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Liquid Crystalline Polymers Containing Heterocycloalkanediyl Groups as Mesogens. 7. Molecular Weight and Composition Effects on the Phase Transitions of Poly(methylsiloxane)s and Poly(methylsiloxane-*co*-dimethylsiloxane)s Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecanyl)-1,3,2-dioxaborinane Side Groups†

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ABSTRACT: The synthesis of poly(methylsiloxane)s with different molecular weights and of poly(methylsiloxane-*co*-dimethylsiloxane)s with different molecular weights and compositions, both containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,2,3-dioxaborinane as side groups, is described. Copolymers containing around 50/50 weight ratios between the polymer backbone and the polymer side chains exhibit two changes in their heat capacity. Sequence distribution considerations, dynamic mechanical thermal analysis measurements, and influence of both molecular weight and copolymer composition on the width of isotropization and transitions are all suggesting that these changes in the heat capacity are most probably associated with two glass transition temperatures. One glass transition temperature was assigned to the independent motion of the polymer backbone and the other to the cooperative (but independent from the polymer backbone) motion of the side groups. Therefore, these copolymers should exhibit an intramolecular microphase-separated morphology. Extrapolation of these two glass transition temperatures suggests that the poly(methylsiloxane) containing mesogenic side groups may also exhibit two glass transition temperatures.

Introduction

Recently we critically reviewed the molecular engineering of thermotropic side-chain liquid crystalline polymers and outlined some of the major problems of synthetic interest which require additional research.[1]

One of the principal problems which deserves additional research is the spacer concept introduced by Ringsdorf et al.[2,3]

This simple and invaluable structural concept led to the development of the entire field of side chain liquid crystalline polymers. However, the spacer concept provides only a partial decoupling of the motions of the side groups from that of the backbone in the liquid crystalline phase.[4-6] Below the glass transition temperature, the motion of the side groups is frozen. This is a very important result based on which many applications of side-chain liquid crystalline polymers are presently considered.

Recently, by analogy with the behavior of block and graft copolymers, we have proposed that highly or even completely decoupled side-chain liquid crystalline polymers would be realized for systems in which the side groups and the polymer backbone are highly immiscible.[7-12] In such systems, for a proper weight ratio between the polymer backbone and its side groups, an intramolecular microphase separation of the side groups from the polymer backbone is realizable and has been observed both by our group[7-12] and by Ringsdorf's group.[13,14] It is expected that for a suitable ratio between the domain sizes of the polymer backbone and the side groups, almost independent motion of the two sybsystems would be achievable. We have observed for a series of systems two changes in heat capacity on the DSC curves and suggested that they are due to the independent motion of the polymer backbone and the cooperative (but independent from the polymer backbone) motion of the side groups. Without any additional support, we have assigned these two changes in the heat capacity to the glass transition temperatures

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† Part 6 in this series: ref 64.

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associated with these two motions.[7-12] However, these two changes in the heat capacity can also be associated with at least two other possible phenomena. Before further discussion of these two possibilities, let us mention that all side-chain liquid crystalline polymers exhibiting two changes in their heat capacity are copolysiloxanes[7-14] and that they contain dimethylsiloxane structural units and siloxane structural units which are substituted with methyl and mesogenic side groups, respectively.

Certainly, the first alternative is that the two changes in the heat capacity are indeed due to the two glass transition temperatures but that these two glass transitions are the result of a microphase-separated block-copolymer type microstructure of the liquid crystalline copolysiloxane as suggested by Ringsdorf and Schneller.[15,16] In this case the two glass transition temperatures would be associated with the poly(dimethylsiloxane) segment and the polysiloxane segment containing mesogenic groups, respectively. The second alternative is that one of the two changes in the heat capacity is due to a glass transition while the other is due to a β-relaxation process.[17]

These are very important issues, since these two possible alternative explanations prevent the establishment of the basic concept supporting a highly decoupled side-chain liquid crystalline system.

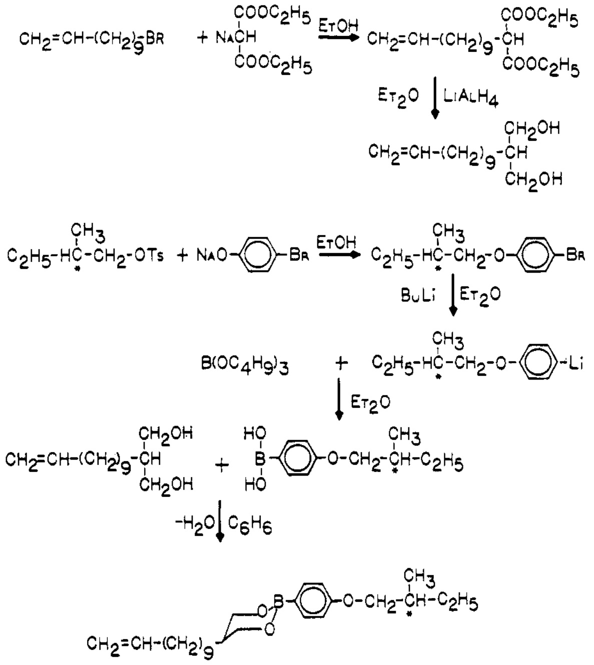
In an intramolecular microphase-separated system as previously suggested,[7-12] the motion of each subsystem would have to be controlled by its own glass transition temperature and therefore the behavior of a system like this differs from that of the partially decoupled systems. Therefore, such a system is of both theoretical and practical interest. However, since the design of such a polymer requires additional knowledge concerning the control of the polymer morphology, we must first try to elucidate the relationship between the two changes in the heat capacity and the three possible origins of these changes. In order to contribute to the interpretation of this issue, we have synthesized several series of homopolysiloxanes and copolysiloxanes with different molecular weights and containing 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,3,2-dioxaborinane as side groups. The goal of this paper is to present the synthesis of these polymers and to discuss their phase behavior in relation to these three alternatives.

Experimental Section

A. Materials. (−)-2(*S*)-Methyl-1-butanol, $[\alpha]_D$ − 7.3°, was obtained from Fluka and was used as received. Dicyclopentadienyl platinum (II) chloride catalyst used in the hydrosilation reaction was prepared according to a literature procedure.[18] Toluene used in the hydrosilation reaction was first refluxed over sodium and then distilled under argon. Trifluoromethanesulfonic acid (CF_3SO_3H, Aldrich) was freshly distilled prior to use. 1,3,5,7-Octamethylcyclotetrasiloxane (D_4), 1,3,5,7-tetramethylcyclotetrasiloxane (D_4'), dimethyldisiloxane, and hexamethyldisiloxane (MM) (all from Petrarch Systems) were distilled from CaH_2. Several commercial samples of poly(dimethylsiloxane)s (Petrarch Systems) with degrees of polymerization of 7, 43, 54, and 56 were used as received.

B. Techniques. ^1H NMR (200 MHz) spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard, unless noted. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station, was used to determine the thermal transitions which were reported as the maxima and minima of their endothermic or exothermic peaks, respectively. In all cases, heating and cooling rates were 20 °C/min, unless otherwise specified. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. All the heating scans produced identical DSC traces and similar results. However, transitions reported were read during the second or third heating and cooling scans unless reported otherwise. A Carl-Zeiss optical polarized microscope (magnification: 100×) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyze the anisotropic textures.[19,20] Molecular weights were determined by gel permeation chromatography (GPC) with a Perkin-Elmer Series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and Sigma 15 data station. High-pressure liquid chromatography (HPLC) determinations were performed with the same instrument. The measurements were made by using a UV detector, THF as solvent (1 mL/min; 40 °C), a set of Polymer Lab gel columns of 10^2, 5×10^2, 10^3, 10^4, and 10^5 Å, and a calibration plot constructed with polystyrene standards. Number-average molecular weights of the poly(methylsiloxane-*co*-dimethylsiloxane)s were also determined by ^1H NMR spectroscopy. Optical rotations were measured at 25 °C on a Perkin-Elmer 241 polarimeter with absolute methanol or chloroform as solvent. Dynamic mechanical thermal analyses were performed on a dynamic mechanical thermal analyzer (DMTA II, Polymer Laboratories) instrument, in the shear mode within the range of frequencies 0.3–200 Hz. Sample thickness was 0.33 mm. The temperature scanning rate was 4 °C/min. Samples were scanned from 140 to 40 °C for each individual frequency. The complex modulus (G^*) was plotted versus temperature, and T_g's were determined as the midpoint of each change in G^*.

Scheme I
Synthesis of 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecen-1-yl)-1,3,2-dioxaborinane



C. Synthesis of Monomers. Synthesis of 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(10-undecen-1-yl)-1,3,2-dioxaborinane. This synthesis is described in Scheme I and is based on a procedure described previously.[10] The only modification in the present case consists in the use of (*p*-[2(*S*)-methyl-1-butoxy]phenyl)lithium instead of (*p*-[2(*S*)-methyl-1-butoxy]phenyl)magnesium bromide in the preparation of *p*-[2(*S*)-methyl-1-butoxy]phenyl)boronic acid. This novel procedure is described below.

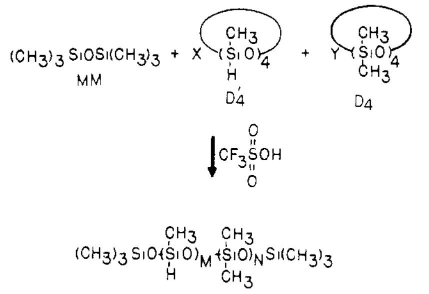
Synthesis of (*p*-[2(*S*)-Methyl-1-butoxy]phenyl)boronic Acid. Into a dry ice–acetone bath cooled solution of *p*-[2(*S*)-methyl-1-butoxy]phenyl bromide[10] (50 g, 0.21 mol) in 200 mL of dried diethyl ether was injected 22.7 mL of butyllithium (10 M solution in hexane) under nitrogen. The stirred solution was allowed to slowly warm to room temperature and then the reaction was allowed to continue for 2 h. After this time the solution was once again cooled with a dry ice–acetone bath. Tri-*n*-butyl borate[10] (63 g, 0.27 mol) was then added dropwise. A large amount of white precipitate formed, and the resulting slurry was allowed to warm to room temperature after which it was left stirring overnight.

Table I
Synthesis and Characterization of Poly(methylsiloxane)s and Poly(methylsiloxane-*co*-dimethylsiloxane)s

D_4', mmol	D_4, mmol	MM, mmol	$\bar{M}_n$ (theoretical)[a]	$\overline{DP}$ (NMR)	compositns and molecular weights determined after hydrosilatn			
					mol % mesogenic structural units		$\bar{M}_n$	
					theoretical[a]	NMR	theoretical[a]	GPC
b			580	7[b]	100	100	3 200	8 900
8.33		8.33	400	14	100	100	1 850	6 500
8.33		4.17	650	22	100	100	3 840	9 500
20.83		6.94	880	27	100	100	5 780	9 800
b			1500	43	100	100	11 500	16 400
b			2270	54	100	100	17 400	21 100
b			3900	56	100	100	29 900	29 900
20.83		0.10	50150	92	100	100	383 400	43 700
80.00		3.21	6140		100	100	45 900	25 500
13.73	54.9	2.70	7240		20	23.3	15 540	26 800
23.92	48.41	2.90	7080		33	38.0	20 300	21 400
23.75	48.18	10.02	2150		33	31.4	5 950	9 400
11.88	24.16	1.0	10170		33	35.3	29 170	35 700
17.84	36.18	1.0	15150		33	35.5	43 700	27 800
17.84	36.22	0.5	30170		33	34.1	87 230	47 000
36.42	36.42	2.9	6900		50	56.0	27 000	25 900
57.58	19.19	3.08	6500		75	82.0	36 400	22 800

[a] Based on the ratio between D_4' (and D_4) and MM without taking into account the formation of cycles. [b] Commercial samples.

Scheme II
Synthesis of Poly(methylsiloxane)s and Poly(methylsiloxane-*co*-dimethylsiloxane)s



The reaction mixture was then acidified with dilute HCl. The ether layer was separated, and the ether was removed in a rotovapor. Approximately 100 mL of H_2O was then added to the residue, and the mixture was placed on a rotovapor at 50 °C to azeotropically remove the 1-butanol formed in the reaction. After all of the butanol was removed, the resulting solid was recrystallized from water/methanol to yield 34 g (79.2%) of white crystals: mp 125–127 °C; ^1H NMR ($CDCl_3$, TMS, δ, ppm)) 1.1 (m, 6 H, CH_3–), 1.2–1.7 (m, 2 H, –CH_2CH–), 1.6 (s, 2 H, B($3H)_2$), 1.9 (m, 1 H, –C*H*–), 3.9 (m, 2 H, –CH_2O–), 7.1 and 8.2 (2d, 4 H, Ar*H*).

D. Synthesis of Polymers. Synthesis of Poly(methylsiloxane)s and Poly(methylsiloxane-*co*-dimethylsiloxane)s. Scheme II illustrates the synthesis of poly(methylsiloxane)s and poly(methylsiloxane-*co*-dimethylsiloxane)s. Poly(methylsiloxane)s were synthesized by the cationic polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D_4'). Poly(methylsiloxane-*co*-dimethylsiloxane)s were synthesized by the cationic copolymerization of 1,3,5,7-tetramethylcyclotetrasiloxane (D_4') with 1,3,5,7-octamethylcyclotetrasiloxane (D_4). The molecular weight of the polymers was controlled in both cases by using the proper amount of hexamethyldisiloxane (MM) as a chain terminator. Polymerizations were performed in bulk at room temperature by using trifluoromethanesulfonic acid as initiator. Reaction time was 24 h in all cases. We can safely assume that after 24 h of reaction time our polymerization systems have reached equilibrium, since the kinetics of equilibration of D_4 and MM derivatives in the presence of triflic acid has been shown to result in equilibrium within a maximum of 12 h of reaction time.[21] An example of polymerization is discussed below.

Into a flame-dried flask fitted with magnetic stirrer and nitrogen inlet–outlet purge system was placed 4.28 g (18 mmol) of D_4, 0.162 g (1 mmol) of MM, and 37 mg of trifluoromethanesulfonic acid.

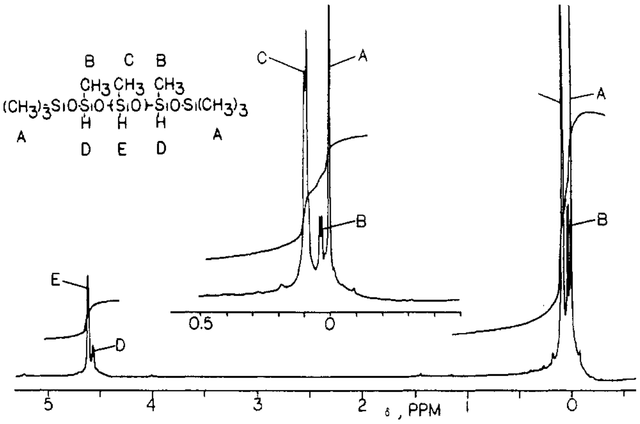


Figure 1. 200-MHz ^1H NMR spectrum ($CDCl_3$, TMS) of poly(methylsiloxane) with DP-7.

The reaction mixture was stirred under nitrogen for 24 h at room temperature. After this time, 70 mg of sodium bicarbonate was added to the reaction mixture to neutralize the initiator, and the reaction mixture was stirred for 1 h. The mixture was then taken up in toluene, filtered, and dried over anhydrous $MgSO_4$. The solution was filtered, and toluene was removed under vacuum. Cyclic compounds were distilled from the resulting polymer under vacuum at 150 °C. Number-average degrees of polymerization of the poly(methylsiloxane)s were determined by 200-MHz ^1H NMR spectroscopy. A typical ^1H NMR spectrum together with its proton assignments is presented in Figure 1. The following relation was used for the calculation of the polymerization degree: $DP = [(C + B)/3]/(A/18)$, where A, B, and C are the integrals corresponding to the A, B, and C resonances from Figure 1. Table I summarizes the reaction conditions and the characterization of the poly(methylsiloxane)s and poly(methylsiloxane-*co*-dimethylsiloxane)s.

Synthesis of Polysiloxanes and Copolysiloxanes Containing Mesogenic Side Groups. Both homopolymers and copolymers were synthesized by the hydrosilation of 2-[4-(2-(*S*)-methyl-1-butoxy)phenyl]-5-(10-undecen-1-yl)-1,3,2-dioxaborinane using dicyclopentadienylplatinum(II) chloride as catalyst in toluene. A detailed procedure for a complete hydrosilation free of side reactions was previously reported[10] and was followed without modification. The purity of the resulting polymers was checked by HPLC. All were purified until they were free of starting materials. Their molecular weights were determined by GPC. The final composition of the copolymers was determined by 200-MHz ^1H NMR spectroscopy. A representative ^1H NMR

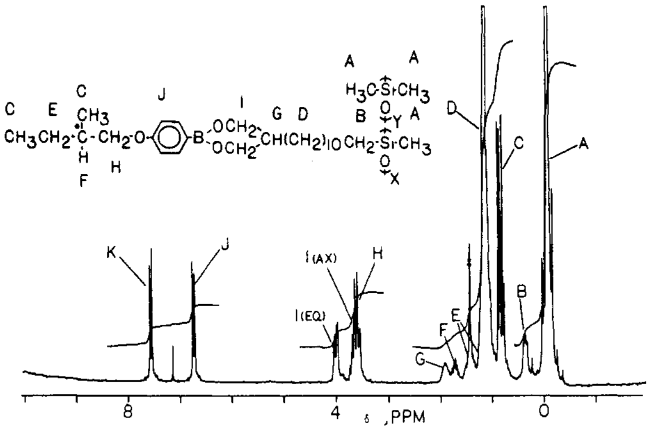


Figure 2. 200-MHz ^1H NMR spectrum ($CDCl_3$, TMS) of the copolysiloxane containing 23.3 mol % structural units with mesogenic groups and M_n = 26 800.

spectrum together with its protonic assignments is presented in Figure 2. The following equation was used to calculate copolymer composition: mole % of structural units containing mesogenic side groups =

$$(B/2)/([A - 3(B/2)]/6 + B/2)$$

Table I summarizes the composition of copolymers as determined after hydrosilation.

Results and Discussion

Some Considerations of the Possible Sequence Distribution in Poly(methylsiloxane-*co*-dimethylsiloxanes)s. The mechanism of cationic ring-opening polymerization of D_4 initiated by trifluoromethanesulfonic acid was investigated by two research groups.[22-24] It has been demonstrated by both groups that there are two different mechanisms which are simultaneously operating and which generate linear polymers and/or cyclic oligomers.

Sigwalt et al.[22,23] suggested that cationic ring opening polymerization of D_4 takes place through tertiary oxonium ions. This propagation reaction is accompanied by backbiting which gives rise to cyclic compounds. Termination provides α,ω-bis(silyl triflate) poly(dimethylsiloxane)s. This derivative cannot undergo homopolycondensation. Hydrolysis of one of the silyl triflate groups gives α-silanol-ω-(silyl triflate) poly(dimethylsiloxane)s. Simultaneously, acidolysis of D_4 leads to $Tf-(SiMe_2-O)_4-H$. This last derivative as well as the higher homologues of α-silanol-ω-(silyl triflate) poly(dimethylsiloxane)s undergo polycondensation, leading through an intramolecular end to end ring closure reaction to macrocycles and through an intermolecular reaction to high polymers. It is essential to mention that in the cationic polymerization of D_4, cyclic compounds containing multiples of D_4 units (D_{4n}) are not kinetically favored, even at the beginning of the reaction. Therefore, according to this reaction mechanism, both the cyclic compounds and the linear polymers obtained under reaction conditions dictated by polymerization kinetics do not predominately contain multiples of D_4 units.

Chojnowski's et al.[24] kinetic scheme is similar to that suggested by Sigwalt's group. However, they suggest that cationic ring-opening polymerization occurs through primary oxonium ions. This implies that ring formation takes place only by intramolecular end to end condensation processes. The continuous population of cyclic oligomers, which, in principle, is a feature of a back-biting mechanism of cyclization, is explained in this second case by the siloxane unit exchange between different polymer chains:[24,25]

$$HO(SiMe_2)_nH + HO(SiMe_2O)_mH \rightleftharpoons HO(SiMe_2O)_{n-1}H + HO(SiMe_2O)_{m+1}H$$

Therefore, this second mechanism suggests that the microstructure of the kinetically obtained poly(dimethylsiloxane) is similar to the one which resulted from Sigwalt's mechanism.

However, as described in the Experimental Section, our polysiloxanes and copolysiloxanes were prepared under equilibrium reaction conditions, i.e., where the comonomer sequence distribution dictated by the kinetics of polymerization is lost. The equilibrium composition of linear siloxanes was determined by Scott[26] and confirmed by other authors[27] to agree with Flory's theory of random reorganization. The kinetically controlled composition of linear oligomers in the cationic equilibration of D_4 with MM was studied by Carmichael and Heffel.[28,29] They observed that in the first stages of the reaction some excess of MD_4M and MD_8M oligomers are formed. This led them to conclude that if D_4 is cleaved by the acid catalyst, it enters the linear molecule as a unit. However, this excess of MD_4M and MD_8M disappears in the course of the redistribution.

The reactivity of D_4 should not be too different from the reactivity of D_4'. We see no reason for a change in the ring strain or the nucleophilicity of cyclic siloxane in going from D_4 to D_4'. Therefore, even the kinetically controlled sequence distribution of poly(methylsiloxane-*co*-dimethylsiloxane)s should be random. By random we mean not only a random distribution of D_4 and D_4' structural units, but a random distribution of D_n and D_n' structural units (n = 1, 2, ...). At equilibrium, the sequence distribution should be as predicted by Flory's theory of random reorganization of linear species.[28]

For the case of copolymers obtained from D_3 and D_4' we would expect a different sequence distribution than in the present case. Due to its higher ring strain and nucleophilicity D_3 is more reactive than D_4' or D_4 and therefore at least the kinetically controlled sequence distribution should contain multiples of D_3 units, i.e., D_{3n}. It is well documented that the microstructure of linear and macrocyclic poly(dimethylsiloxane)s obtained by cationic polymerization of D_3 contains multiples of D_3 units.[30]

In conclusion, we can safely assume that the sequence distribution of D and D′ units of the poly(methylsiloxane-*co*-dimethylsiloxane)s prepared under equilibrium conditions is random. However, we cannot automatically assume that this is the case for commercially available samples which are of an unknown synthetic origin.

The random sequence distribution of D and D′ units in poly(methylsiloxane-*co*-dimethylsiloxane)s does not support the idea that the two changes in the heat capacity of the DSC curves of liquid crystalline copolysiloxanes are due to two glass transitions associated with a block copolymer type microstructure of the liquid crystalline copolysiloxanes.

Evidence for Two Glass Transition Processes in Copolymers. As previously discussed[10] copolymers containing about 50 wt % mesogenic units display two relaxation processes resulting in a stepwise increase of the specific heat capacity which can be observed on the DSC trace from Figure 3. The magnitude of these two stepwise variations of ΔC_p is of the same order as the one observed for the case of the glass relaxation of flexible chain molecules. This strongly suggests that both relaxation processes are primary relaxation processes, i.e., are due to relaxation processes involving the freezing of cooperative motions. We have assigned the relaxation process occuring at low temperature to the glass transition temperature of

Table II
Thermal Transitions and Thermodynamic Parameters for Polysiloxanes Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,3,2-dioxaborinane Side Groups and Varying Degrees of Polymerization

$\overline{\mathrm{DP}}$ (NMR)	$\bar{M}_w/\bar{M}_n$ (GPC)	phase transitions (°C) and corresponding enthalpy changes (kcal/mru[a])															
		heating									cooling						
7	1.17	g	−5	s	10	(0.12)[b]	s	72	(1.9)	i	i	64	(1.9)	s	6	(0.10)	s
15	1.14	g	9	s	25	(0.16)	s	93	(2.1)	i	i	85	(2.0)	s	20	(0.15)	s
22	1.17	g	10	s	24	(0.15)	s	98	(2.0)	i	i	87	(2.0)	s	16	(0.13)	s
27	1.45	g	10	s	21	(0.11)	s	95	(1.8)	i	i	85	(1.8)	s	13	(0.10)	s
43	1.60	g	10	s	21	(0.10)	s	99	(1.9)	i	i	90	(1.8)	s	15	(0.09)	s
54	1.63	g	10	s	21	(0.08)	s	98	(1.6)	i	i	87	(1.5)	s	16	(0.09)	s
56	1.81	g	10	s	21	(0.13)	s	98	(1.8)	i	i	90	(1.7)	s	14	(0.10)	s
92	1.72	g	10	s	24	(0.11)	s	104	(1.8)	i	i	94	(1.7)	s	17	(0.12)	s

[a] mru = mole repeat unit. [b] Values in parentheses are enthalpy changes in kcal/mru. Abbreviations: g, glassay; s, smectic; i, isotropic.

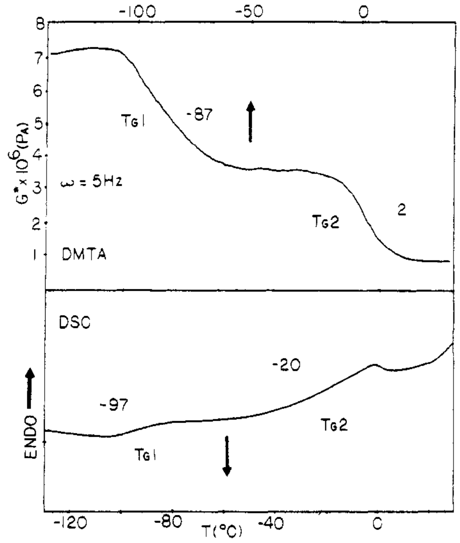


Figure 3. DMTA and DSC traces for the copolysiloxane containing 23.3 mol % structural units with mesogenic groups and M_n = 26 800.

the microphase-separated polymer backbone. The relaxation process at high temperature was assigned to a glass transition associated with the cooperative (but independent from the polymer backbone) motion of the side groups.

Discrimination between primary (cooperative) and secondary relaxation processes (characterized by local motions) can be made by investigating the dependence of the frequency of these motions on temperature. This can be done by using the WLF equation and/or by determining the activation energy of the relaxation process.[31-36]. Secondary (β) relaxation processes usually display constant activation energy over a considerable temperature range, whereas the primary or glass process (α) displays an effective activation energy which increases drastically as the static glass transition temperature is approached. A secondary process is thus characterized by a straight line on the activation diagram, i.e., in a plot of the logarithm of the frequency versus the inverse temperature, whereas the glass transition process yields a line which strongly bends.[31,34]

Figure 3 presents a representative DSC curve and a G^*–T (°C) plot resulting from DMTA measurements of a copolymer which has 22.3% structural units containing mesogenic groups. Due to the difference between the frequencies of the DSC and DMTA experiments, the temperature at which the two sets of relaxation processes occur is slightly shifted. However, both experiments provide clear evidence for two relaxation processes. Figure 4 displays the plots of ln ω versus $1/T$. Both plots suggest β relaxation processes since their ln ω versus $1/T$ dependences are linear. However, even a cooperative relaxation process can exhibit such a linear dependence for the narrow ranges of frequencies used in the experiment described here.[34,37]

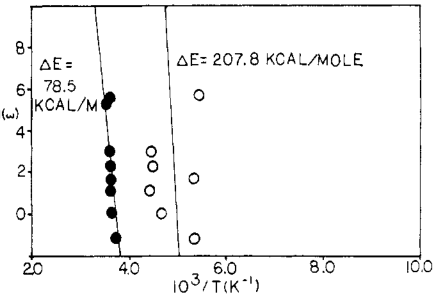


Figure 4. ln ω versus $1/T$ (K^{-1}) plots for copolysiloxane containing 23.3 mol % structural units with mesogenic groups and M_n = 26 800: ●, relaxation process at low temperature (T_{g1}); ○, relaxation process at high temperature (T_{g2}).

The temperature dependence of the relaxation frequency for the case of a secondary relaxation can be expressed as follows:[34,38] $\omega = \omega_0 \exp(-E_\beta/kT)$. The determination of the activation energy assuming β relaxation processes for the plots in Figure 4 lead to E_a = 207.8 kcal/mol for the relaxation process at low temperature and E_a = 78.5 kcal/mol for the relaxation process at high temperature. These activation energy values are higher than expected for β relaxation transitions and are within the values expected for the activation energies of glass transition temperatures.[31,37] Therefore, dynamic mechanical thermal analysis results strongly support the conclusion that both changes in the heat capacity of the DSC curves are due to glass transition temperatures.

Influence of Molecular Weight on the Phase Behavior of Homopolymers. The influence of molecular weight on the phase beahvior of liquid crystalline polymers was recently reviewed.[1] We will briefly consider a few results from the literature of liquid crystalline polymers containing flexible spacers.

Regardless of the nature of the polymer backbone, liquid crystalline transition temperatures increase up to a certain molecular weight and then remain roughly constant independent of molecular weight.[39,41] In the case of liquid crystalline polysiloxanes, phase transitions become independent of molecular weight for degrees of polymerization higher than 10.[40] It has been suggested that the increased phase transition temperature is due to the increased packing density of the mesogenic side groups of the higher molecular weight polymer.[40] Table II summarizes the phase transition temperatures for the liquid crystalline polysiloxanes of different degrees of polymerization. All polymers and copolymers discussed in this paper display two smectic mesophases.[10] However, the nature of these

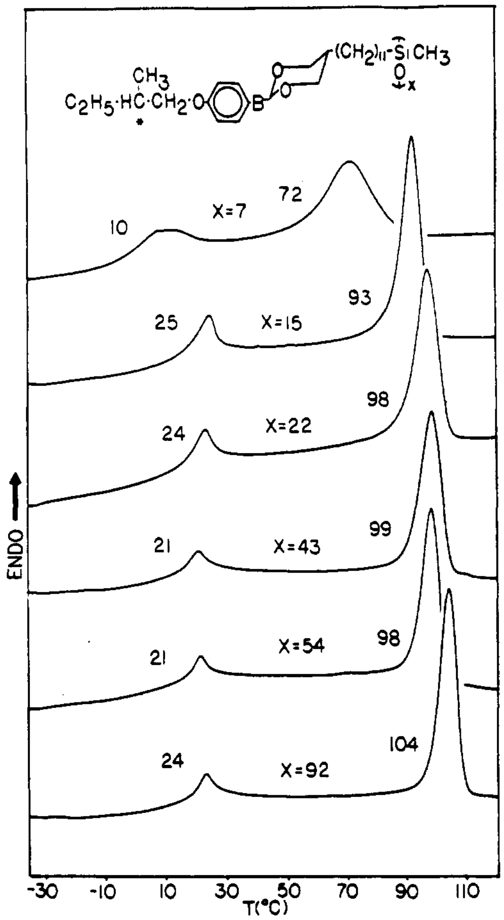


Figure 5. Normalized DSC heating scans (20 °C/min) for some representative liquid crystalline polysiloxanes with different degrees of polymerization.

mesophases is not important to the present discussion. Figure 5 presents some representative heating DSC curves for this series of polymers, while Figure 6 presents the cooling curves for the same polymers. Both smectic–smectic and smectic–isotropic phase transitions summarized in Table II are plotted as a function of degrees of polymerization in Figure 7. These results agree with the data obtained by Finkelmann et al.[40] That is, phase transition temperatures increase up to degrees of polymerization of about 15 after which they are molecular weight independent. This degree of polymerization corresponds to a $\bar{M}_n$ (as determined by GPC measurements) of 6500. Therefore, it is safe to assume that number-average molecular weights larger than 6500 will not have a significant influence on the polymer phase transitions under consideration.

Two very important points are missing from previous experiments concerning the influence of molecular weight on phase transitions.[39,40] The first one refers to the dependence of the enthalpy change associated with the liquid crystalline transition on polymer molecular weight. Finkelmann et al. unpublished data have shown that within the experimental error of the DSC measurements, the enthalpy change is independent of polymer molecular weight.[42] Our results from Table II seem to support the idea that enthalpy changes are molecular weight independent. Experimental results from our laboratory carried out with liquid crystalline polymers containing different polymer backbones also agree with Finkelmann's results.[42]

The second point missing from previous publications on this topic[39,40] refers to the shape of the DSC peak associated with liquid crystalline phase transitions. This

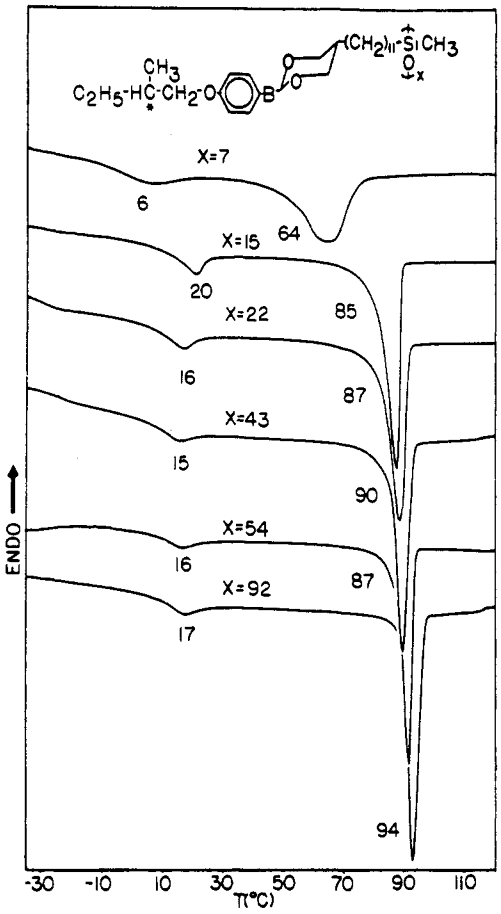


Figure 6. Normalized DSC cooling scans (20 °C/min) for some representative liquid crystalline polysiloxanes with different degrees of polymerization.

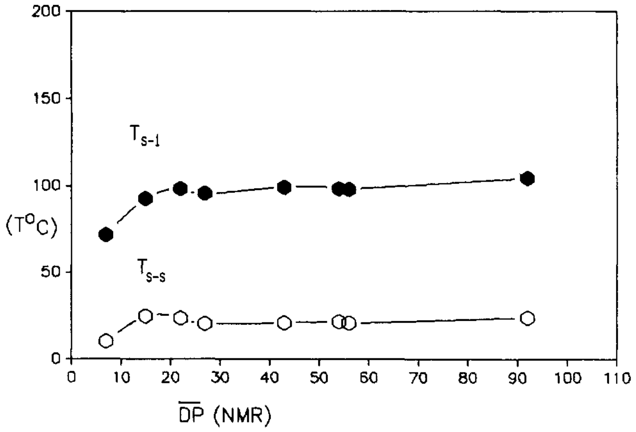


Figure 7. Dependence of T_{s-s} and T_{s-i} versus polymerization degree for liquid crystalline polysiloxanes. Data from Table II.

subject has been discussed by Blumstein for the case of thermotropic main-chain polymers containing flexible spacers.[43] In contrast to low molar mass liquid crystals which are composed of single molecular species, liquid crystalline polymers and oligomers are characterized by a variety of molecular species due to the polydispersity of molecular mass, composition (for the case of copolymers), chain end concentration, etc. This results in the appearance of a liquid crystalline–isotropic or liquid crystalline–liquid crystalline biphase, the width of which depends on the average molecular mass and the global polydispersity of the sample. The sharp transition points from low molar mass liquid crystals are replaced in polymers by averaged values. The width of this biphase has never

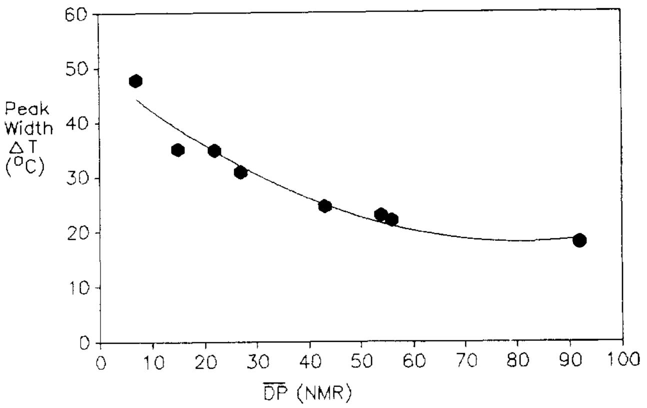
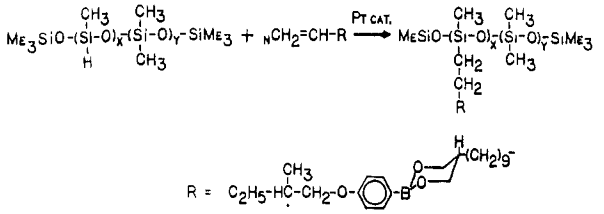


Figure 8. Width of the isotropic–smectic transition as a function of liquid crystalline polysiloxane molecular weight.

been considered for side-chain liquid crystalline polymers. The simplest way to characterize this biphase is by determining the width of the endothermic (from the heating scan) or exothermic (from the cooling scan) DSC peaks associated with the phase transition.[43] For the case of main-chain liquid crystalline polymers, it has been demonstrated that the width of the nematic–isotropic biphase is inversely proportional to the decrease of the polymer molecular weight.[43]

A short inspection of the DSC traces presented in Figures 5 and 6 shows that an identical trend appears for side-chain liquid crystalline polysiloxanes. The width of the smectic–isotropic (Figure 5) or isotropic–smectic (Figure 6) phase transition is much wider for lower molecular weight polymers. The peak widths determined from the cooling scans of the DSC curves from Figure 6 are plotted in Figure 8 as a function of the degree of polymerization. We can propose several possible explanations for this behavior. For polymer samples having the same molecular weight polydispersities, the width of this transition should be larger at low molecular weights than at high molecular weights. This statement can be understood if we consider again the plots from Figure 7. This figure can easily demonstrate that for low molecular weight polymers, the difference between the T_{s-i} of two different molecular weights which are present within the same polymer sample is wider than for two polymers with high molecular weights. This is because this transition is strongly molecular weight dependent within the range of low molecular weights, while it is almost molecular weight independent for higher molecular weight ranges. Therefore, the difference between the T_{s-i} for two low molecular weight polymers should be larger than the difference between T_{s-i} of two higher molecular weight polymers. However, due to the same molecular weight effect we would expect to see no difference between the width of the smectic–isotropic transitions above the range of molecular weights where phase transitions are molecular weight independent. As Figure 8 shows, this is not the case. There is a continuous decrease in the width of this phase transition even for the range of molecular weights where the temperature of this transition is only slightly molecular weight dependent. A possible cause of this trend is due to the polymer polydispersity. However, as we see from Table II, for the range of low molecular weights, polydispersities are very narrow, while for higher molecular weight polymers there is an inversion in the trend of polydispersity. This inversion is not followed by the trend in the width of the isotropic transition temperature (Figure 8). Low molecular weight polymer samples have very narrow polydispersities in comparison with higher molecular weight polymer samples (Table II). This means that the explanation correlating the width of the phase transition based upon the dependence of the phase transition on molecular weight cannot alone explain this behavior.

Scheme III
Synthesis of Liquid Crystalline Polysiloxanes and Copolysiloxanes



The influence of polymer chain ends on phase transitions also has to be considered. All these polymers contain two trimethylsiloxy chain ends (Scheme III). These chain ends can drastically affect the phase behavior of the polymer if they are miscible or partially miscible with the mesogenic structural units. Consider the lowest molecular weight polymer sample, which has a degree of polymerization of 7 (Table II). If the chain ends are considered as structural units in a "copolymeric" architecture which contains both mesogenic and nonmesogenic (the chain ends) units, then the lowest molecular weight copolymer contains 22.2 mol % of nonmesogenic units derived from these two chain ends. The mol % concentration of these chain ends decreases according to the degrees of polymerization from Table II, to 8.3, 6.9, 4.4, 3.6, 3.4, and reaches 2.1 for the polymer with a polymerization degree of 92. Certainly, a larger difference in concentration of structural units derived from chain ends is found for the samples with degrees of polymerization of 7 and 15. Therefore, we would expect these two samples to show the largest difference in peak widths. This expectation does not correspond completely with the data from Figure 8.

We have observed the same trend in the peak width dependence versus polymer molecular weight for a series of liquid crystalline polymethacrylates which were synthesized by group transfer polymerization.[41] The influence of the polymer chain ends in this case, although large, is expected to be almost undetectable because of the nature of the polymer chain ends resulting from the group transfer polymerization technique.

Two model compounds were considered of possible help in elucidating this problem. The first one is a 1,3,5,7-tetramethylcyclotetrasiloxane containing mesogenic side groups.[11] The peak width of its isotropic–liquid crystalline transition is 16.7 °C, which is much narrower than of the linear heptamer. The cyclic compound (a mixture of four stereoisomers with identical molecular weights) does not contain trimethylsiloxy chain ends, and this together with the monodisperse nature of this sample can be the reason for the difference between the peak width of these samples. However, we should not neglect the difference between the restricted conformation of the crowned cyclic tetramer and the random coil conformation of the linear compounds. The second model prepared is a tetramethyldisiloxane containing two mesogenic units and no trimethylsiloxy chain ends ($R-Si(CH_3)_2-O-Si(CH_3)_2-R$) where R is the mesogenic side group. The isotropization transition for this dimer occurs at 49 °C on the heating scan and at 43 °C on the cooling scan. The peak width of this transition on the cooling scan is 34 °C. This width is narrower than of the heptamer but is larger than the peak width of the cyclic tetramer and is within the same range with values for the next two molecular weight homopolymers. Since

Table III
Thermal Transitions and Thermodynamic Parameters for Copolysiloxanes Containing 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,3,2-dioxaborinane Side Groups and Varying Composition

structural units containing side groups		GPC		phase transitions (°C) and corresponding enthalpy changes (kcal/mrmu[a])																	
mol % (NMR)	wt % (NMR)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	heating											cooling						
23.3	65	26 800	2.95	g_1	−98	g_2	−8	s	−7	(0.16)[b]	s	37	(1.3)	i	i	31	(1.3)	s	−14	(0.12)	s
38.0	79	21 400	2.02	g_1	−81	g_2	−8	s	−6	(0.22)	s	47	(1.3)	i	i	41	(1.2)	s	−13	(0.21)	s
56.0	89	25 900	2.17	g_1	−66	g_2	5	s	9	(0.23)	s	75	(1.8)	i	i	67	(1.8)	s	2	(0.19)	s
82.0	97	22 800	1.49			g_2	8	s	18	(0.24)	s	92	(2.0)	i	i	83	(2.0)	s	13	(0.26)	s
100.0	100	25 500	2.10			g_2	8	s	20	(0.13)	s	90	(1.8)	i	i	81	(1.7)	s	13	(0.12)	s

[a] mrmu = mole repeat mesogenic units. [b] Values in parentheses are enthalpy changes in kcal/mrmu. Abbreviations: g_1, g_2, glassy; s, smectic; i, isotropic.

this dimer has no trimethylsiloxy chain ends and is monodisperse, we would expect it to dissplay a narrower peak width than even the high molecular weight polymers. It seems that the results from studies of these two model compounds are not conclusive enough to evaluate this problem. Additional model compounds would be needed to solve this problem. At the present time, we suggest that the concentration of the polymer chain ends is not sufficient to explain this trend in the peak width–molecular weight dependence. The last possible explanation we can propose at the present time is that in addition to the miscibility of the polymer chain ends, the miscibility of the polymer backbone and the polymer side groups also influence this peak width. Lower molecular weight polysiloxane segments are much more miscible with glassy oligomers than with higher molecular weight homologues,[44–46] and the same should be true for their miscibility with liquid crystal oligomers. However, with only the data from experiments described in this subsection we cannot argue more on this statement.

As we can observe from Table II, all homopolymers exhibit a single glass transition temperature. This glass transition temperature is independent of molecular weight for polymers with degrees of polymerization higher than 22.

Influence of Copolymer Composition on the Phase Behavior of Copolymers. A series of copolysiloxanes with molecular weights higher than the molecular weight which influences phase transitions but with different compositions was synthesized (Table III). We tried as much as possible to obtain copolymers exhibiting the same molecular weight. As we can observe from the data collected in Table III, all these copolymers exhibit two glass transition temperatures. Since the sequence distribution of the dimethylsiloxane and methylsiloxane containing mesogenic structural units is random, the only explanation we can support at the present time is that the low glass transition temperature is indeed due to the independent motion of the microphase separated main chain, while the high glass transition temperature is due to the independent (from the polymer backbone) but cooperative motion of the side groups.

Recently, Ringsdorf et al.[13,14,47] have demonstrated a similar morphology in side-chain liquid crystalline copolysiloxanes containing paired mesogens. On the basis of X-ray diffraction experiments, they have suggested a microphase separated model which consists of two sublayers. One layer contains the irregularly arranged main chain, while the other one is formed by the side chains.[13,47] A microphase-separated system like the copolysiloxane containing paired mesogens as side groups is characterized by a low dependence of phase transitions versus copolymer composition. Simultaneously, a nonmicrophase separated liquid crystalline copolymer shows a very sharp dependence of phase transitions versus composition.[4] This is a expected behavior for an intramolecularly microphase separated system, for example, a graft copolymer. Although the weight ratio of the two subsystems drastically affects the polymer morphology, the physical parameters of each subsystem are affected mostly at the two extremes in copolymer composition. However, in a single phase graft copolymer, physical parameters are weight averaged values of those of the individual systems and therefore undergo continuous change. It is therefore of interest to observe the relationship between phase transitions and copolymer composition for our case.

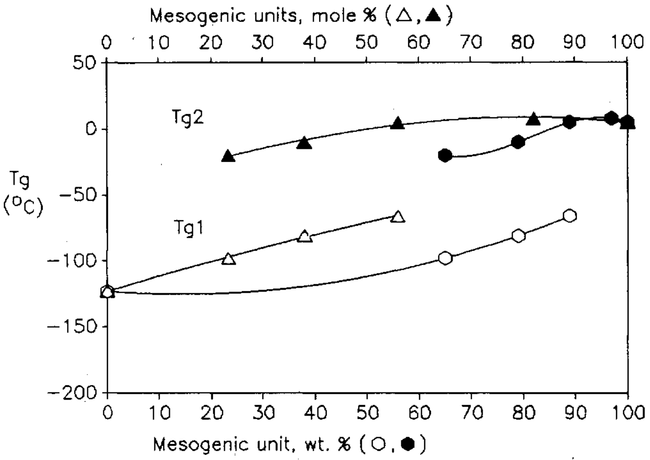


Figure 9. The dependence of the two glass transition temperatures of copolysiloxanes as a function of concentration of mesogenic structural units in copolysiloxanes.

Figure 9 presents the dependence of the two glass transition temperatures on the mole percent and respectively weight percent of structural units containing mesogenic units. There is a very small dependence of T_g versus copolymer composition independent of the mode in which these data are plotted. However, for the case of the liquid crystalline homopolymers, and copolymers containing less than 10 mol % or wt % dimethylsiloxane structural units, we can detect only the high glass transition temperature on the DSC curves. We have to carefully examine the dependence of the high-temperature glass transition on copolymer composition, especially, for the range of mole percent composition approaching the liquid crystalline homopolymer. From 50 to 100 mol % structural units containing mesogenic groups, this T_g is composition independent. This result can suggest that the glass transition temperature of the homopolymer might correspond to the glass transition of the side groups. Additional work to confirm this extrapolation is required and is in progress in our laboratory.

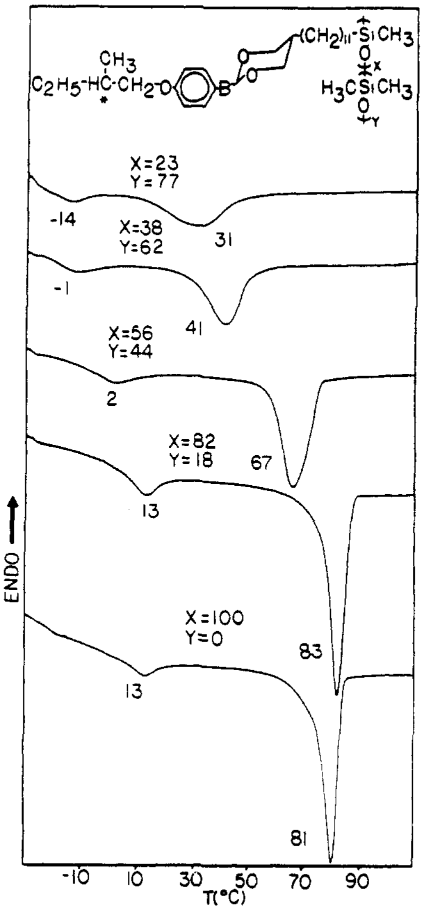


Figure 10. Normalized DSC heating scans (20 °C/min) for liquid crystalline copolysiloxanes with different composition.

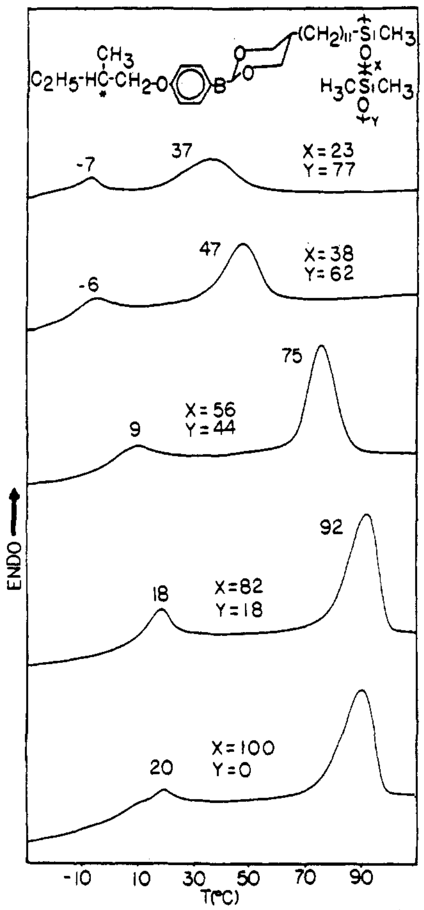


Figure 11. Normalized DSC cooling scans (20 °C/min) for liquid crystalline copolysiloxanes with different composition.

Figures 10 and 11 present some representative DSC curves for these copolymers. It is of interest to follow not only the trend in the thermal transition temperatures but also the shape of these peaks as well as the enthalpy change associated with these transitions. The trend in liquid crystalline transition temperature–copolymer composition is illustrated in Figure 12. The decrease in thermal transition temperatures obtained by diluting the mesogenic units with nonmesogenic units resembles the trend observed by microphase separated copolysiloxanes containing paired mesogens,[4] assuming that corrections for the difference between the weight of paired and single mesogens are considered. At the same time, the width of the smectic–isotropic or isotropic–smectic transition dependence is strongly composition dependent. In this case, the width of this transition increases with increasing nonmesogenic units content (Figures 10, 11, 13). A possible explanation for this behavior is that a lower concentration of side groups gives a larger percentage of the side groups being solubilized into this high molecular weight backbone.

Influence of Molecular Weight on the Phase Behavior of Copolymers. Table IV presents phase transitions for a series of copolysiloxanes containing an average of 35 ± 3.2 mol % structural units with mesogenic side groups and different degrees of polymerization. All polymers exhibit two glass transition temperatures. Both glass transition temperatures are almost independent of molecular weight. This behavior is expected since the molecular weights of these polymers are higher than the values for which the molecular weight influences phase transitions for the homopolymers. Representative heating and cooling DSC traces from these polymers are presented in Figures 15 and 16. Both the smectic–smectic and the

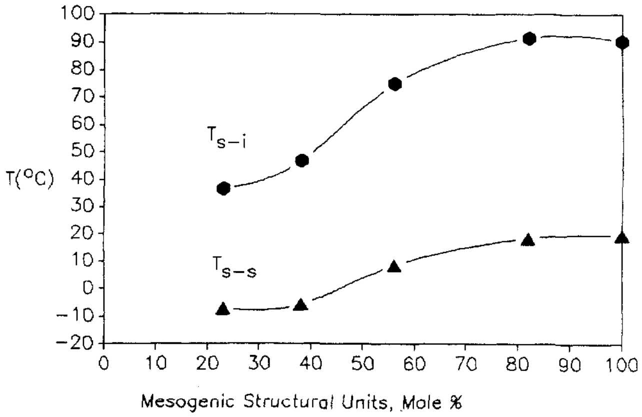


Figure 12. Dependence of $T_{s\text{-}s}$ and $T_{s\text{-}i}$ on liquid crystalline copolysiloxane composition.

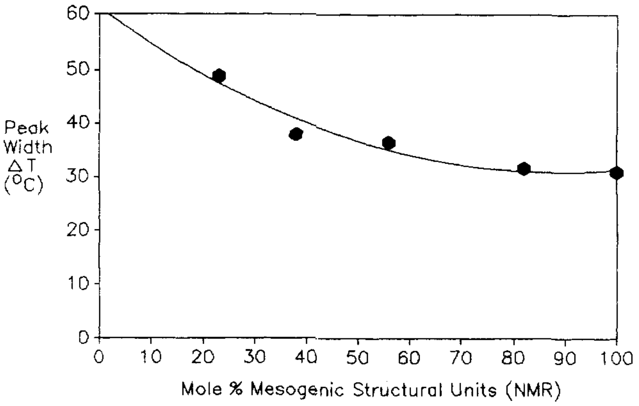


Figure 13. Dependence of isotropic–smectic peak width on liquid crystalline copolysiloxane composition.

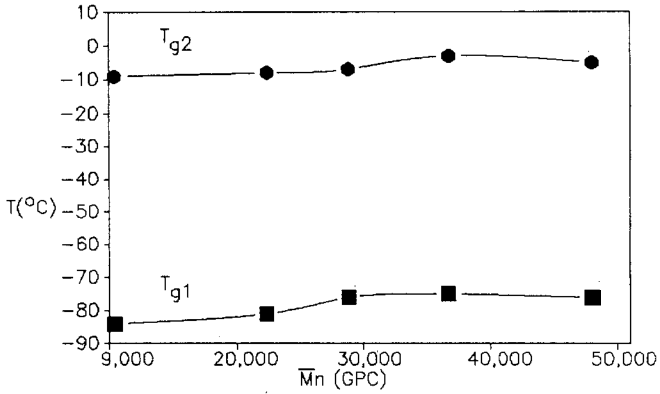


Figure 14. The dependence of the two glass transition temperatures of liquid crystalline copolysiloxanes on their molecular weight. All samples contain 35 ± 3.2 mol % structural units with mesogenic groups.

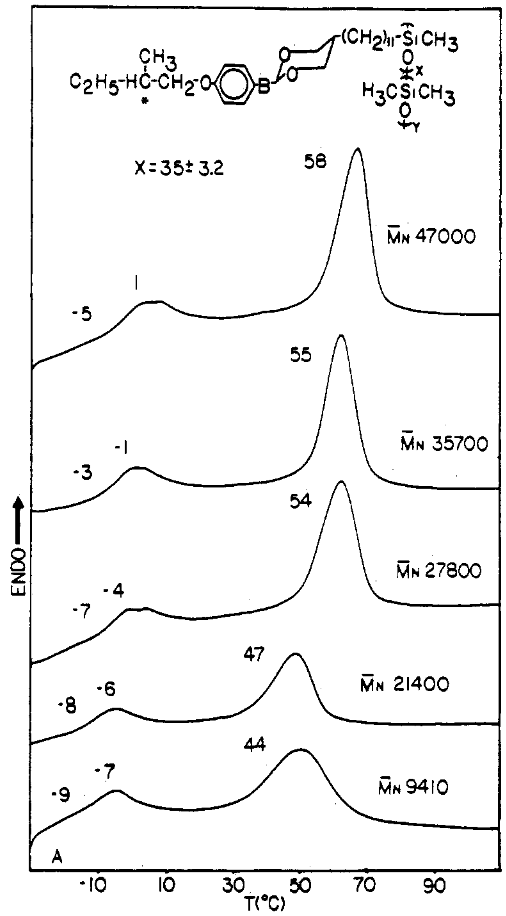


Figure 15. Normalized DSC heating scans (20 °C/min) for liquid crystalline copolysiloxanes containing 35 ± 3.2 mol % structural units with mesogenic groups and different degrees of polymerization.

smectic–isotropic transitions are very little affected by molecular weight differences. This is best illustrated by the plots for Figure 17. The only parameters which is still strongly influenced by copolymer molecular weight within this range of molecular weights is the peak width of the smectic–isotropic transition. However, since both copolymer compositions and molecular weight are not very uniform, the dependence of peak width on molecular weight presented in Figure 18 should be considered with reservations.

Figure 19 represents plots of the two glass transition temperatures of copolymers as a function of weight percent of mesogenic units from both Table III (or Figure 9) and Table IV (or Figure 14). This plot is pertinent since both sets of data were obtained with copolymer molecular weights which basically do not affect the values of the two glass transition tempertures. Figure 19 supports the proposal we were previously trying to establish from a limited number of experiments (Figure 9); i.e., the single glass transition temperature of the homopolymer might represent the glass transition temperature of the side groups. Also, it is possible that the homopolymer exhibits a glass transition temperture due to the polymer backbone. However, due to the very low weight percent of the polymer backbone, it might not be possible to detect on the DSC curves of the homopolymer such a small change in the heat capacity corresponding to this glass transition

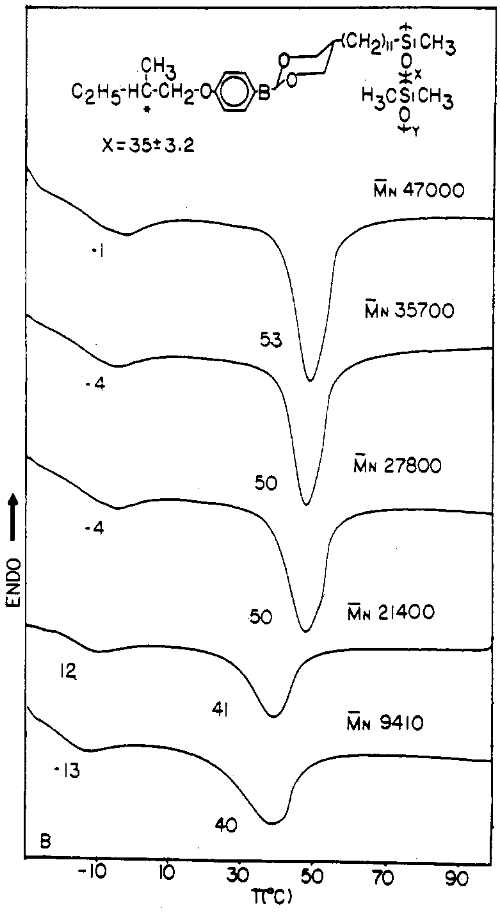


Figure 16. Normalized DSC cooling scans (20 °C/min) for liquid crystalline copolysiloxanes containing 35 ± 3.2 mol % structural units with mesogenic groups and different degrees of polymerization.

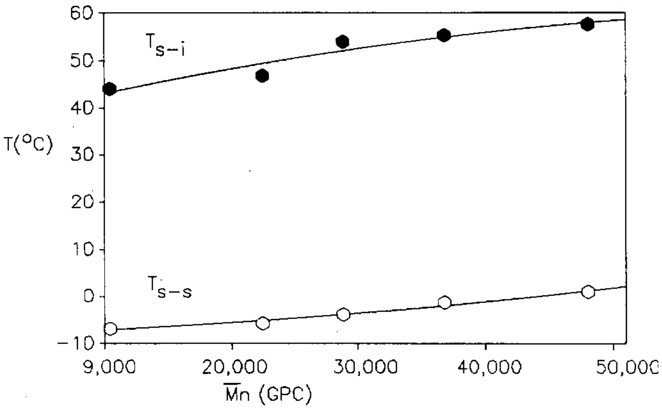


Figure 17. The dependence of the T_{s-s} and T_{s-i} of liquid crystalline copolysiloxanes on their molecular weight. All samples contain 35 ± 3.2 mol % of structural units with mesogenic groups.

Table IV

Thermal Transitions and Thermodynamic Parameters for Copolysiloxanes Containing 35 ± 3.2 mol % Structural Units with 2-[4-(2(*S*)-Methyl-1-butoxy)phenyl]-5-(11-undecan-1-yl)-1,3,2-dioxaborinane Side Groups and Varying Degrees of Polymerization

NMR mesogenic structural units, mol %	GPC		phase transitions (°C) and corresponding enthalpy changes (kcal/mrmu[a])																	
	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	heating											cooling						
31.4	9400	1.70	g_1	−84	g_2	−9	s	−7	(0.14)[b]	s	44	(1.5)	i	i	40	(1.4)	s	−13	(0.14)	s
38.0	21 400	2.02	g_1	−81	g_2	−8	s	−6	(0.22)	s	47	(1.3)	i	i	41	(1.3)	s	−12	(0.21)	s
35.5	27 800	2.06	g_1	−76	g_2	−7	s	−4	(0.20)	s	54	(1.8)	i	i	50	(1.8)	s	−4	(0.19)	s
35.3	35 700	2.05	g_1	−75	g_2	−3	s	−1	(0.20)	s	55	(1.7)	i	i	50	(1.8)	s	−4	(0.15)	s
34.1	47 000	1.71	g_1	−76	g_2	−5	s	1	(0.15)	s	58	(1.9)	i	i	53	(2.0)	s	−1	(0.15)	s

[a] mrmu = mole repeat mesogenic units. [b] Values in parentheses are enthalpy changes in kcal/mrmu. Abbreviations: g_1, g_2, glassy; s, smectic; i, isotropic.

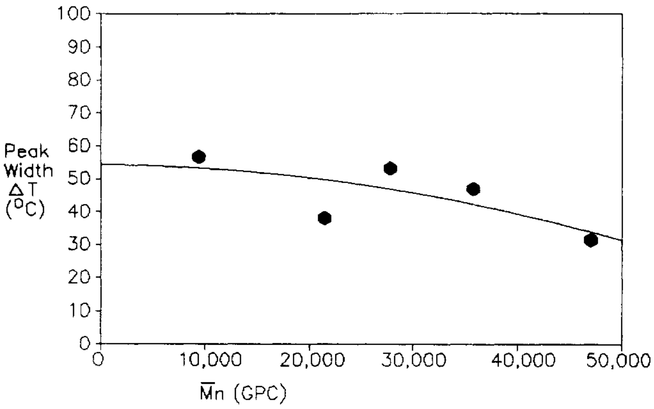


Figure 18. Dependence of isotropic–smectic peak width of liquid crystalline copolysiloxanes containing 35 ± 3.2 mol % structural units with mesogenic groups versus molecular weight.

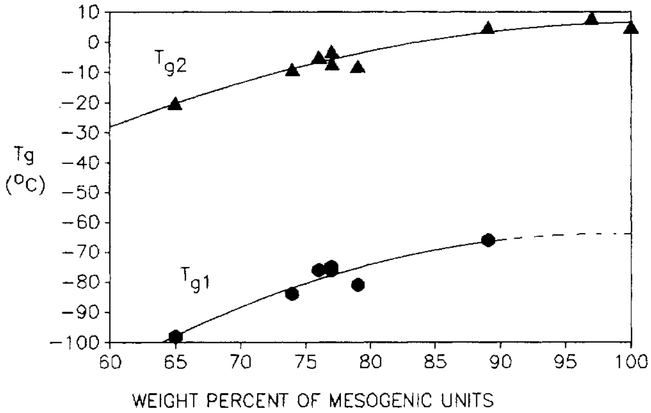


Figure 19. The dependence of the two glass transition temperatures of liquid crystalline copolysiloxanes on copolymer composition. Data from Tables III and IV are included.

temperature. More sensitive techniques are required to demonstrate if this assumption is correct.

Finally, we should consider the relationship between the width of the isotropic–smectic or smectic–isotropic transition, and its possible role in detecting, at least in a qualitative nature, different "degrees of liquid crystallinity". The meaning of "degree of liquid crystallinity" refers in this present case to the fraction of liquid crystalline side groups which are microphase separated from the polymer backbone. Presently there is not technique which can be used to directly demonstrate microphase separation in these copolymers. This is because both glass transition temperatures are below room temperature and therefore electron-microscopy studies cannot be performed.

As Blumstein has mentioned,[43] the width of the liquid crystalline isotropic phase transition is proportional to the quantity of anisotropic–isotropic biphase available at this transition temperature. However, we have recently shown for the case of main-chain liquid crystalline polymers that nonequilibrium states of liquid crystallinity existing at the isotropic-liquid crystalline phase transition are also available in the anisotropic phase. This quantity was termed "degree of liquid crystallinity" and was quantitatively determined.[48] This "degree of liquid crystallinity" dictates the temperature, the width, and the enthalpy change associated with the liquid crystalline isotropic transition peak.[48,49]

The origin of the biphase in main-chain liquid crystalline polymers is of course different from the origin of the biphase in the copolymers presented here. This biphase is kinetically controlled in the case of main-chain copolymers, while it seems to be thermodynamically controlled in the side-chain copolymers used in this study. However, we can be certain that the width of the transition peak can be used to quantitatively estimate the proportion of biphasic material in our side-chain liquid crystalline copolysiloxanes.

In our opinion, microphase-separated side-chain liquid crystalline copolymers do not represent a completely unusual idea for the field of polymer science. Independent motions of the main chain and side groups in nonliquid crystalline comblike polymers have been proposed for a large number of polymer systems, of particular interest being poly(dialkyl itaconate)s,[50,51] poly(α-amino acids) containing different side chains,[52-56] and copolymers of α-olefins with maleic anhydride.[57,58] Even for the field of side-chain liquid crystalline polymers we think our findings do not represent an unexpected result. Lipatov et al.[59-62] have predicted and demonstrated that side-chain liquid crystalline homopolymers containing long alkyl groups, i.e., more than 10 methylenic units as the tail of the mesogenic units and attached directly to the polymer backbone, exhibit a two-phase morphology. However, in thier case there is a microsegregation of the alkyl chain ends (soft phase) from the aromatic part (hard phase) of the mesogenic unit. Although their systems are different from ours, it is of interest to remark that in both cases in order to observe microphase separation, the system had to contain at least 10 methylenic units within the flexible spacer or in the tail part of the flexible spacer.

Krigbaum has first suggested that side-chain liquid crystalline polymers might have a microphase structure with clusters of mesogenic side groups embedded in a continuous phase formed by the polymeric backbone.[63] His idea corresponds to the microphase-separated systems described in our work and the work of Ringsdorf et al.

Acknowledgment. Financial support from the National Science Foundation (DMR-86-02435) is gratefully acknowledged. We also thank Professor H. Ringsdorf for providing two of his manuscripts prior to publication and for helpful and critical discussions.

Registry No. (*S*)-$C_2H_5CH(CH_3)CH_2OC_6H_4$-*p*-Br, 110458-69-0; $B(OC_4H_9)_3$, 688-74-4; (*S*)-$(HO)_2BC_6H_4$-*p*-$OCH_2CH(CH_3)C_2H_5$, 110458-70-3; $H_2C{=}CH(CH_2)_9CH(CH_2OH)_2$, 108414-88-6; 2-[4-(2(*S*)-methyl-1-butoxy)phenyl]-5-(10-undecen-1-yl)-1,3,2-dioxaborinane, 117893-73-9.

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