IIci computer, to identify likely molecular conformations.

Light microscopy to identify and photograph liquid crystalline phases was performed on a Leitz Laborlux 12 POL polarizing microscope equipped with a Canon T90 camera. A Linkam 26-THM-600S heating/freezing stage with micromanipulator and 26-PR-600 controller were used to view microstructures at elevated temperatures (600°C maximum). Samples of the polymeric products were held between 18 mm diameter round coverslips, and were loaded into the heating stage in the drybox. The coverslips had previously been treated by a cleaning procedure similar to that recommended[24] as a general procedure for glass substrates used in liquid crystal microscopy. Coverslips were washed in 5% KOH/ethanol for one hour, rinsed in 5% H_2SO_4, followed by water and acetone rinses. They were then dried in a 120°C oven for one hour, and were stored in the drybox until used. All openings into the heating stage were sealed with rubber fittings, to retain the nitrogen atmosphere acquired in the drybox. Specimens on the heating stage were observed through a 32 × (0.40 numerical aperture) objective lens, while specimens at ambient temperature could be observed at up to 100 × (1.32 numerical aperture) with an oil immersion objective. Microstructures characteristic of elevated temperatures

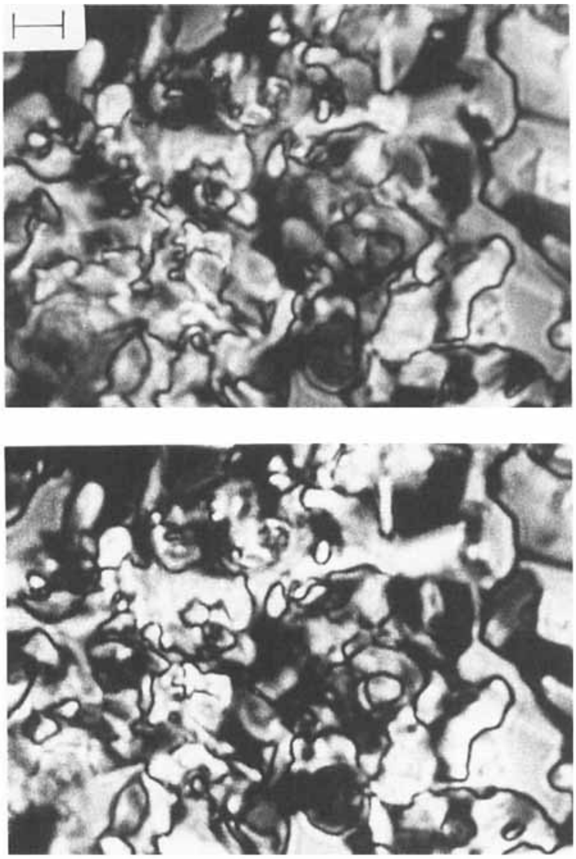


FIGURE 2 Thermotropic nematic schlieren texture of the soluble polymer obtained by reacting xylene solutions of biscatechol silane, bis(4-*t*-butyl-catechol) silane and hydroquinone in a 1:1:1 mole ratio. The specimen was quenched from 300°C. The scale bar represents 10 μm. Crossed polars rotated 15° between top and bottom micrographs.

were preserved to ambient temperature by quenching,[25] so that photomicrographs could be obtained at high resolution.

Thermal analysis was carried out with a Seiko Instrument Co. Differential Scanning Calorimeter DSC 100 (range 0°C–600°C) and SSC 5000 Series Thermal Analysis Disk Station. Specimens were 10 mg. (approximately) sealed samples scanned at 5°C/min or 10°C/min.

RESULTS AND DISCUSSION

Spectroscopic Characterization

The bis(1,2-dioxyphenyl) silane and bis(4-*t*-butyl-1,2-dioxyphenyl) silane polymer precursors were characterized by ^{1}H-NMR and DRIFT spectra. The NMR spectra

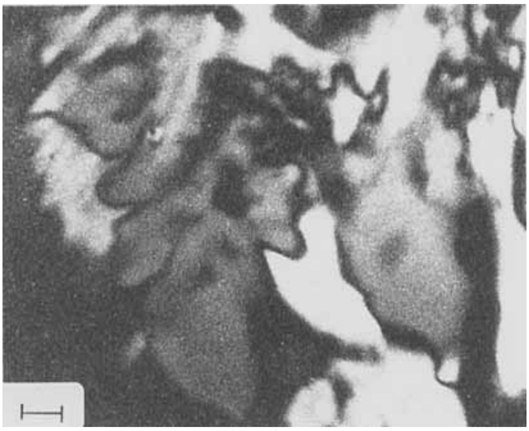


FIGURE 3 Thermotropic inversion wall texture of the soluble polymer obtained by reacting chloroform solutions of biscatechol silane and bis(4-*t*-butyl-catechol) silane in a 1:1 mole ratio. The specimen was quenched from 180°C. The scale bar represents 5 μm.

were compared to literature values[22] and the compounds were found to have no unreacted catechol and only minor solvent residue present. Samples stored in the drybox or in sealed vials were found to have an indefinite shelf life. This was confirmed by comparing the DRIFT spectra of both bis(1,2-dioxyphenyl) silane and bis(4-*t*-butyl-1,2-dioxyphenyl) silane with literature values.[21,22]

DRIFT spectra of the polymer products as recovered from both xylene and chloroform show that the polymers are susceptible to slow hydrolysis in air, but have an indefinite shelf life in the drybox. In all cases where hydroquinone was a reactant, DRIFT spectra of the polymer products confirm the participation of hydroquinone in the reaction: either the 1467 cm^{-1} component of the strong hydroquinone aromatic doublet at 1467–1515 cm^{-1} is missing or it is significantly reduced, and the 1515 cm^{-1} component is shifted slightly. Polymers retain the $\bar{\nu}$ O—H (i.e., intermolecular O—H stretching) of hydroquinone at 3400–3600 cm^{-1}. More detailed polymer syntheses and spectroscopic characterization[26] will be published at a later date.

Molecular Modelling

The energy-minimized conformation predicted for the homopolymer of bis(1,2-dioxyphenyl) silane (Figure 1a) corresponds closely to the published x-ray structure.[27] The substitution of a single 1,2-dioxyphenyl group by a 1,4-dioxyphenyl group does not alter the linear, extended trajectory of the energy-minimized molecular conformation (Figure 1b). Even replacing both 1,2-dioxyphenyl bridges between adjacent Si atoms with 1,4-dioxyphenyl linkages does not change the overall rod-like aspect of the molecules (Figure 1c). Therefore, all the polymers described here are candidates for forming nematic phases, unless there is an overriding preference for crystallization. However, we expect that crystallization will be inhibited if there is no blockiness in the sequence of 1,2-dioxyphenyl and 1,4-dioxyphenyl linkages along the polymer chains.

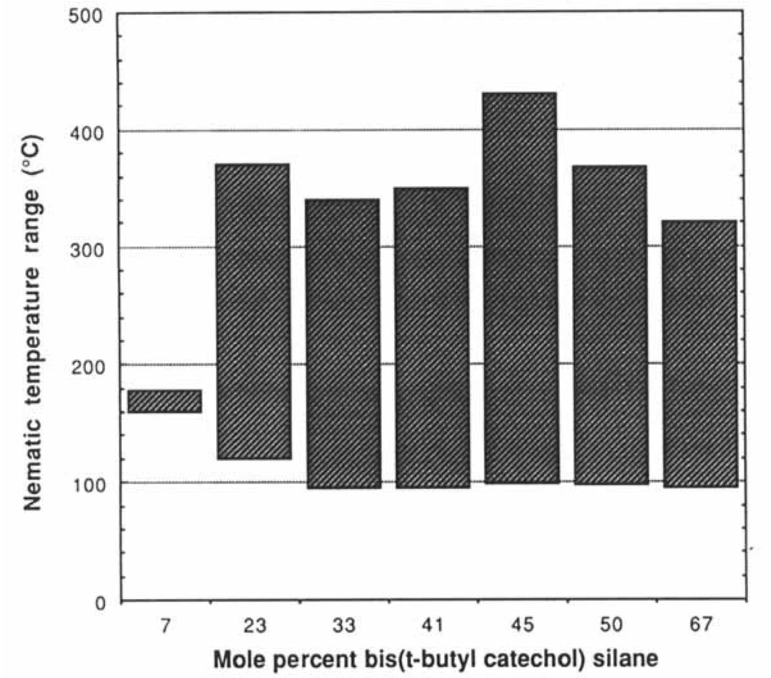


FIGURE 4 Nematic range of polymers prepared from xylene solutions of biscatechol silane and bis(4-*t*-butyl-catechol) silane. Data were obtained by transmitted polarized light microscopy of specimens on a sealed heating stage. The upper limit of the nematic range is masked by specimens tending to form homeotropic textures, and by the onset of degradation.

Transmitted Polarized Light Microscopy

No liquid crystalline phases were observed in samples of bis(1,2-dioxyphenyl) silane or bis(4-*t*-butyl-1,2-dioxyphenyl) silane when examined individually. This is consistent with the results of Eaborn and Hartshorne[3] that the dioxy silanes in general have not shown liquid crystalline behavior. Liquid crystalline phases also were not detected in homopolymers prepared from these individual monomers, or in copolymers prepared from mixed solutions of bis(1,2-dioxyphenyl) silane and hydroquinone. In these cases, it appears that the molecular structure is sufficiently regular to promote crystallization relative to liquid crystallinity.

The remaining types of polymer formed thermotropic nematic phases, and additionally formed lyotropic nematic phases in xylene. The conditions giving rise to liquid crystallinity varied with (1) the ratio of monomers in the polymerization mixture; (2) the temperature at which the polymerization reaction occurred; and (3) the reaction (reflux) time.

All the nematic polymers demonstrated a strong tendency to form *homeotropic* textures, i.e. large areas of the microstructures are dark at all rotations of the crossed polars; the remaining areas of the microstructure exhibited either schlieren textures containing both integral-strength and half-integral-strength disclinations (Figure 2) or domain textures with inversion walls (Figure 3). Because samples were viewed in a sealed heating stage, we could not confirm the nematic nature

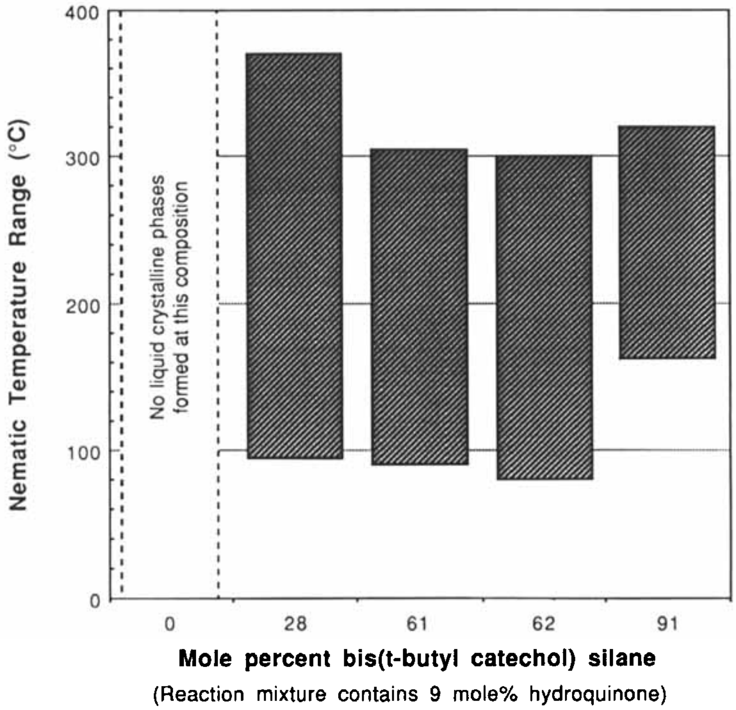


FIGURE 5 Nematic range of polymers prepared from xylene solutions of biscatechol silane, bis(4-*t*-butyl-catechol) silane and hydroquinone. The relative amount of hydroquinone was constant, at 9 mole% of dissolved reactants. Data were obtained by transmitted polarized light microscopy of specimens on a sealed heating stage. The upper limit of the nematic range is masked by specimens tending to form homeotropic textures, and by the onset of degradation.

of the entire sample by shearing the top cover slide. But, it is still possible to demonstrate that the dark regions coexisting with the schlieren or domain textures are in the nematic state: if there were an equilibrium between nematic and truly isotropic material, we would expect the regions of definitive texture to decrease continuously in size as a function of increasing temperature. Instead, we observe that regions of schlieren or domain texture remain unchanged from the temperature at which they first appear, up to the temperature at which they abruptly become isotropic. Not all regions of schlieren or domain texture in a given sample become isotropic at the same temperature, however. Our estimates of the nematic range of a material (Figures 4 and 5) are therefore obtained from microscopic observation of several samples at each composition: the solid-liquid crystal melting transition is identified at the temperature where areas of schlieren or domain texture first appear reversibly on heating, and the nematic-isotropic clearing transition is *at least* as high as the temperature where the last area of distinguishable texture reversibly disappears. In many samples, this temperature overlaps the onset of degradation.

The initial solids precipitated from the three-component polymerization reactions have high melting points (>500°C). Precipitation occurs when the amount of hydroquinone in the reaction mixture exceeds approximately 9 mole%. These con-

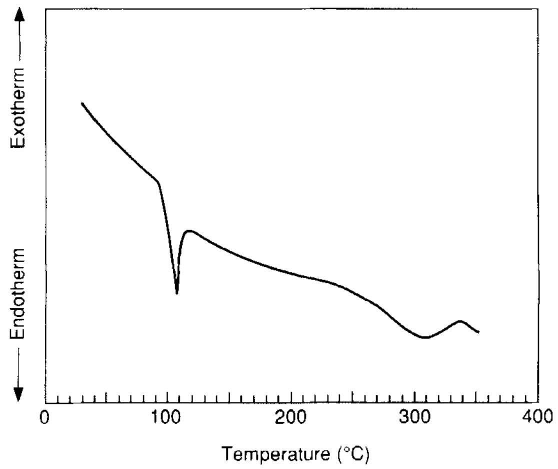


FIGURE 6 DSC heating trace of soluble polymer recovered from reaction of biscatechol silane and bis(4-*t*-butyl-catechol) silane (1:1 mole ratio) in xylene solution. A well-defined endotherm corresponding to the onset of liquid crystallinity at 94°C is seen. A broader endotherm centered at approximately 310°C may indicate the transition to the isotropic phase; its high-temperature side leads into the irregular oscillations that are characteristic of specimen degradation.

centrations of hydroquinone are apparently sufficient to promote a significant degree of cross-linking between the polymer chains,[28] rendering them insoluble.

Differential Scanning Calorimetry

A typical DSC trace of a sample being heated is shown in Figure 6. On initial inspection, the trace appears to exhibit a steeply tilting baseline. However, this feature is preserved at both higher and lower heating rates, and so cannot be a simple baseline artifact. Instead, we identify it as the low-temperature side of a broad "background" endotherm, extending over more than 200°C, and upon which more well-defined endotherms are superimposed. This type of behavior has been observed previously for organic thermotropic random copolymers,[25,29] where it has been interpreted as the melting of highly localized regions of order that arise from chance association between identical random monomer sequences on adjacent molecules.[30] Because a wide range of sequences and lengths are involved, they melt out over a wide range of temperatures. In the present case, we regard the broad DSC endotherms as supporting evidence that we have succeeded in preparing *random* copolymers. The sharp endotherm with an onset temperature of 94°C in Figure 6 corresponds to the temperature at which light microscopy first reveals liquid crystallinity in specimens of this composition. Light microscopy also suggests that the endotherm centered at approximately 310°C coincides with the nematic-to-isotropic transition in this material—though simultaneous specimen degradation at this temperature makes definitive textures difficult to obtain.

CONCLUSIONS

1. Copolymers synthesized from biscatechol silane and bis(4-*t*-butyl-catechol) silane consist of rod-like molecules that form nematic liquid crystalline phases.

The nematic phases form both thermotropically and lyotropically, in the latter case with xylene as the solvent.

2. Similar observations pertain to copolymers synthesized from biscatechol silane, bis(4-*t*-butyl-catechol) silane and hydroquinone.
3. Many of these liquid crystalline polymers are nematic over a wide temperature range, with the reversible clearing point for some compositions exceeding 400°C.

Acknowledgments

The authors are grateful to Dr. David Treadwell for helpful discussions, and to Susan Abrams and Dr. Paul Yager for access to and training on DSC equipment. Funding was provided by the Air Force Office of Scientific Research (AFOSR) through grant No. F49620-89-C-0059, and by the Washington Technology Centers.

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