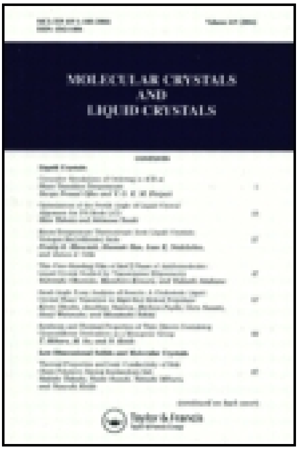

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Probe-Solute Study of Mesomorphic Polysiloxane (MEPSIL) Solvents. Synthesis and Characterization of Some Ester-Linked Copolymer Mepsil Stationary Phases

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PROBE-SOLUTE STUDY OF MESOMORPHIC POLYSILOXANE (MEPSIL) SOLVENTS. SYNTHESIS AND CHARACTERIZATION OF SOME ESTER-LINKED COPOLYMER MEPSIL STATIONARY PHASES

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Abstract The synthesis and characterization of several mesomorphic copolymer sidechain siloxanes is presented and discussed from the standpoints of the extent of pendant substitution as well as composition. For a given copolymer, both the glass-mesomorphic and mesomorphic-isotropic transition temperatures were found to increase, although not linearly so, with increasing substitution up to ca. 70% extent of reaction (determined by FT-NMR and elemental analysis), beyond which, however, there was then little further change in either. In addition, the glass-mesomorphic transition temperature increased more slowly than that for the mesomorphic-isotropic transition as the copolymer composition was varied. The findings confirm the results reported some time ago that even partially-reacted poly(mesomorph-co-hydro)siloxanes can exhibit liquid-crystalline properties over extensive temperature ranges; as well as the contention that judicious adjustment of the makeup of sidechain siloxanes can provide a variety of materials that are useful both as gas- and liquid-chromatographic stationary phases.

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INTRODUCTION

Laub and coworkers[1-4] were the first to demonstrate that mesomorphic sidechain polysiloxane[5] (MEPSIL) solvents, Figure 1, particularly nematic materials, constitute highly effective gas-chromatographic (GC) stationary phases from the standpoints both of selectivity and thermal stability. For example, one of the MEPSIL's they synthesized exhibited a glass/nematic transition at 364 K and a nematic/isotropic transition at 590 K (polymer IV.F of ref. 3). In addition, the high degree of shape selectivity e.g. for benzopyrene solutes persisted well beyond the upper transition temperature.[3] However, the volatility ("column bleed") of all mesomorphic polysiloxanes synthesized to date is still unacceptable at much above 550 K. Also, high glass transitions preclude the use of MEPSIL's for volatile solutes such as the xylenes.

We therefore undertook some time ago to widen the mesomorphic range of MEPSIL phases, with the particular view of lowering the glass transition temperature, and at the same time increasing their thermal stability. We report in this work the results of an attempt to achieve a broadened nematic range by fabricating copolymers comprised of one monomer that exhibits a favorably-low glass transition despite an unacceptably-low isotropic transition, together with a second monomer that gives a high isotropic transition yet which has the disadvantage of a high glass transition. The former is thus intended to serve as a kind of internal plasticizer of the copolymer.[4]

In addition, in seeking to reduce the volatility of MEPSIL solvents, we have also carried out sidechain attachment reactions such that some hydride hydrogens were left on the polysiloxane backbone. These unreacted sites would then be available for chemical attachment to GC column packings (or, in the case of open-tubular systems, to GC column walls), as well as for crosslinking.

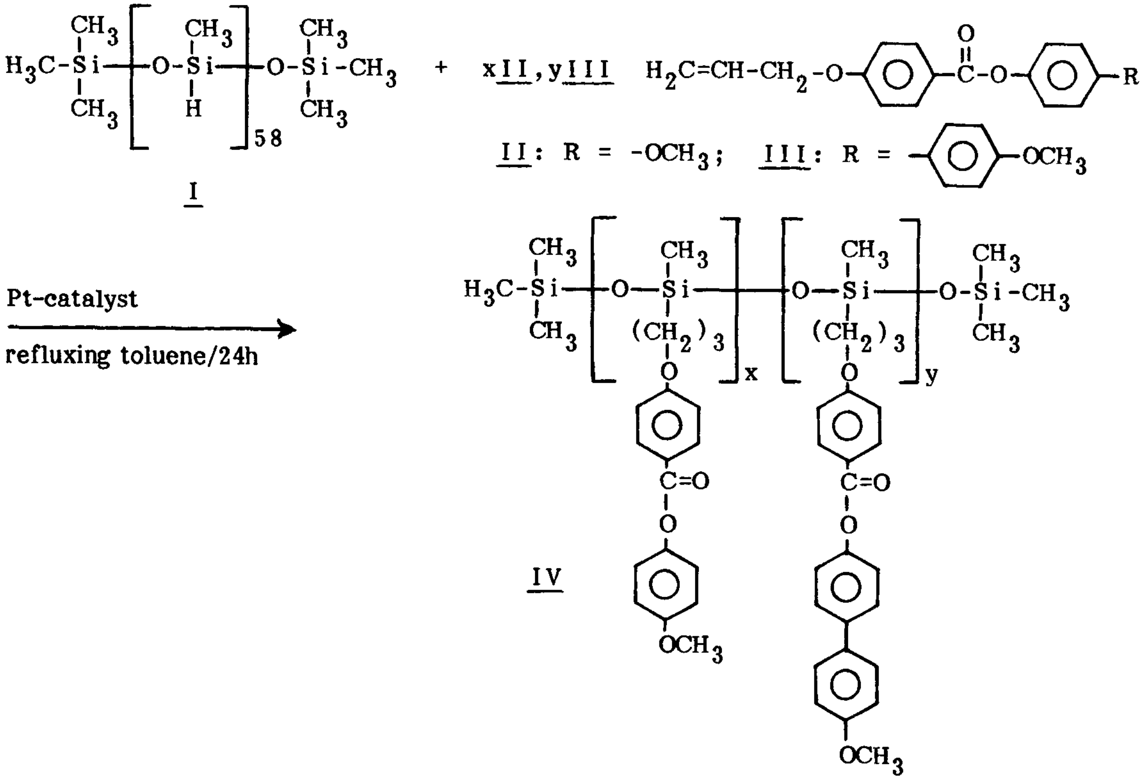


FIGURE 1. Synthesis of mesomorphic polysiloxane (MEPSIL) solvents.

However, it was not known at the outset how limiting the extent of substitution might affect the glass-mesomorphic and mesomorphic-isotropic transition temperatures.

EXPERIMENTAL

SYNTHETIC PROCEDURES

Monomers

The monomers, [4-(allyloxy)benzoyl]-4-methoxylphenyl (II) and 4-[[4-(allyloxy)benzoyl]oxy]-4'-methoxybiphenyl (III), were synthesized as reported previously by Laub, et al.,[4,6] except that 4-hydroxy-4'-methoxybiphenyl was obtained from 4,4'-biphenol with the methylating agent methyl tosylate instead of dimethyl sulfate.[7]

poly(Methyl[hydro-co-methoxybiphenyl]siloxanes)[7]

Depending on the desired extent of sidechain substitution, an amount of monomer III and 280 mm^3 (4.66 mmol) of poly(methylhydrosiloxane) (PMHS) (I) were dissolved in 200 cm^3 of freshly distilled predried toluene in a 250-cm^3 three-necked round-bottom flask equipped with a magnetic stirrer, a thermostated oil-bath, and a reflux condenser. The solution was then charged with an injection of 100 mm^3 of a mixture of 1.1 mg dicyclopentadienylplatinum(II) chloride catalyst[3,4] in 1 cm^3 of HPLC-grade dichloromethane, following which it was allowed to reflux for 24 h under a blanket of dry nitrogen. The solution became opaque upon cooling if the extent of substitution was at least 55%; the solution volume was otherwise reduced by evaporation under a stream of nitrogen until the formation of a milky white precipitate was observed. The crude product, IV, was then collected by centrifugation at 4°C, subsequently washed twice with dry benzene, recollected by centrifugation, and the benzene decanted. Centrifuge tubes containing the washed product were then placed in a vacuum line at 5 torr in order to remove residual benzene. The yields generally fell between 20 and 50% for PMHS of degree of polymerization 58, but were in any event dependent upon the molecular weight of PMHS (when this was low, only a small fraction of the product precipitated from solution). The liquid-crystalline properties of the polymers were determined by optical microscopy and differential scanning calorimetry; the extent of monomer substitution and accompanying phase transition temperatures are presented in Table I.

TABLE I. Transition Temperatures of MEPSIL Polymers IV (x = 0)

Mol % y	T_{g-n}/K	T_{n-i}/K
0	137	-
56	368	220
71	404	573
77	403	573
79	407	573
99	412	592

poly(Methyl[methyl-co-methoxybiphenyl]siloxanes)

The synthesis of copolymers of this type was as described in Figure 1, except that poly(methyl[methyl-co-hydro]siloxane) (PMMHS) was employed as the starting reagent instead of PMHS. Several products exhibited smectic phases, for example, that with 30 mol % methoxybiphenyl monomer III/70 mol % co-methyl sidechains gave a T_{g-s} of 361 K and a T_{s-n} of 454 K.

poly(Methyl[methoxyphenyl-co-methoxybiphenyl]siloxanes)

The synthesis of these copolymers was also as described above, except that various amounts of both monomers II and III were employed in the reaction sequence. The phase transitions as a function of copolymer composition are summarized in Figure 2.

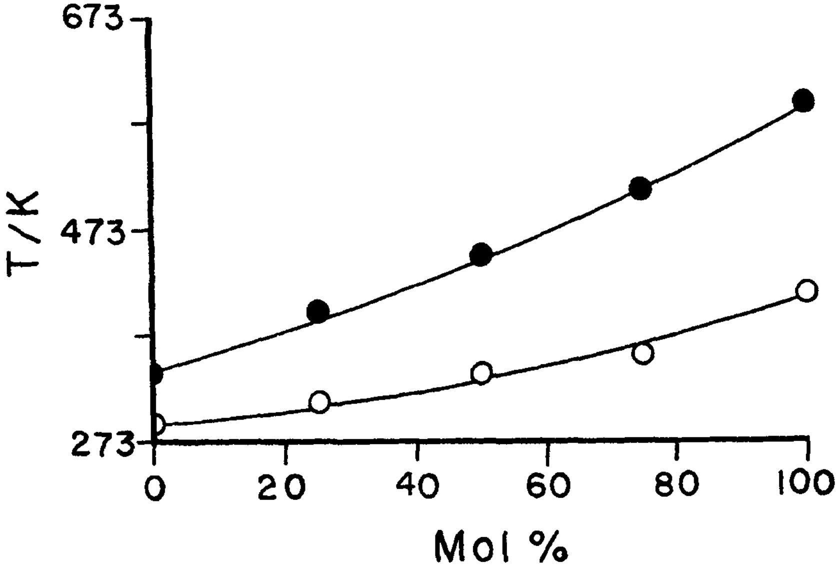


FIGURE 2. T_{g-n} (open circles) and T_{n-i} (closed circles) for copolymers IV of indicated composition (cf. Figure 1).

ANALYTICAL TECHNIQUES[7]

The extent of sidechain substitution was determined by Fourier-transform infrared spectroscopy (FT-IR), Fourier-transform nuclear magnetic resonance spectroscopy (FT-NMR), and elemental analysis.

FT-IR

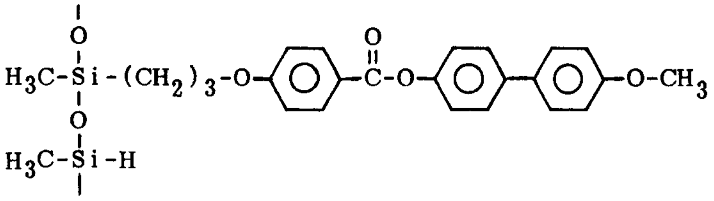
We attempted, first, to quantitate the amount of the methoxybiphenyl monomer III that was attached to the polymer backbone by application of Beer's law to the absorbance at 1732 cm^{-1} exhibited by KBr pellets of the samples. However, the results were unsatisfactorily imprecise, due most likely to pellet inhomogeneity.

Elemental Analysis

We found elemental analysis to be an accurate method for assessment of the extent of low to moderate sidechain attachment. Moreover, it is straightforward to relate the carbon content of a MEPSIL homopolymer to pendant substitution; a plot of the results for polymer IV made from neat monomer III is provided as an example in Figure 3. However, as shown, the accuracy of the method deteriorates rapidly at high ordinate values.

FT-NMR

NMR is often used to monitor the progress of hydrosilation reactions, where the disappearance of the band due to the Si-H proton is employed for quantitation. However, we have found that the method can detect residual Si-H to no better than 20 mol %. Therefore, peak-ratio methods were devised, which are at least as accurate as elemental analysis. Consider, for example, the partially-reacted homopolymer IV made from monomer III:



There are 6 Si-CH_3 protons, whose NMR signal appears at $\delta = 0.2$ ppm. Let the intensity of this peak be equal to I_a; the intensity per proton is therefore $I_a/6$. The signals for the protons of the -OCH_3 and -CH_2O- groups overlap at ca. 4 ppm. Let this intensity be equal to I_b. Now, supposing that there were 100% substitution at both silicon atoms, the maximum number of sidechain methyl- and methylene-group protons is 10. The band at 4 ppm should therefore have an intensity I_b of $10(I_a/6)$. Thus, the extent of reaction R is given by: $R/\% = 100(I_b/10)/(I_a/6) = 60(I_b/I_a)$.

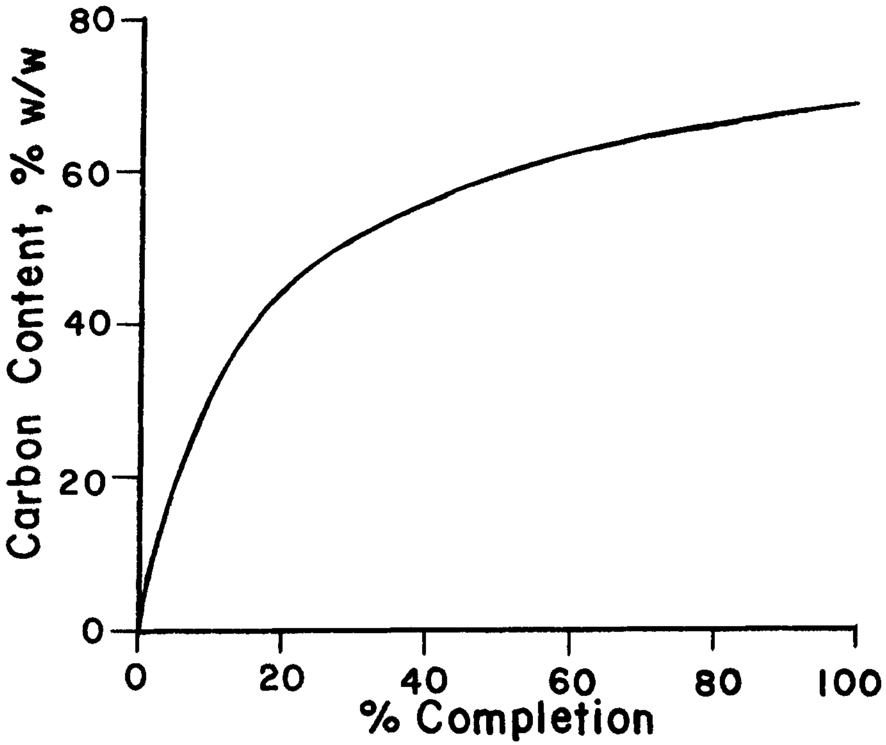


FIGURE 3. Carbon content as a function of extent of reaction (polymer IV with monomer III).

DISCUSSION AND CONCLUSIONS

Figure 4 summarizes the extent to which the phase transitions of methyl(hydro-co-methoxybiphenyl) and methyl(methyl-co-methoxybiphenyl) MEPSIL solvents depend upon the extent of sidechain substitution. Beyond 50% reaction, the phase transition temperatures of the former clearly increase faster with increasing substitution than do those for the latter copolymers. A likely reason for this is that intermolecular association of the methoxybiphenyl sidechains is less hindered by intervening Si-H protons than by methyl groups. The phase transitions of the methyl(hydro-co-methoxybiphenyl) polymers thus increase rapidly beyond 50% substitution.

The respective glass-nematic and nematic-isotropic transition temperatures in any event become identical beyond ca. 70% backbone substitution. These findings therefore substantiate the hypothesis made some time ago[3] that the potential exists for chemical attachment of partially-reacted MEPSIL's to silica surfaces (e.g., fused-silica GC column walls; HPLC silica packings) via simple thermal-induced dehydration without destroying the liquid-crystalline properties of the polymers.

Figure 2 also illustrates the broad range of transition temperatures that can be realized with MEPSIL copolymers, which, if nothing else, reveals the particularly interesting possibility of their application as chemically-bound stationary phases to room-temperature HPLC separations. However, it is also fair to say that the most desirable situation would be a single MEPSIL polymer that exhibited a glass/nematic transition at less than 273 K, and an upper nematic/isotropic transition at in excess of 623 K. We hope soon to report further and substantial progress toward achieving this goal.

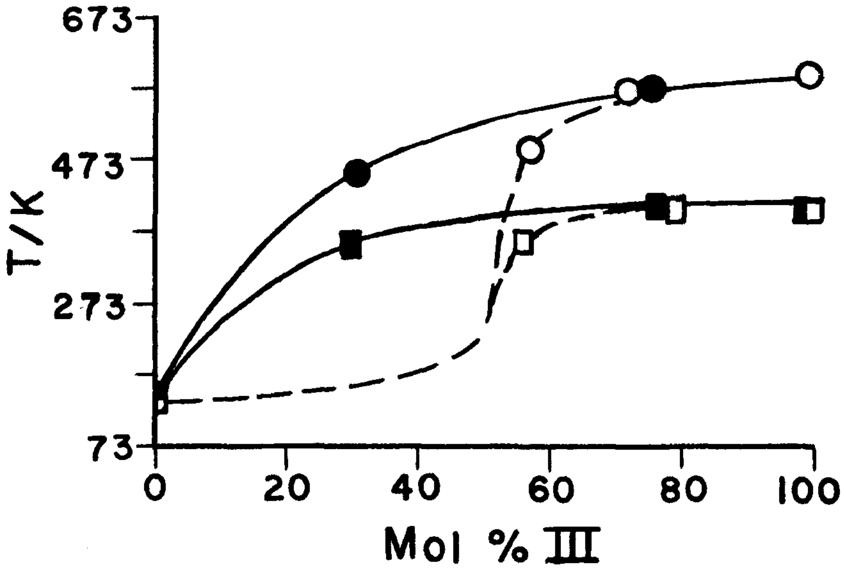


FIGURE 4. Plots of transition temperatures T/K as a function of the extent of substitution of methoxybiphenyl monomer III onto PMHS (dashed lines) and PMMHS (solid lines) polymer backbones. Squares: T_{g-n}; circles: T_{n-i}.

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