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G. M. Janini [a], A. M. Al-ghoul [a] & G. H. Hovakeemian [b]
[a] Department of Chemistry, Kuwait University, Kuwait, 13060, Kuwait
[b] Kuwait Institute for Scientific Research, Kuwait, Kuwait
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Effect of Molecular Structure on the Properties of Schiff's Base Side-Chain Liquid Crystal Polysiloxanes

G. M. JANINI and A. M. Al-GHOUL

Department of Chemistry, Kuwait University, Kuwait 13060, Kuwait

and

G. H. HOVAKEEMIAN

Kuwait Institute for Scientific Research, Kuwait, Kuwait

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A series of smectic liquid crystal polymers with a polysiloxane backbone and Schiff's base side-chains is presented.

In a three-step procedure, hydroxy-terminated Schiff's bases were first prepared and then converted to allyloxy-terminated derivatives. Only few of the resulting monomers were liquid crystals, even though all were potentially mesomorphic.

When attached to a polysiloxane backbone *via* a 3-carbon spacer, all resulting polymers were smectic. Where comparisons were possible, the mesophase ranges for the polymers were greater than those for the corresponding side-chain precursors.

Interesting trends were observed in the effect of the length of the alkyl and alkoxy terminal substituent on the liquid crystal properties. The chloro-terminated side-chain precursors did not exhibit liquid crystal properties, but gave the widest mesomorphic range polymers. The high transition enthalpies for the mesomorphic–isotropic transition are indicative of a smectic mesophase. The transition temperatures and entropies for the smectic–isotropic transitions for an alkoxy terminated series show odd–even alternations.

INTRODUCTION

Over the years a large and varied number of liquid crystal materials have been synthesized and their properties characterized.[1] The effect of chemical structure on liquid crystal properties has also been extensively investigated and correlations have been established whereby liquid crystal properties can be predicted with a reasonable degree of certainty.

In contrast, main-chain polymeric liquid crystals have been introduced only in the fifties,[2–4] and only in this decade have side-chain liquid crystal polymers been recognized. During this period, several hundred polymers of this latter variety have been synthesized.[5–13] The idea is to link monomeric mesogens or potential me-

sogens to a preferably flexible main chain polymer *via* a flexible spacer. The first side-chain polymer to be synthesized had a polymethacrylate backbone.[5,9] To date, almost all such polymers are polymethacrylates or polysiloxanes. In a noted exception, a polychloroacrylate was synthesized,[14] but substitution of chloro for methyl had almost no effect on the mesomorphic behavior of the polymer.

The nature of the backbone, the mesogenic side-chain, and the length of the flexible spacer are the three main factors which are observed to influence the structure, texture and thermal stability of the mesophase.[15] As the mesogenic segments are attached to the polymer backbone, their translational and rotational motions are restricted to some degree, irrespective of the length of the spacer. Very long spacers (> six carbons) promote smectic mesophases, while very short spacers (< three carbons) restrict the tendency of the side chains to organize into a mesomorphic state.[5,6,15]

For polymethacrylate and polyacrylate side-chain polymers with identical side chains and spacers, the glass transition temperature is lower for the more flexible polyacrylate.[12,15] The polysiloxane backbone, which is known for its extremely high flexibility, provides mesomorphic polymers with the lowest glass transition temperatures of all known mesomorphic polymers.[15]

Most of the polymeric liquid crystals synthesized to date contain a carboxylic-acid ester linkage in the mesogenic core. Liquid crystal side-chain polymers with Schiff's base central side-chain linkage (—CH=N—) were first synthesized by Janini *et al.*[16] as alternatives to those with ester linkages (—COO—). It was established that the introduction of the more rigid Schiff's base linkage increased the clearing point of a polymer compared with that with the more flexible ester linkage. Moreover, and by analogy with conventional polymers, when side-chain polymers were synthesized by using amide linkages, highly rigid polymers were obtained with very high melting points (> 350°C). This precludes the formation of a mesophase, because it is well known that amide groups, in a polymer backbone decrease the segmental motions of polymers due to the stiffening effect of intermolecular hydrogen bonding.[17]

For some side-chain polymers with lateral substituents (CH_3 group) presented by Gemmell *et al.*,[18] it was found that all the polymers were glassy, indicating that the lateral methyl group very effectively inhibits crystalline packing of the side chains. This conclusion was later confirmed by Mauzac *et al.*,[19] who showed that the introduction of a lateral substituent into the aromatic core of the mesogenic moiety disfavors the mesogenic character.

On the other hand, Finkelmann *et al.*[20] concluded that the polarity of substituents may influence the type of mesophase in the polymer. For example, only smectic homopolymers were observed when polar substituents (for example Cl_) were introduced in the *para*-position. Nematic homopolymers were obtained only if less highly polar substituents (for example CH_3O—) were introduced in the *para*-position. This explained why side-chain polymers with cyano-terminal substituents tend usually to be smectic. Furthermore, increasing the monomer length-to-breadth ratio is generally found to raise the clearing point. This was observed by Janini and coworkers,[16] who showed that a biphenyl system with a methoxy terminal tail

exhibited higher a clearing point in comparison to a biphenyl system with no terminal CH_3O.

The odd-even effect, which is well known for monomeric liquid crystals and main chain polymers, has also been reported for side chain polymers synthesized by Gemmell *et al.*[18]

In this work we present the synthesis and characterization of a series of mesomorphic polysiloxanes with Schiff's base side chains. The Schiff's base link was selected in order to investigate the synthetic procedures needed to arrive at polymers with certain desired properties for use as stationary phases in gas-liquid chromatography (GLC). Of particular importance was the synthesis of polymers with a low melting point, a wide mesomorphic (preferably) nematic temperature range and a high thermal and chemical stability at elevated temperatures.

EXPERIMENTAL

Chemicals

The starting materials in this study were mainly purchased from commercial suppliers.

All of the aldehydes, unless otherwise mentioned, were purchased from the Eastman Kodak Company. *p*-Anizaldehyde and 4-chloroaniline were obtained from the Aldrich Chemical Company. 4-Hydroxybenzaldehyde and *p*-aminophenol were obtained from Fluka Chemie. All solvents were supplied by Alltech associates and used without further purification, except for toluene and tetrahydrofuran which were first dried over sodium and distilled before use.

The poly(hydrogenmethylsiloxane) (PMHS; $\overline{DP}$ = 58) which contains reactive hydrogen on each monomeric unit, was obtained from silar. Low to intermediate molecular weight material, as well as any additives were removed by precipitation of the desired fraction from solutions in benzene by the addition of methanol.[21]

The aldehydes were cleaned by vacuum distillation or washing with aqueous Na_2CO_3. 4-Hydroxybenzaldehyde was recrystallized from water to give fine needles, which were dried overnight under vacuum at 50°C. Simple distillation was performed on the allyl bromide. The amines were purified from oxidation products by recrystallization from appropriate solvents.

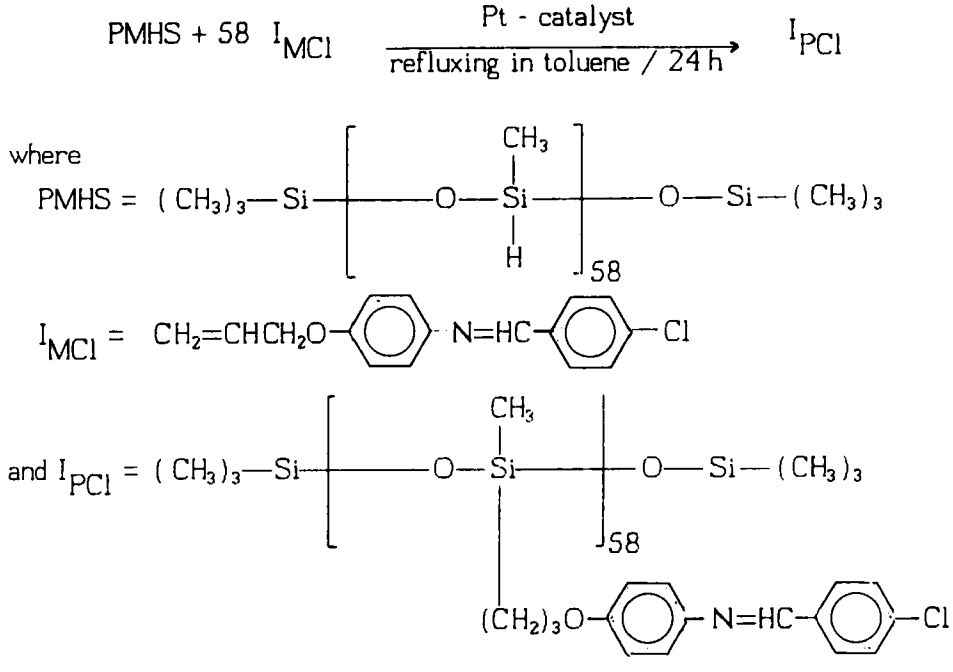
Synthetic procedures

Schiff's bases were obtained by condensation of the aromatic aldehyde with an aromatic amine. In most reactions, the solvent was absolute ethanol, and in some cases catalytic amounts of benzenesulphonic acid were added to speed-up the reaction. The Schiff's base products (mostly solids) were collected and washed with hot ethanol, and in some cases were recrystallized prior to use.

In all cases the Williamson synthesis was carried out using absolute methanol or propan-2-ol as solvent; appropriate amounts of the hydroxy Schiff's base and po-

tassium hydroxide were dissolved up and the allyl bromide was then added dropwise. The mixture was then boiled for 6 h.

The hydrosilation procedure is outlined below for one of the polymers with a chloro terminal substituent.



The three synthetic steps for the formation of MEPSIL (I_{PCl}) are described in details in the following.

4-(4-Hydroxyphenyliminomethyl)chlorobenzene (I_{Cl}). *p*-Aminophenol (5.0 g; 45.8 mmol) was dissolved in 80 cm^3 of absolute ethanol contained in a flask fitted with a stirrer, reflux condenser and $CaCl_2$ drying tube. A solution of 7.08 g of *p*-chlorobenzaldehye (10% excess over 45.8 mmol) in 10 cm^3 of absolute ethanol was then added quickly and the resulting mixture was boiled for 6 h. The precipitate formed upon cooling to room temperature was collected by filtration, washed twice with warm ethanol and finally recrystallized from ethanol to give 8.49 g (80.0%) of product (m.pt. 183°C) [Infra-red (KBr disc), —CH=N— at 1628 cm^{-1}].

Table I lists the symbols, names and melting points of all the Schiff's bases. The melting points of all compounds were determined accurately by DSC analysis using a Du Pont 990 thermal analyzer at a heating rate of 10 $Kmin^{-1}$. An indium sample was used as calibrant. The samples were examined under a dry nitrogen flow.

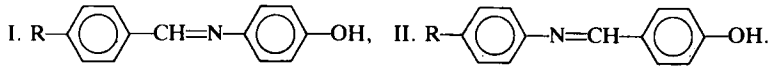
N-(4-chlorobenzylidene)-4-allyloxyaniline (I_{MCL}). A solution of 1.14 g KOH (17.27 mmol) in 40 cm^3 of propan-2-ol was added to a hot solution of I_{Cl} (4 g in 20 cm^3 of propan-2-ol; 17.27 mmol) while stirring. The dark clear solution was transferred to a two necked flask equipped with reflux condenser, drying tube and

TABLE I

Symbols, names and melting points of the hydroxy-terminated Schiff's bases[a]

Symbol[b]	Nomenclature	R—	m.pt. °C $k-i$[c]
I. I_{OM}	4-(4-Hydroxyphenyliminomethyl)methoxybenzene	CH_3O—	185
I_{OE}	4-(4-Hydroxyphenyliminomethyl)ethoxybenzene	C_2H_2O—	182
I_{OP}	4-(4-Hydroxyphenyliminomethyl)propoxybenzene	C_3H_7O—	180
I_{OB}	4-(4-Hydroxyphenyliminomethyl)butoxybenzene	C_4H_9O—	150
I_M	4-(4-Hydroxyphenyliminomethyl)toluene	CH_3—	198
I_E	4-(4-Hydroxyphenyliminomethyl)ethylbenzene	C_2H_5—	169
I_P	4-(4-Hydroxyphenyliminomethyl)propylbenzene	C_3H_7—	155
I_B	4-(4-Hydroxyphenyliminomethyl)butylbenzene	C_4H_9—	153
I_{Cl}	4-(4-Hydroxyphenyliminomethyl)chlorobenzene	Cl—	183
I_{CN}	4-(4-Hydroxyphenyliminomethyl)benzonitrile	CN—	182
II. II_{OM}	4-(4-methoxyphenyliminomethyl)phenol	CH_3O—	212
II_{Cl}	4-(4-chlorophenyliminomethyl)phenol	Cl—	182
II_{CN}	4-(4-cyanophenyliminomethyl)phenol	CN—	169

[a]The general formulae of the compounds are:



[b]The symbol was chosen to be indicative of the chemical composition of the compound. For example I_{OM} is structure I with a methoxy end group (OM).

[c]Crystalline-to-isotropic transition.

dropping funnel. The solution was heated until boiling, and a solution of 1.96 cm^3 of allyl bromide (30% excess over 17.27 mmol) in 20 cm^3 propan-2-ol was added dropwise over 4 h. The reaction mixture was boiled for an additional 2 h.

Some of the solvent (20 cm^3) was removed by distillation and the supernatant solution was decanted. Cream crystals formed immediately upon cooling. The precipitate was filtered, and washed first with water and twice with propan-2-ol to give white crystals. The dried solid was crystallized from propan-2-ol to give white crystals (80% yield), m.p. 114°C.

The product I_{MCl}, as well as all other side-chain precursors, was characterized by ^{1}HNMR (Bruker AM-300). The samples were dissolved in $CDCl_3$ and tetramethylsilane (TMS) was added as an internal reference. The NMR data are shown below.

^{1}H-NMR ($CDCl_3$, TMS, δ, ppm):

δ 8.39, *s*, 1 H, —CH=N—,

δ7.79, *d*, 2H, J = 8.4 Hz, ArH α to —CH=N—,

δ 7.4, *d*, 2H, J = 8.4 Hz, ArH α to —CH=N—,

δ 7.2, *d*, 2H, J = 8.4 Hz, ArH α to the allylic system,

δ 6.92, *d*, 2H, J = 8.8 Hz, ArH α to Cl—,

δ 6.07, *d* of *d* of *t*, 1H, —CH=CH_2—,

δ 5.43, *d* of *d* of *d*, 1 H; H_1

δ 5.27, *d* of *d* of *d*, 1 H; H_2

δ 4.53, *d* of *t*, 2H, —OCH_2CH=CH_2.

Table II lists the allyl ethers and their symbols, and Table III summarizes the phase transition temperatures for these compounds. The liquid crystalline properties of the mesomorphic compounds were examined by polarizing microscopy (Reichert, Austria). The transition temperatures were determined accurately by DSC at heating and cooling rates of 5 or 10 $Kmin^{-1}$. Monotropic liquid crystals were detected on cooling.

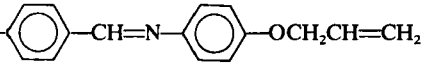
The purity of the hydroxy- and the allyloxy- derivatives was assured by recrystallizing each product. Schiff's bases are known to hydrolyze readily, but all our products were kept dry and were only dissolved in water-free organic solvents. The NMR spectra showed no sign of —CHO hydrogen (δ > 10). The DSC thermograms gave sharp endothermal peaks comparable in width to the peak generated by a pure benzoic acid standard. Furthermore, HPLC analysis of the hydroxy-derivatives

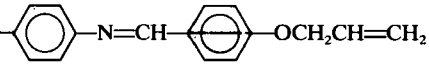
TABLE II

Names and symbols of the allyloxy-terminated Schiff's bases.[a]

Symbol[b]	Nomenclature	R—
I. I_{MOM}	*N*-(4-methoxybenzylidene)-4-allyloxyaniline	CH_3O—
I_{MOE}	*N*-(4-ethoxybenzylidene)-4-allyloxyaniline	C_2H_5O—
I_{MOP}	*N*-(4-propoxybenzylidene)-4-allyloxyaniline	C_3H_7O—
I_{MOB}	*N*-(4-butoxybenzylidene)-4-allyloxyaniline	C_4H_9O—
I_{MM}	*N*-(4-methylbenzylidene)-4-allyloxyaniline	CH_3—
I_{ME}	*N*-(4-ethylbenzylidene)-4-allyloxyaniline	C_2H_5—
I_{MP}	*N*-(4-propylbenzylidene)-4-allyloxyaniline	C_3H_7—
I_{MB}	*N*-(4-butylbenzylidene)-4-allyloxyaniline	C_4H_9—
I_{MCl}	*N*-(4-chlorobenzylidene)-4-allyloxyaniline	Cl—
I_{MCN}	*N*-(4-cyanobenzylidene)-4-allyloxyaniline	CN—
II. II_{MOM}	*N*-(4-allyloxybenzylidene)-4-methoxyaniline	CH_3O—
II_{MCl}	*N*-(4-allyloxybenzylidene)-4-chloroaniline	Cl—
II_{MCN}	*N*-(4-allyloxybenzylidene)-4-aminobenzonitrile	CN—

[a]The listed compounds are of the general structures:

I. R—  —OCH_2CH=CH_2

II. R—  —OCH_2CH=CH_2

[b]The symbols were selected in the same manner as in Table I, where the added M stands for monomer.

TABLE III

Transition temperatures of the monomers presented in Table II.

Compound	R—	Transition Temperatures (in °C) $k-i$	$k-n$	$n-i$
I. I_{MOM}	CH_3O—	111	(79)*	(98)*
I_{MOE}	C_2H_5O—	133	(108)*	(126)*
I_{MOP}	C_3H_7O—	127 (115)*	—	—
I_{MOB}	C_4H_9O—	114	(109)*	(113)*
I_{MM}	CH_3—	71	—	—
I_{ME}	C_2H_5—	71	—	—
I_{MP}	C_3H_7—	—	60	74
I_{MB}	C_4H_9—	—	43	64
I_{MCl}	Cl—	114	—	—
I_{MCN}	CN—	—	82	113
II. II_{MOM}	CH_3O—	111	(79)*	(98)*
II_{MCl}	Cl—	76	—	—
II_{MCN}	CN—	—	85	103

[a]The heating and cooling rate on DSC was 5°C/min. k = crystalline, n = nematic, i = isotropic.
[b]( )* indicates monotropic liquid crystal transitions. For I_{MOP}, the value (115)* represents the freezing point of the compound.

and GLC analysis of the allyloxy-derivatives showed that the purity of each product was better than 98%.

Synthesis of the polymer I_{PCl}. Purified PMHS was used for the preparation of I_{PCl}. A 0.9 g sample (3.31 mmol) *N*-(4-chlorobenzylidene-4-allyloxyaniline, I_{MCl} (a 10 mol% excess over the Si-H groups present in the PMHS (~58)) was dissolved in 50 cm^3 of dry freshly distilled toluene. PHMS (0.18 g or 5.14×10^{-5} mol) was added to the solution, the reaction mixture was heated to 110°C, and 100 μg of a platinum catalyst per g of product was pipetted in as a solution of 1 mg catalyst/1 cm^3 of methylene chloride (HPLC-Grade). The platinum catalyst (dicyclopentadiene platinum(II)chloride; m.p. 218°C) was synthesized as described elsewhere.[21] The reaction mixture was then boiled for 24 h. The extent of the reaction was monitored by I.R. analysis by following the disappearance of the Si-H absorption band at 2180 cm^{-1}.

At the end of the reaction, the solvent was evaporated to 20 cm^3, and the solution cooled. 100 cm^3 of methanol (HPLC-Grade) were then poured into the polymer solution slowly with stirring. The polymer was precipitated and collected by centrifugation at 2000 rpm for 15 min using a Beckman Centrifuge Model TJ-6, connected to Refrigeration Unit Model TJ-R. The supernatant was discarded and the resulting white polymer was redissolved in dry, freshly distilled THF (HPLC-Grade), and precipitated again using methanol. This process was repeated five times, and finally the polymer (I_{PCl}) was dried in a vacuum oven at 40°C overnight. The resulting polymer (60% yield) had the transition temperatures: k 73 s 223 i.

The phase transitions of this polymer and all other polymers were first roughly determined by microscopic observation. All of the polymers were smectic in character as shown by polarizing microscopy and miscibility studies using a polymer of

TABLE IV

Transition temperatures of the resulting polymers[a]

	Polymer[a]	R—	Transition Temperatures, °C $g-s$	$k-s$	$s-i$
I.	I_{POM}	CH_3O—	—	108	141
	I_{POE}	C_2H_5O—	—	108	181
	I_{POP}	C_3H_7O—	—	74	139
	I_{POB}	C_4H_9O—	88	—	179
	I_{PM}	CH_3—	—	62	75
	I_{PE}	C_2H_5—	—	58	86
	I_{PP}	C_3H_7—	—	58	81
	I_{PB}	C_4H_9—	—	53	103
	I_{PCl}	Cl—	—	73	223
II.	II_{POM}	CH_3O—	—	100	123
	II_{PCl}	Cl—	—	73	203
III.	I_{PCP}	C_3H_7O—		70	203
		Cl—	—		

[a] k = crystalline, s = smectic, i = isotropic, g = glassy. The symbols were selected in the same manner as in Table II. Here P stands for polymer.

known nematic character (immiscible). However, we were not able to determine the type(s) of smectic phase exhibited by these polymers by polarizing microscopy alone.

The transition temperatures $T_{k\text{-}s}$ and $T_{s\text{-}i}$ were determined accurately from the endothermal peaks recorded on DSC. In all cases, heating and cooling rates were 5 or 10 K min^{-1}.

Table IV summarizes the transition temperatures (in °C) for the resulting polymers.

RESULTS AND DISCUSSION

The objective of this study was to investigate synthetic procedures whereby Schiff's base liquid crystals with an allyloxy terminal group could be prepared and subsequently attached as side chains to a siloxane based polymer backbone. Considering the need for thermally stable liquid crystals to be used as stationary phases in GLC, a clearer understanding of the effect of molecular structural changes on liquid crystalline properties would allow more accurate prediction of the types of compounds likely to exhibit the best properties for this particular application.

A number of monomeric Schiff's base liquid crystalline stationary phases have been introduced over the last decade, the best known being the commercially available materials, BMBT, BBBT and BPhBT developed by Janini and co-workers.[22-24] Many of the shortcomings of these compounds, most notably, their volatility at high temperatures may be avoided if they are incorporated as side chains in a polymeric structure. Moreover, enhanced liquid crystalline properties are also

expected for the resulting polymers, as observed when other liquid crystal side-chain precursors were similarly treated.

In this work, we report the synthesis and characterization of a series of Schiff's base side-chain polymers with different terminal functional groups.

Table I lists the hydroxy-terminated Schiff's bases which are the precursors for the allyloxy-terminated materials listed in Table II. Table III presents the transition temperatures recorded for the latter materials. Inspection of the data presented in Table III reveals several characteristic trends.

Most of the alkoxy-terminated compounds I_{MOM}–I_{MOB} exhibit monotropic liquid crystal phases, whereas the analogous alkyl-terminated series I_{MM}–I_{MB} does not show liquid crystal properties for the first two members I_{MM} and I_{ME}. The other two members (I_{MP} and I_{MB}) are liquid crystalline. In both series, as the number of carbon atoms in the terminal substituent is increased, the melting points decrease. These results are in agreement with results reported for other Schiff's base series.

The effect of the nature of the terminal substituent on the nematic thermal stability shows trends similar to those previously reported for other liquid crystal systems.[1] Accordingly both materials with a CN-terminal group (I_{MCN} and II_{MCN}) behave as expected and promote a nematic state. As shown in Table III, the order of substituent efficiency in promoting the nematic state is: CN > OCH_3 > Cl > CH_3.

Compounds I_{MOM} and II_{MOM}; I_{MCN} and II_{MCN} are identical in molecular shape, but differ in the location of the atoms in the central linkage. Such structural variations will only affect the electronic distribution, and consequently the polarizability and the dipole moments of the molecules, but not their length-to-breadth ratios. Both I_{MOM} and II_{MOM} exhibit identical liquid crystalline properties. The inversion of the atoms in the central imino-linkage has no appreciable effect on the phase transition temperatures, indicating that both have equivalent nematic thermal stability. When analyzed by GLC on nonpolar OV-101 and polar OV-17 columns, both compounds gave identical retention times under the same chromatographic conditions, indicating similar volatility and polarity. In contrast, the pair of compounds I_{MCN} and II_{MCN} show differences in their macroscopic properties as a result of subtle differences in their molecular structures. Both gave identical retention times on a non-polar OV-101 column. However, II_{MCN} is retained slightly longer on a polar OV-17 column indicating that it is more polar than I_{MCN}. Comparable results were obtained when several pairs of Schiff's bases with different terminal substituents were similarly treated.[27]

Table IV lists the phase transition temperatures for the side-chain Schiff's base polymers as determined by combined DSC and polarizing microscopy. The results show some characteristic trends which will now be discussed.

It has been observed that the melting points or glass transition temperatures of polymers are usually lower than those of their side-chain precursors, but exceptions to this are not unlikely, and we observe that polymer I_{PB} (k 53 s) has a melting point that is slightly higher than that of the precursors alkene I_{MB} (k 43 i).

When we study the effect of the chain length of the alkyl terminal substituent of the mesogenic side chain, we observe that the melting point decreases with increasing chain length. For the alkoxy series it decreases and then increases again.

A similar trend is reported by Finkelmann *et al.*,[6] but Harvath *et al.*[28] report an opposite trend, where the transition temperature increases with increasing length of the substituent. It is to be noted that for series of monomeric liquid crystals, no specific trends in melting points occur with increasing terminal substituent chain length.[1]

All the polymers reported in Table IV were crystalline in nature, except I_{POB} which was glassy. Similar studies indicate that polymers with five or more carbons in the alkoxy chain are expected to be glassy. Furthermore, all the polymers were mesomorphic, irrespective of the nature of their side-chain precursors. The increase in order of the system on going from precursor to polymer is manifested in the fact that all the polymers exhibited the more ordered smectic phase, rather than the nematic state of their respective precursors. Non liquid-crystalline precursors also gave mesomorphic polymers. In fact non liquid-crystalline I_{MCI} and II_{MCI}, having in common a chloro-terminal group, gave polymers with the highest clearing points and the widest mesomorphic ranges. This result could not have been predicted from established trends for monomeric liquid crystals, as it is known that the chloro-terminal substituent is weaker than the methoxy group in promoting mesomorphic properties. Thus it is apparent that more systematic investigations on the effects of changes in structure on the properties of these relatively new types of liquid crystal materials are needed.

Figure 1 shows the dependence of the clearing temperatures of the polymers on the number of carbons in the *n*-alkoxy (upper curve) and *n*-alkyl (lower curve) terminal substituents. Considering the *n*-alkoxy terminated series we observe a significant odd-even variation, with the polymers with an even number of carbons having higher clearing temperatures than those with an odd number of carbons. This trend is well known for low molar mass mesogens.[1,29,30] Although it was not specifically discussed by the authors, we observed a similar trend in the data presented in Table I of Reference 6. For yet another polymeric systems,[28] it was simply reported that the clearing points increase with increase in the length of the alkoxy substituent. The odd-even effect has never been reported for polymeric systems except for main-chain polymers and for the spacer in side-chain polymers.[18] The data presented by Gemmell *et al.*[18] show that an even number of carbons and oxygen in the spacer promotes higher clearing points for the polymer.

Turning our attention to the alkyl terminated polymers, we notice a slight odd-even variation in the clearing points. In contrast to the trends observed for alkyl terminated monomeric liquid crystals, including those reported in Table II, the polymers with an even number of carbons in the alkyl terminal substituent exhibit higher clearing points. This unusual trend shows that polymeric liquid-crystalline systems are complicated and that more systematic studies are needed before one can make sweeping generalizations.

The enthalpies (ΔH) of the smectic–isotropic transitions for the alkoxy series (polymers I_{POM}–I_{POB}) are listed in Table V, together with the corresponding transition temperatures. Table V also lists the entropies of transition (ΔS). Only the *n*-alkoxy series was considered for this determination, because of the easily measured DSC peaks obtained for the clearing points. As can be seen from Table V, the values of the heat of transition associated with the smectic to isotropic changes

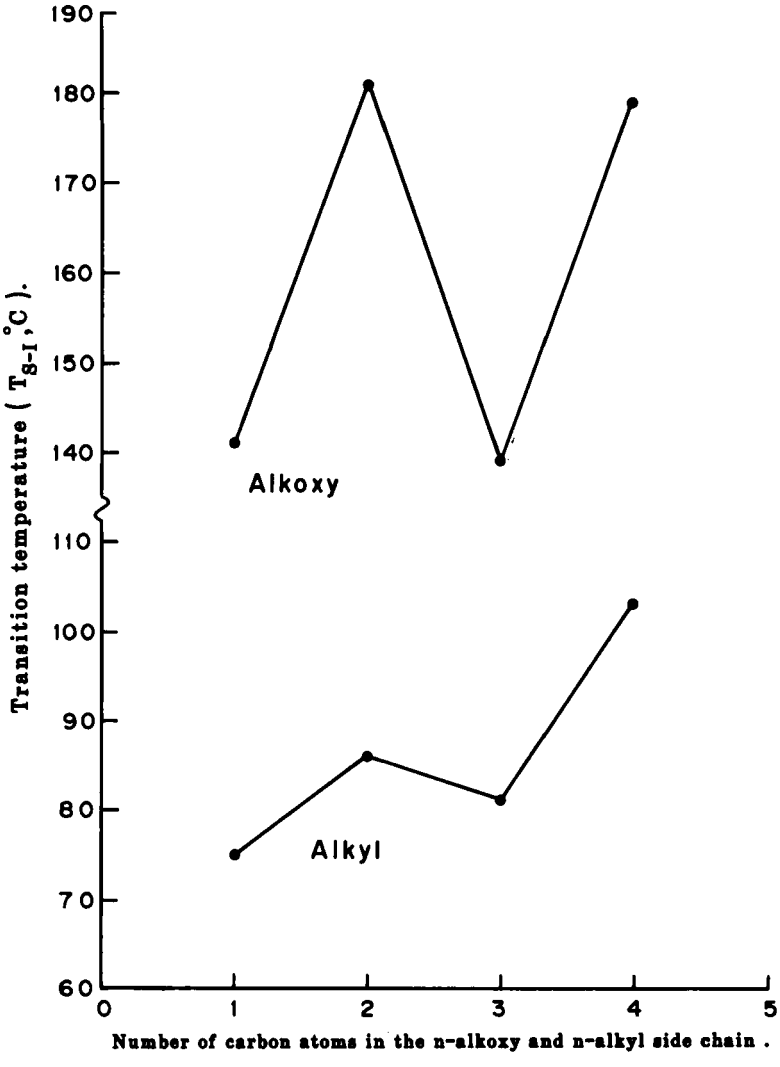


FIGURE 1 Plots of liquid crystal transition temperatures *v* *n*-alkoxy- and *n*-alkyl-chain length for side-chain length for side-chain Schiff's base polysiloxanes.

range from 1.69 to 3.69 Jg^{-1}. The transition heats are compared to those measured by different workers[10,18,19,31] for comparable polysiloxane systems with different spacer lengths (m) and different terminal tails. It is observed that for $m = 3$ or 4 and R = CN, the ΔH values range from 1.59 to 3.2 Jg^{-1}.[18,19] For other homologous series with $m = 3$, the transition enthalpies range from 2.0 to 6.4 Jg^{-1}.[31] Higher values were also reported for other types of smectic polymers.[10,31] It seems to be a general trend that the heat associated with the smectic to isotropic transition increases with increasing alkyl chain length or spacer length; however, the influence of the length of the tail is more important than that of the spacer.

TABLE V

Transition temperatures, enthalpies and entropies of the S–I transition for polymers I_{POM}–I_{POB}.

Polymer	R—	T(K)	ΔH (Jg^{-1})	ΔS ($Jg^{-1}K^{-1}$)
I_{POM}	CH_3O—	414.15	1.69	4.08×10^{-3}
I_{POE}	C_2H_5O—	454.15	2.14	4.72×10^{-3}
I_{POP}	C_3H_7O—	412.15	2.87	6.95×10^{-3}
I_{POB}	C_4H_9O—	452.15	3.69	8.18×10^{-3}

The entropy data for the smectic–isotropic transitions are given in Table V and presented graphically in Figure 2. It is observed that ΔS increases with increasing terminal alkoxy chain length. Furthermore a likely odd-even alternation in ΔS values is apparent. While odd-even alternations in ΔS values are known for monomeric liquid crystals,[1,29,30] no comparable data are reported for polymeric liquid

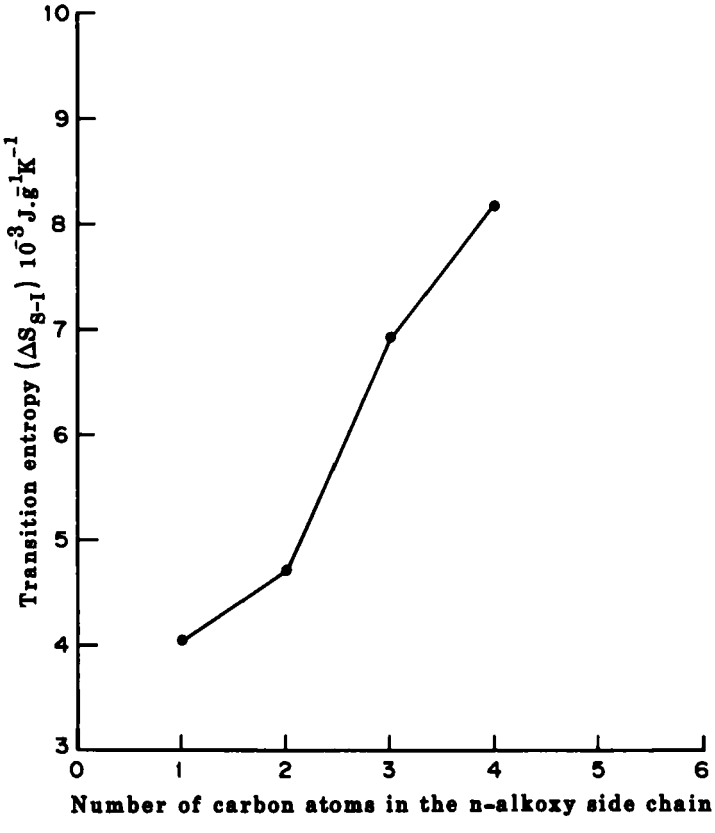


FIGURE 2 Plot of liquid crystal transition entropies *v* *n*-alkoxy-chain length of the alkoxy terminated side-chain polysiloxanes.

crystals. It is therefore apparent that collection of more thermodynamic data for polymeric systems is needed before one can establish common trends in ΔH and ΔS values.

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