methanol should be added to keep the loss of volatiles to a minimum.

Registry No. Chloroform, 67-66-3; 1,1,1-trichloroethane, 71-55-6; trichloroethylene, 79-01-6; carbon tetrachloride, 56-23-5; bromodichloromethane, 75-27-4; 1,1,2-trichloroethane, 79-00-5; tetrachloroethylene, 127-18-4; 1,2-dibromoethane, 106-93-4; bromoform, 75-25-2; 1,1,2,2-tetrachloroethane, 79-34-5; benzene, 71-43-2; toluene, 108-88-3; chlorobenzene, 108-90-7; *p*-xylene, 106-42-3; *o*-xylene, 95-47-6; *p*-chlorotoluene, 106-43-4; *o*-chloro-toluene, 95-49-8.

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Synthesis and Properties of High-Temperature Mesomorphic Polysiloxane Solvents: Biphenyl- and Terphenyl-Based Nematic Systems

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The synthesis and characterization of a variety of mesomorphic (liquid--crystalline) side-chain polysiloxane (MEPSIL) solvents, said to be useful as gas chromatographic stationary phases, are described and discussed. The synthetic scheme is based upon the hydrosilation reaction that occurs when 4-(allyloxy)benzoyl esters are contacted with poly(methylsiloxane) in the presence of a dicyclopentadienylplatinum(II) catalyst, while product characterization is carried out by IR, NMR, GC, DSC, elemental analysis, and direct-observation hot-stage light-polarized microscopy. Selectivity of the **MEPSIL** phases is shown to differ very substantially from those exhibited by all other common GC solvents. The MEPSIL found overall to be the best suited as a GC stationary liquid exhibits a melting point of 139 $^{\rm o}{\rm C}$ (k \rightarrow n) and a nematic/isotropic (n \rightarrow I) transition temperature of 319 °C, while the practical operating limits of the material span 150 to in excess of 300 °C.

The development and optimization of chromatographic techniques for maximal resolution in minimal time of analysis, coupled with maximum sample throughput, continue to represent a substantial problem when dealing with analytes comprised of structurally related isomers. Among the most notably difficult of these are polycyclic aromatic hydrocarbons (PAH) which are, at the very least, ubiquitous environmental pollutants produced by the incomplete combustion of organic matter. Moreover, some of the most efficient carcinogens known at present are members of, or products derived directly from, this class of compounds. In addition, the carcinogenic and mutagenic properties of these materials are frequently found to be isomer specific. Major efforts have therefore been directed in chromatography at the separation of these species (1).

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²Present address: Department of Chemistry, University of Kuwait, Kuwait, Kuwait. Reverse-phase packings and selective detection in column-liquid (2) and supercritical fluid (3) chromatographic techniques have been utilized for the separation of PAH isomers in a number of cases; however, the present state of technology in each of these methods precludes the high column efficiency necessary for analysis of complex mixtures comprised of large numbers of components.

In gas-liquid chromatography (GLC), studies of the separation of PAH have been concerned mainly with the fabrication of open-tubular columns of ever-higher efficiency with "slightly polar" phases such as SE-52 and SE-54. And, while some degree of success has certainly attended these efforts (4, 5), it is nonetheless fair to say that the resolution of isomers such as anthracene/phenanthrene, benz[a]anthracene/triphenylene/chrysene, and benzo[a]pyrene/benzo[e]pyrene/ perylene/benzofluorenes is not entirely satisfactory, particularly when quantitation of these materials is attempted at parts-per-billion levels in natural or industrial matrices.

In contrast, it has been recognized for some time that liquid-crystalline (mesomorphic) stationary phases (the nematic state in particular) provide enhanced GLC separations of many isomeric species, including PAH, that are difficult or impossible to resolve by other traditional chromatographic techniques (1, 6-13). Unlike most other common GLC solvents that provide separations based upon solute vapor pressure and/or differential solubility arising from specific energetic interactions, nematic stationary phases yield separations based upon differences in solute molecular shape or, in the instance of cholesteric phases, solute chirality. Simply put, rodlike mesomorphs exist in the bulk-liquid state in well-ordered domains such that the more rodlike the solute isomer, the more readily it is accommodated into the nematic matrix and, hence, the longer it is retained. Thus, mesomorphic solvents provide selectivity on an entirely different basis from all other GLC stationary phases.

However, the liquid-crystal phases reported to date suffer from column bleed as a result of volatility at high temperatures, poor column efficiency as a result of slow kinetics of mass transfer, and restricted useful nematic ranges. Even so, Laub and his co-workers (14-18) have argued that a suitable member representative of this class of materials must be defined in order, if nothing else, to identify a standard set of stationary phases (i.e., no more than a half dozen or so solvents) with which all GLC separations can be achieved (19–26). Accordingly, and in attempts at overcoming the limitations of mesomorphic materials, Laub, Roberts, and Smith (18) blended N,N'-bis(p-butoxybenzylidene)- α,α' -bi-p-toluidine (BBBT; nematic) stationary phase with SE-52. This resulted in much improved column efficiency but, in spite of the reduction of column bleed in approximate accord with Raoult's law, there remained the inconvenience of fabrication of blended-phase systems; nor could the useful temperature range of the liquid-crystalline phase be expanded.

As a result, the synthesis of nematic siloxane polymers exhibiting high column efficiency as well as low bleed, yet providing high selectivity over a wide temperature span, was undertaken by us several years ago, the preliminary results of which we have reported elsewhere (17, 27). The compounds synthesized initially comprised a series of grafted polymers in which the liquid-crystalline side chains resembled the teeth of a comb, attached with flexible spacers, running the length of the polymer backbone. However, in independent evaluations carried out by others on materials synthesized in this laboratory (28), the earlier versions of these species, since christened by us MEPSIL (mesomorphic polysiloxanes), were found to suffer from the drawbacks of comparatively meager column efficiency and poor thermal stability arising from incomplete substitution of all available hydrogen on the starting poly(methylsiloxane), as well as polymer cross linking. Moreover, the batch-to-batch reproducibility of the synthetic procedures, as well as yields, was poor. We therefore undertook to clarify, then simplify, the synthesis scheme, and then to synthesize and characterize fully a variety of MEPSIL products. We report in this work the results for biphenyland terphenyl-based nematic systems. In addition, and for the first time, we provide in detail descriptions of each synthetic step, including equivocal aspects that we have come across during the course of our studies, in order to encourage continued investigations of these materials by others (29).

EXPERIMENTAL SECTION

Materials. Poly(methylsiloxane) of the general formula



was obtained from Silar, Petrarch, or Wacker Chemie (Munich, West Germany). All other chemicals and reagents were from Aldrich Chemical Co.

Apparatus and Equipment. Differential scanning calorimetry (DSC) was performed with a Perkin-Elmer Model DSC-2. Light microscopy was carried out with a Leitz (West Germany) microscope equipped with a cross-polarized light source and fitted with a Reichert (Austria) hot stage. Viscosities were measured with an Ostwald tube at 25 °C (30) utilizing water as a reference. Systems were thermostated with a Neslabs RTE-8 water bath. Gel permeation chromatography (GPC) was conducted with a TSK-3000 column (Varian) and THF solvent, with a Varian Model 5000 liquid chromatograph and Varian Variable UV-Vis detector set at 220 nm. The gas chromatograph used throughout was a Carlo Erba 4160. Chromatograms were obtained on a 1-mV full-scale Linear strip chart recorder at the highest electrometer setting of the GC. Pyrex glass-capillary columns (15 m \times 0.25 mm i.d.) were drawn with a Shimadzu GDM-1 glass-drawing machine. Mass spectral data were acquired with an AEI MS-9 mass spectrometer. Infrared spectrometry was performed with a Perkin-Elmer Model 337, while nuclear magnetic resonance spectrometry was carried out with a Varian Model HA-100. The rotating-disk thin-layer chromatograph was an Hitachi CLC-5 equipped with a 5-cm spacer ring. Elemental analyses were



Figure 1. Reaction scheme for synthesis of MEPSIL solvents.

performed by Galbraith Laboratories. The centrifuge was a Du Pont Sorval Model RC-5B refrigerated superspeed.

GC Column Fabrication and Utilization. Drawn tubes were leached with 20% HCl overnight and subsequently flushed with 0.75 M HCl and then water. They were dried at 250 °C, followed by silvlation with hexamethyldisilazane as described by us previously (14, 31). After being rinsed with methanol and dried with nitrogen, a typical column was filled with a solution of 1.6 mg cm⁻³ MEPSIL polymer in chloroform, calculated so as to produce a film thickness of ca. 0.1 μm . One end was then sealed and the other end attached to a vacuum pump, and the entire column placed in a water bath at 35 °C in order to hasten the evaporation of volatile solvent. Columns were conditioned at 300 °C with hydrogen (the carrier gas in all instances) until a stable base line was obtained at the maximum sensitivity of the instrument. The mobile phase was split at a ratio of 50:1 in order to maintain an average linear velocity of 40 cm s⁻¹ as measured from the retention time of methane.

Synthetic Procedures. The general reaction scheme is shown in Figure 1. Poly(methylsiloxane) (I) is contacted (refluxing toluene solvent; 24 h) with monomer II containing a vinyl group whereupon, in the presence of a platinum catalyst III, hydrosilation takes place yielding the desired mesomorphic polysiloxane (MEPSIL) IV.

Preparation and Properties of Reactant Polymer I. Poly-(methylsiloxane) materials vended commercially are polydisperse, and it was found to be beneficial from the standpoint of product reproducibility to remove low- to intermediate molecular weight homologues. This was carried out just prior to use of the polymer in grafting reactions by isothermal dissolution of the starting material twice from benzene by the addition of methanol at 20°C (32). Thus, 20 cm³ polymer was taken up in 80 cm³ benzene and placed in a 250-cm³ separatory funnel to which had been attached a glass water jacket. Methanol (140 cm³) was then added gradually with mechanical stirring with a glass rod. The solution was allowed to stand for 2 h, whereupon two phases separated. The lower layer (ca. 80% v/v of the starting polymer) was then drawn off and the procedure was repeated with it with 80 cm³ benzene and 100 cm³ methanol. The recovered polymer was then placed in a vacuum line at 10^{-3} torr for 12 h in order to remove any residual dissolved methanol. The product was stored under nitrogen; recoveries amounted routinely to 40% v/v, i.e., 8 cm³ of polymer. The appearance of gas bubbles upon the addition of methanol indicated that the solution temperature was too high: methanol reacts with siloxane hydrogen at elevated temperatures to produce molecular hydrogen (given off as a gas) and poly-(methoxymethylsiloxane).

The densities of the starting polymers (Silar, I.A.1; Petrarch, I.B.1; Wacker, I.C.1) were all ca. 0.98-1.02 g cm⁻³ at 25 °C. The averages of three repetitive determinations of viscosities at 25 °C were as follows: I.A.1, (value not quoted by the manufacturer), 28.8 mm² s⁻¹ found; I.B.1, 15-30 mm² s⁻¹ stated by the manufacturer, 26.4 mm² s⁻¹ found; I.C.1, 30 mm² s⁻¹ stated, 31.9 mm² s⁻¹ found. The stated molecular weights were 3500 for I.A.1 (n = 58 in Figure 1) and 2270 for I.C.1 (n = 38), although the viscosities belie these values. No molecular weight information was provided for I.B.1 although, considering the viscosity data, it must presumably be less than ca. 2500 (n = 40). The high molecular weight fraction of the Silar polymer, I.A.2, was used throughout in what follows.

Synthesis of 4-(Allyloxy)benzoyl Chloride. The spacer group linking the polymer backbone with the mesomorphic side-chain unit comprised throughout this work 4-(allyloxy)benzoic acid ester, the acid chloride precursor to which was synthesized in two stages. First, 4-(allyloxy)benzoic acid was prepared as follows: into a 1-L three-neck round-bottom flask equipped with a reflux condenser, an addition funnel, a heating bath, and a magnetic stirrer was placed 90 g (0.65 mol) of 4-hydroxybenzoic acid; to this was added 400 cm³ of methanol at 25 °C, which produced a brown solution. To this solution was added dropwise 105 g (1.9 mol) of potassium hydroxide in 125 cm³ of distilled water. The reaction was heated to reflux and 90 g (0.74 mol) of allyl bromide was then added over a 1-h period. The reaction mixture was allowed to reflux for 8 h at which point 250 cm³ of methanol was removed by single-stage distillation. The remainder of the reaction mixture was cooled to 25 °C and added to 1 dm³ of distilled water. The aqueous solution was extracted three times with 200 cm³ of diethyl ether to remove organic impurities and the ether layer was discarded. The remaining aqueous phase was heated to 40 °C in a fume hood and neutralized with 300 cm³ of 20% aqueous HCl, which caused the product to precipitate. The crude acid was recovered by suction filtration and purified by recrystallizing twice from ethanol, yielding 107 g (60%), mp 165 °C.

4-(Allyloxy)benzoyl chloride was then prepared as follows: to a 100-cm³ round-bottom flask equipped with a reflux condenser, a drying tube, a magnetic stirrer, and a heating bath was added 50 g (0.28 mol) of 4-(allyloxy)benzoic acid prepared as above, 50 cm³ (0.42 mol) of thionyl chloride, and 10 drops of dimethylformamide. The reaction mixture was protected from moisture and allowed to stir overnight at room temperature. It was then heated to 60 °C for 2 h to ensure complete reaction. The excess thionyl chloride was removed in vacuo and the crude product was vacuum distilled at 100 °C/1 torr yielding 50 g (90%) as a pale yellow liquid which was stored in a tightly sealed glass bottle.

Synthesis of [4-(Allyloxy)benzoyl]-4-methoxyphenyl Monomer II.A. Into a 250-cm³ three-neck round-bottom flask equipped with a reflux condenser, a drying tube, a dropping funnel, and a magnetic stirrer was placed 14 g (0.11 mol) of 4-methoxyphenol, 150 cm³ of dry THF, and 16 cm³ of pyridine. The mixture was protected from moisture with nitrogen. Over a 2-h period, 22 g (0.11 mol) of 4-(allyloxy)benzoyl chloride in 20 cm³ of dry pyridine was added through the dropping funnel. The mixture was stirred at room temperature for 4 h after the addition was completed. It was then heated to 60 °C for 2 h; after cooling, the reaction mixture was added to 200 cm³ of distilled water and then neutralized with 20% aqueous hydrochloric acid. The solution was then extracted three times with diethyl ether, the organic phase being saved. The ether was removed by rotary evaporation and the crude product, II.A, was recrystallized twice from ethanol yielding 20 g (64%), mp 87-88.5 °C.

Synthesis of 4-[[4-(Allyloxy)benzoyl]oxy]-4'-methoxybiphenyl Monomer II.B. To 400 cm³ of 10% aqueous sodium hydroxide cooled to 0 °C in an ice bath was added 75 g (0.40 mol) of 4,4'dihydroxybiphenyl with vigorous stirring. Fifty grams (0.40 mol) of dimethyl sulfate was then added under a nitrogen atmosphere to the reaction mixture over a period of 1 h, again with vigorous stirring. After the addition was complete, the resultant precipitate was removed by filtration with a sintered glass filter and redissolved in 400 cm³ of 10% aqueous sodium hydroxide. The solution was heated briefly to boiling and allowed to cool, followed by filtration. The solid mass was placed in 2 dm³ of water, heated to boiling, and this time filtered while hot. The filtrate was then heated to 70 °C, and 20% aqueous hydrochloric acid was added until the solution became acidic. The product thereupon precipitated as white crystals, which were recrystallized twice from ethanol yielding 24 g (30%) of 4-hydroxy-4'-methoxybiphenyl.

Next, into a 250-cm³ three-neck round-bottom flask equipped with a dropping funnel, a reflux condenser, and a magnetic stirrer was placed under a nitrogen blanket 12 g (0.06 mol) of 4hydroxy-4'-methoxybiphenyl, prepared as above, dissolved in 100 cm³ of dry pyridine. To this solution was added 12 g (0.06 mol) of 4-(allyloxy)benzoyl chloride dissolved in 20 cm³ of pyridine over a 1-h period with stirring. The mixture was stirred for an additional 3 h at room temperature, and then heated to 60 °C for 2 h. It was cooled again to room temperature, and then added to 400 cm³ of distilled water, following which the mixture was acidified with 20% aqueous hydrochloric acid. The resultant precipitate was removed by suction filtration and washed with 400 cm³ of distilled water. The crude solid, II.B, was recrystallized twice from acetone yielding 15 g (70%), mp 147–148.5 °C.

Synthesis of 4-[[4-(Allyloxy)benzoyl]oxy]-4'-methoxy-p-terphenyl Monomer II.C. Into a 2-dm³ three-neck round-bottom flask equipped with an addition funnel, a reflux condenser, and a mechanical stirrer was placed 11 g (0.45 mol) of magnesium turnings and 8 cm³ of *p*-bromoanisole dissolved in 200 cm³ dry tetrahydrofuran (THF). A small crystal of iodine was introduced and the reaction mixture, under nitrogen, was heated to reflux with a water bath. After the reaction had begun, 48 cm³ of p-bromoanisole dissolved in 900 cm³ of THF was added over a 1-h period with stirring. To the product mixture, i.e., p-anisylmagnesium bromide, still under nitrogen, was added 25 g (0.22 mol) of 1,4-cyclohexadienone dissolved in 220 cm³ of THF over a 35-min period. Vigorous stirring was continued for an additional hour. The resultant solution was then poured into 1 dm³ of 10% aqueous ammonium chloride. The organic phase was recovered in a separatory funnel, washed with water, and dried over sodium sulfate. The solvent was removed by rotary evaporation, yielding 57 g of an oil. This was redissolved in 1.30 dm³ of toluene containing 3.6 g of *p*-toluenesulfonic acid. The reaction mixture was refluxed for 6 h, water produced during the reaction being removed with a Dean-Stark trap. The solution was then cooled in ice water, and the solid precipitate, 4,4'-dimethoxy-p-terphenyl, was removed by filtration yielding 10 g (15%), mp 270-275 °C.

Next, in a 1-dm³ three-neck round-bottom flask equipped with a reflux condenser, a pressure-equalizing addition funnel, a magnetic stirrer, and an oil bath was placed the above-described 10 g (0.034 mol) of 4,4'-dimethoxy-*p*-terphenyl in 600 cm³ of dry benzene, the mixture then being taken to reflux. To this solution was added 11 cm³ of 1 M boron tribromide in benzene over a 2-h period. The mixture was refluxed an additional 2 h and then cooled to room temperature. Subsequently, it was added to 4000 cm³ of water, the organic phase was removed, and the aqueous phase extracted with two 500-cm³ portions of warm toluene. All of the organic phases were combined and reduced to dryness by rotary evaporation. The crude product, 4-hydroxy-4'-methoxy*p*-terphenyl, was purified by rotating-disk thin-layer chromatography (33, 34) with silica stationary phase and dichloromethane mobile phase; the yield was 0.3 g (3%).

Finally, into a 25-cm³ round-bottom flask equipped with a reflux condenser, a magnetic stirrer, and an oil bath was placed the above-described 0.3 g (0.0011 mol) of 4-hydroxy-4'-methoxy-*p*-terphenyl and 0.5 g (0.0025 mol) of 4-(allyloxy)benzoyl chloride in 15 cm³ of dry pyridine. The mixture was refluxed for 24 h; after cooling to room temperature, it was added to 30 cm³ of distilled water and acidified with 20% aqueous hydrochloric acid. The precipitate was filtered off and washed with 50 cm³ of fast-urated aqueous sodium bicarbonate, and then 75 cm³ of distilled water. The crude product, II.C, was purified by rotating-disk thin-layer chromatography, yielding 0.2 g (41%).

Synthesis of [4-(Allyloxy)benzoyl]biphenyl Monomer II.D.Into a 250-cm³ round-bottom flask equipped with a reflux condenser and a magnetic stirrer was placed 4.85 g (0.029 mol) of 4-phenylphenol dissolved in 50 cm³ of dry pyridine under nitrogen. To this solution was added 5.7 g (0.029 mol) of 4-(allyloxy)benzoyl chloride with stirring. The mixture was stirred for 3 h at room temperature and then heated to 60 °C for an additional 2 h. After the reaction mixture had cooled, it was added to 200 cm³ of water, and then acidified with 20% aqueous hydrochloric acid. The resultant precipitate was removed by suction filtration and washed with 200 cm³ of distilled water. The crude product, II.D, was recrystallized from 1:1 v/v acetone:ethanol yielding 7 g (75%), mp 138–140 °C.

Synthesis of [4-(Allyloxy)benzoyl]-p-terphenyl Monomer II.E. To a vigorously stirred suspension of 50 g (0.22 mol) of p-terphenyl in 250 cm³ of refluxing glacial acetic acid was added a solution of 35 cm³ red fuming nitric acid and 55 cm³ of acetic acid over a 4-h period. The mixture was then cooled in an ice bath, whereupon the solid yellow precipitate, 4-nitro-p-terphenyl, was removed by filtration with a sintered glass funnel. The crude product was recrystallized from nitromethane yielding 50 g (85%), mp 209-213 °C.

Next, into a 2-dm³ three-neck round-bottom flask equipped with a mechanical stirrer, a reflux condenser, a dropping funnel, and an oil bath was placed 20 g (0.07 mol) of 4-nitro-*p*-terphenyl, prepared as described above, and 1 dm³ of 95% ethanol. After warming to 50 °C, 0.1 g of a catalyst consisting of 10% palladium on charcoal was added and stirring was commenced. Ten cubic centimeters of hydrazine hydrate was then added from the dropping funnel over a period of 30 min. After the addition was complete, another 0.1 g of catalyst was added and the mixture then refluxed for 4 h. The hot solution was filtered through Celite to remove the catalyst and the filtrate taken to dryness with a rotary evaporator. The crude product, 4-amino-*p*-terphenyl, was purified by rotating-disk thin-layer chromatography. The yield was 17 g (85%), mp 200-202 °C.

4-Hydroxy-p-terphenyl was then prepared as follows: in a 1-dm³ three-neck round-bottom flask fitted with a mechanical stirrer, a dropping funnel, and a thermometer was placed 8.9 g (0.036 mol) of 4-amino-p-terphenyl in 250 cm³ of glacial acetic acid. The mixture was heated to 70 °C with stirring. Next, 32 cm³ of concentrated sulfuric acid was added dropwise as the mixture was cooled to 0 °C in an ice-salt bath. A solution of 3.4 g of sodium nitrite in 15 cm³ of water was then added over a 20-min period. Stirring was continued for 15 min, following which 250 cm³ of ice water containing 4 g of urea was added in small portions. The mixture was filtered by suction while being maintained at 5 °C. Separately in a 2-dm³ one-neck round-bottom flask was placed 500 cm³ of water and 120 cm³ of concentrated sulfuric acid. The mixture was heated to reflux, to which was added the cold diazonium solution over a 20-min period, refluxing then being continued for an additional 30 min. The mixture was then cooled and the crude product, 4-hydroxy-p-terphenyl, was purified by sublimation at 170 °C/0.2 torr yielding 0.5 g (5%), mp 273-276 °C

Finally, into a 50-cm³ round-bottom flask equipped with a reflux condenser, a magnetic stirrer, and an oil bath was placed 0.43 g (0.0017 mol) of 4-hydroxy-p-terphenyl and 0.5 g (0.0025 mol) of 4-(allyloxy)benzoyl chloride dissolved in 20 cm³ of dry pyridine. The mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was added to 50 cm³ of distilled water, and then acidified with 20% aqueous hydrochloric acid. The precipiate was filtered and washed with 100 cm³ saturated aqueous sodium bicarbonate, followed by 100 cm³ of distilled water. The crude product, II.E, was recrystallized from toluene yielding 0.5 g (72%).

Synthesis of Dicyclopentadienylplatinum(II) Chloride Catalyst III. The catalyst used for all grafting reactions was dicyclopentadienylplatinum(II) chloride, III. We found that the synthesis of this material described by Stille and Fox (35) did not proceed as described and that what yields were obtained were poor; we therefore developed a synthetic route to the catalyst that was based upon those reported by Kharasch and Ashford (36) and Drew and Doyle (37). Thus, 2.76 g of hydrated chloroplatinic acid was dissolved in 6 cm³ of glacial acetic acid in a 25-cm³ flask. The solution was diluted with 10 cm³ of water and then heated to 70 °C. Two cubic centimeters of dicyclopentadiene was then added to the reaction vessel, and the mixture was stirred vigorously for 24 h at this temperature. The crude product was collected by filtration, decolorized with charcoal, and finally recrystallized twice from tetrahydrofuran, yielding 1.2 g (71%), mp 218 °C. The structure was verified by NMR and by MS. Synthesis of MEPSIL Polymers IV.A–E. Into a 250-cm³

Synthesis of MEPSIL Polymers IV.A–E. Into a 250-cm³ round-bottom flask modified with a stopcock and an injection port was placed 2.3×10^{-3} mol of 4-allyloxybenzoyl ester II (e.g.,



Figure 2. Gel permeation chromatograms (a) of reactant-polymer I.A.1 as received and (b) after fractional dissolution twice from benzene: column, TSK 3000H; detection at 220 nm; 0.05 absorbance units full scale; flow rate, 1.0 cm³ min⁻¹ of tetrahydrofuran mobile phase.

1.0 g of II.B) dissolved in 100 cm³ of dry and freshly distilled toluene. Into this was pipetted 0.15 g (4.29 \times 10⁻⁵ mol; 60.1 g equiv⁻¹) of starting polymer I.A.2, i.e., a 10% excess of monomer over a mole ratio of 1:1 based upon siloxane hydrogen. The flask was then equipped with a reflux condenser and the contents were protected from moisture and air with a stream of nitrogen. The reaction mixture was heated to boiling, and 100 μ g of catalyst per gram of product, III, was then injected with a syringe as a solution (1 mg cm⁻³) in dichloromethane. The mixture was refluxed under nitrogen atmosphere at 110 °C for 24 h. The solution was then cooled and the product precipitated by the addition of an excess of methanol. Following this, the product was collected by centrifugation at 15000 rpm for 20 min. The supernatant was discarded and the polymer taken up in toluene, following which it was reprecipitated with methanol and collected once more by centrifugation. The wet gellike material was partially dried under a stream of nitrogen, drying being taken to completion in a vacuum oven at 110 °C for 24 h.

Replicate elemental analyses were performed on MEPSIL IV.B. Anal. Calcd. for $Si_{60}C_{1396}H_{1410}O_{291}$: Si, 6.86; C, 68.39; H, 5.79; O, 18.96 w/w. Found: Si, 6.96; C, 67.48; H, 5.81; and O, 19.47 w/w.

RESULTS AND DISCUSSION

Reactant-Polymer Preparation. Figure 2 illustrates the effects of the clean-up procedure on the molecular weight distribution of the reactant polymer I. The trace shown in (a) is the gel permeation chromatogram of starting material as received from Silar (I.A.1), while that in (b) (I.A.2) shows the GPC obtained after fractional dissolution. The polydispersity has clearly been reduced substantially. The material in (b), the higher molecular weight fraction of the starting polymer, was utilized in all subsequent reactions except as noted.

Extent of Completion of Reaction. The extent of completion of hydrosilation had previously been assessed by us by grating IR, where the Si–H absorption band at 2180 cm⁻¹ was monitored. We have since found this method to be insensitive above ca. 75% completion and so utilized throughout this work the proton NMR band seen for Si–H. Typical NMR spectra of unreacted polymer I.A.2 (a), monomer II.B (b), and fully reacted polysiloxane polymer IV.B (c) are given as examples in Figure 3. The band-broadening seen in (c) is characteristic generally of the NMR spectra of side-chain polymers.

Transition Temperatures of Homomonomer MEPSIL Solvents. Table I lists the transition temperatures of mo-



Figure 3. Proton NMR spectra (a) of unreacted starting poly(methylsiloxane) I.A.2, (b) (4-allyoxybenzoyl)-4'-methoxybiphenyl starting monomer II.B, and (c) fully reacted MEPSIL IV.B.

nomers II.A-E as well as those of the resultant MEPSIL polymers IV.A-E. These data demonstrate that attachment of the low molecular weight mesomorphs utilized in this work to a polymeric backbone via a flexible spacer does not result in destruction of the liquid-crystalline nature of the monomers but does alter their transition temperatures, although the extent to which this occurs is at present difficult to predict in advance. For example, mesomorphic monomers may give polymers that do not exhibit liquid crystallinity, while the converse is also true, that is, nonmesomorphic monomers in some instances yield mesomorphic polymers (cf. MEPSIL IV.A).

Dependence of Transition Temperatures on Reactant-Polymer Molecular Weight. We observed during the course of these studies that utilization of reactant polymers of different average molecular weights with the same mesomorphic monomer produced MEPSIL's with different melting points but with identical mesomorphic-isotropic transition temperatures. Thus, MEPSIL's IV.B (reactant-polymer I.A.2, n = 58 in Figure 1) and IV.F (reactant-polymer I.C.1, n = 38) gave melting points of 139 and 91 °C, respectively, but near-identical nematic-isotropic transitions of 319 and 317 °C. The former data are a consequence of the dependence of the melting point on precise close packing of the molecules in the solid state, where polymers with different molecular weights pack differently. On the other hand, the only ordering



Figure 4. Plots of log t_R' against reciprocal absolute temperature for benzo[a]pyrene (upper curve) and benzo[e]pyrene solutes with MEPSIL IV.B stationary phase. Polymer transition temperature is indicated by the vertical dashed line at 319 °C.

that occurs in the liquid-crystalline state is an averaged parallel orientation of the long axis of the mesomorphic side chains, which are free to cluster regardless of the length of the backbone to which they are attached. Thus, mesomorphic-isotropic transition temperatures hardly appear to be affected by the reactant-polymer molecular weight.

Transition Temperatures of Comonomer MEPSIL Solvents. Mesomorphic transition temperatures of MEP-SIL's can be altered by the attachment of additional nonmesomorphic segments to the polymer backbone, analogous to our previous finding that dilution of low molar-mass liquid crystals substantially lowers their transition temperatures (17). We provide illustration of this in Table I, where MEPSIL IV.G was synthesized with a Petrarch reactant-polymer comprised of

units (i.e., methylsiloxane + dimethylsiloxane) in the number ratio 10/17. This MEPSIL gave a nematic/isotropic transition temperature of 169 °C, fully 150° lower than the corresponding MEPSIL IV.B. In addition, a smectic phase was observed for the former which extended from the melting point, 88 °C, to 115 °C, whereas the melting point of MEPSIL IV.B was 139 °C. Thus, although the melting points of MEPSIL's can be lowered by attachment of methyl groups to the polymer backbone, the upper (nematic/isotropic) transition temperatures are thereby reduced also. Even so, we believe at the present time that with the proper choice of backbone length, mesomorphic group, spacer, and percent nonmesomorphic side chains, MEPSIL's with melting points of close to room temperature as well as nematic/isotropic ranges of in excess of 300 °C may in fact be realized.

Comparison of Transition Temperatures of MEPSIL Solvents in Bulk-Liquid and Thin-Film States. We show in Figure 4 plots of log (adjusted retention time, $t_{\rm R}$) against reciprocal absolute temperature observed for benzo[a]pyrene (upper curve) and benzo[e]pyrene with MEPSIL IV.B. The abscissa encompasses the transition of the polymer from the nematic state to the isotropic (DSC: 319 °C; vertical line in Figure 4), which is clearly visible as a discontinuity in each set of retention data. The transition temperature of meso-



 Table I. Transition Temperatures^a of Parent 4-(Allyloxy)benzoyl Ester Monomers II.A-II.E and Resultant MEPSIL

 Polymers IV.A-IV.G

^aDSC, GLC, microscopy: g, glassy; k, crystalline; s, smectic; n, nematic; i, isotropic. ^bn = 38. ^cMethylsiloxane/dimethylsiloxane number ratio of 10/17.

morph IV.B in the thin-film state (i.e., GLC) hence appears to be identical with that observed for the bulk liquid (DSC), as was true also for all other MEPSIL solvents studied here. However, this may not be the case generally. Depending on the nature of the substrate upon which the liquid crystal is coated, there is the possibility that, in fact, the transition temperature might well be altered substantially. For example, separation of the two test solutes is clearly preserved (albeit diminished) with the isotropic form of MEPSIL IV.B at well in excess of 320 °C whereas, even with stationary phases that give rise to strongly energetic solute/solvent interactions (e.g., Lewis acids), the separation of benzo[a]pyrene from benzo-[e]pyrene is notoriously difficult at these temperatures. Thus, there appears to exist some residual ordering of the MEPSIL solvent in the thin-film state.

Of compelling interest in this regard is the alignment of liquid crystals within what are said to be "boundary layers" existing at liquid/solid interfaces: such "boundaries" extend over several thousand angstroms in some cases, and transitions within such layers (whether first or second order is not clear at present) differ measurably from those observed for the bulk liquid (38-42). The matter is currently under further study, and we intend reporting shortly our work on separations carried out with MEPSIL phases in the isotropic as functions of the film thickness as well as column-wall surfaces derivatized with silylating reagents comprising a variety of chemical types.

Practical Operating Temperature Limits of MEPSIL Solvents. We found that plots of log (adjusted retention) of all test solutes with MEPSIL IV.B increased monotonously with reciprocal absolute temperature from 300 to 100 °C, which indicates that there is no change in the physical state of the mesomorphic melt on cooling to this limit. That is, MEPSIL phases can be supercooled substantially below their nominal melting points. However, by way of contrast, we show in Figure 5 plots exemplifying the relative separations (α values; here, $\alpha = k'_{anthracene}/k'_{phenanthrene}$) and resolution (R_s) as functions of temperature that are typical of those that we observed throughout this work. While the separation factor continues to increase as the temperature is decreased, the



Figure 5. Plots of α values and resolution R_s against temperature for anthracene and phenanthrene solutes with MEPSIL IV.B.

resolution, which takes account of peak widths as well as peak positions, shows a maximum at ca. 150 °C. That is, there was a substantial decrease in column efficiency (increased peak broadening) near the nominal melting point. We therefore consider 150 °C to be the lower practical operating limit of MEPSIL IV.B.

The upper practical operating limits of MEPSIL phases are governed primarily by two considerations, namely, the mesomorphic-isotropic transition temperatures (beyond which, generally, the selectivity of the phases is substantially reduced) and the thermal stability of the materials. As illustrated in Figure 4, MEPSIL IV.B is in fact selective to well in excess of 320 °C; however, the thermal stability of similar compounds synthesized by us previously precluded continuous operation at much above 300 °C. Therefore, in order to test the stability



Figure 6. Separations of (a) three-, (b) four-, and (c) five-ring PAH with MEPSIL IV.B. Solutes: fluorene (1); phenanthrene (2); anthracene (3); fluoranthene (4); pyrene (5); 1,2-benzofluorene (6); 2,3-benzofluorene (7); triphenylene (8); benz[*a*] anthracene (9); chrysene (10); benzo[*b*] fluoranthene (11); benzo[*k*] fluoranthene (12); benzo[*a*] pyrene (13); perylene (14); and benzo[*a*] pyrene (15). Column temperatures: (a), 180; (b), 235; (c), 275 °C isothermal.

of materials synthesized in this work, the number of theoretical plates for benzo[a]pyrene and the resolution of benzo[a]pyrene/benzo[e]pyrene with several MEPSIL's were determined as functions both of temperature and time. For MEPSIL IV.B, both N and R_s were found to be constant to within 5% over 1 week of continuous operation at 280 °C.



Figure 7. Programmed-temperature separation of common PAH. Solutes numbered as in Figure 6. Additional solutes: 1,2,3,4-dibenzanthracene (16); benzo[*ghi*]perylene (17). Column temperature: 140 °C/3 min; 140–280 °C at 4 °C min⁻¹.

Moreover, only gradual deterioration was observed when columns containing this phase were operated continuously at or above 300 °C. Thus, MEPSIL IV.B can be used at least for brief periods (as in temperature programming) at upward of as much as 300 °C without seriously affecting column performance. The practical operating temperature limits of the phase therefore encompass virtually the entire mesomorphic range exhibited by the material. This was observed to be the case generally for all MEPSIL solvents synthesized in this work.

Column Efficiency of MEPSIL Solvents. MEPSIL phases were found in this work to provide satisfactory column efficiency (see chromatograms presented below), which we ascribe mainly to the unique flexibility of the polysiloxane backbone and its concomitant low surface tension. Thus, glass-capillary columns containing MEPSIL IV.B yielded about 2450 plates/m, N/m (chrysene solute; 230 °C), which compares favorably with about 3000 N/m we have observed elsewhere (14, 31) for columns of identical dimensions that contain SE-30 and SE-52. [In contrast, we have found, e.g., that BBBT (monomeric liquid crystal) yields on average only 880 N/m (14).]

Practical Application of MEPSIL Solvents. To illustrate the practical utility of the mesomorphic polysiloxane solvents synthesized in this work, we present as examples the separation of three-, four-, and five-ring PAH with MEPSIL IV.B in Figure 6. Figure 7 then provides the programmed-temperature separation of a synthetic mixture of 17 of the three-to-five-ring PAH encountered most frequently inter alia in environmental samples.

We note in passing that the elution order of the five-ring PAH with conventional polymeric liquid phases is benzo-[e]pyrene, followed by benzo[a]pyrene, and perylene (1, 15, 17). In contrast, the elution pattern of these solutes with mesomorphic polysiloxanes is consistent with the degree of their rodlike geometry, the more rodlike being retained longer. Thus, benzo[e]pyrene elutes first (and well before the rest) with MEPSIL IV.B, followed by perylene, and then benzo-[a]pyrene.

Selection of a Representative MEPSIL Solvent as a Standard GLC Phase. As mentioned at the outset, it was our intention to synthesize a mesomorphic polysiloxane that would provide satisfactory column efficiency, as well as selectivity on a basis entirely different from conventional phases, in our efforts at defining a set of standard GLC solvents. To date, we have selected and characterized a standard "boiling-point" phase (either OV-1 or SE-30, whose physico-



Figure 8. Plots of retention indices for PAH numbered as in Figures 6 and 7 with OV-101 and OV-17 (43) and MEPSIL IV.B stationary phases. Lines were drawn between points without regard for intermediate compositions. Data for the lower five compounds correspond to 230 °C, remaining at 270 °C.

chemical and chromatographic properties are virtually equivalent), as well as a solvent of some aromatic content. OV-7 (22–26). On the basis of the results of this work, we tentatively select MEPSIL IV.B as representative of nematic polysiloxanes, since it provides the broadest nematic range, highest column efficiency, and greatest thermal stability of the MEPSIL's synthesized by us thus far. Accordingly, we illustrate graphically in Figure 8 the variation of retention indices (hence separations) of selected PAH on passing from the conventional ("nonpolar") phase OV-101, through ("polar") OV-17, to (mesomorphic) MEPSIL IV.B solvent. On the basis of these data, we anticipate that the selectivity afforded by the nematic polysiloxane will differ equally as substantially from those exhibited by OV-1 (separations based on solute volatility) and OV-7 (London interactions), the first two of our set of standard phases. The matter is currently under further study, the results of which we hope soon to report.

Generality of the Synthetic Scheme. Finally, we note that the synthetic procedure outlined in Figure 1 is completely general and should therefore prove useful in the fabrication of polysiloxanes comprised of side chains with other specific functional groups, e.g., chiral centers, Lewis acid sites, and so forth. The only requirement of monomer starting material is that an hydroxyl group be present for attachment, via esterification, to the 4-(allyloxy)benzoyl spacer. However, even this may not be necessary since intermediates can be linked directly to the polymer backbone through hydrosilation if the monomer itself possesses active hydrogen, as is the case, for example, with Schiff bases (6-9, 44). In addition, we of course recognize the potential for attachment of liquid-crystal monomers to silica packings utilized commonly in liquid chromatography, for which we are currently developing appropriate derivatizing agents.

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