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Synthesis and Characterization of Poly(methylsiloxane)s Containing 5-[S(-)-2-Methyl-1-butyl]-2-[4-(11-undecan-1-yloxy)phenyl]-1, 3, 2-dioxaborinane and 2-{4-[S(-)-2-Methyl-1- butoxy]phenyl}-5-(11-undecan-1-yl)-1, 3, 2-dioxaborinane Constitutional Isomeric Side Groups

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SYNTHESIS AND CHARACTERIZATION OF POLY(METHYLSILOXANE)S CONTAINING 5-[S(-)-2-METHYL-1-BUTYL]-2-[4-(11-UNDECAN-1-YLOXY)PHENYL]-1, 3, 2-DIOXABORINANE AND 2-{4-[S(-)-2-METHYL-1-BUTOXY]PHENYL}-5-(11-UNDECAN-1-YL)-1, 3, 2-DIOXABORINANE CONSTITUTIONAL ISOMERIC SIDE GROUPS

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ABSTRACT

The synthesis and characterization of a poly(methylsiloxane) (16) and a poly(methyl-co-dimethylsiloxane) (17) containing 5-[S(-)-2-methyl-1-butyl]-2-[4-(11-undecan-1-yloxy)phenyl]-1, 3, 2-dioxaborinane mesogenic units are presented. Their mesomorphic behavior is compared to that of a poly(methylsiloxane) (18) and a poly(methyl-co-dimethylsiloxane) (19) containing the 2-{4-[S(-)-2-methyl-1-butoxy]-phenyl}-5-(11-undecan-1-yl)-1, 3, 2-dioxaborinane constitutional isomeric side groups. 16 exhibits a monotropic s_A mesophase which undergoes the isotropic-anisotropic transition at 27°C while 18 an enantiotropic s_A mesophase which undergoes isotropization at 99°C. Both 16 and 18 display side chain crystallization. An explanation for the difference between the behavior of 16, 17 and of 18, 19 is provided.

INTRODUCTION

Previous publications from our laboratory reported the results of our investigations on the molecular engineering of phase transitions of side chain liquid crystalline polymers by using constitutional isomers of rigid rod-like mesogenic groups.[1-6] Homopolymers based on constitutional isomeric rigid rod-like mesogens exhibit almost identical phase behavior.[1-3, 6] However, since their structural units are isomorphic within their mesophase and nonisomorphic within their crystalline phase, copolymers based on constitutional isomeric mesogens exhibit an isotropization temperature which is about the weight averaged value of their homopolymers and a highly depressed melting transition temperature. Consequently, copolymerization of these constitutional isomeric mesogens can be used to transform virtual or monotropic mesophases into enantiotropic mesophases.[4, 5]

In a previous publication we have reported that isotropization temperatures of homopolymers containing constitutional isomeric mesogens based on a combination of rigid rod-like and flexible moieties are highly different. For example, the isotropization temperature of poly{1-(4-methoxy-4'-biphenyl)-2-[4-(11-methacryloylundecanyl-1-oxyphenyl)]ethane} is 108°C higher than that of its poly{1-[4-(methacryloylundecanyl-1-oxy)-4'-biphenyl]-2-(4-methoxyphenyl)-ethane} constitutional isomer.[7]

This paper describes the synthesis and characterization of poly(methylsiloxane) (16) and poly(methyl-co-dimethylsiloxane) (17) containing 5-[S(-)-2-methyl-1-butoxyl]-2-[4-(11-undecan-1-yloxy)phenyl]-1, 3, 2-dioxaborinane side groups and compare it to that of poly(methyl-siloxane) (18) and poly(methyl-co-dimethylsiloxane) (19) which were synthesized as reported previously.[8-11]

EXPERIMENTAL

Materials

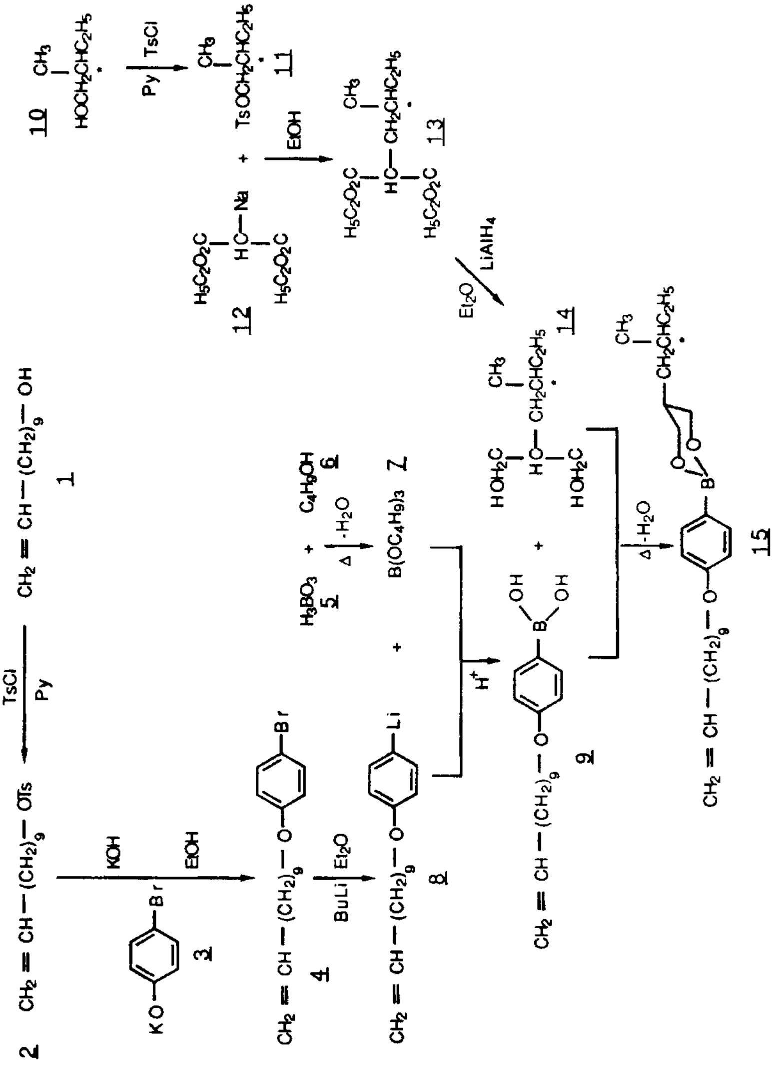
Poly(methylhydrosiloxane) (M_n= 1,500, reported by Petrarch; DP= 43, determined by ^{1}H-NMR spectroscopy), poly[(50-55%)-methylhydro-co-(45-50%)-dimethylsiloxane] (M_n= 900-1,000, DP=12), platinum divinyltetramethyldisiloxane complex in xylene solution (all from Petrarch), p-bromophenol, diethyl malonate (both from Aldrich) and S(-)-2-methyl-1-butanol ($[\alpha]_D$ -7.3°, from Fluka) were used as received. Toluene used in the hydrosilation reaction was first refluxed over sodium and then was distilled under argon. All other solvents and reagents were purified by standard methods.

Techniques

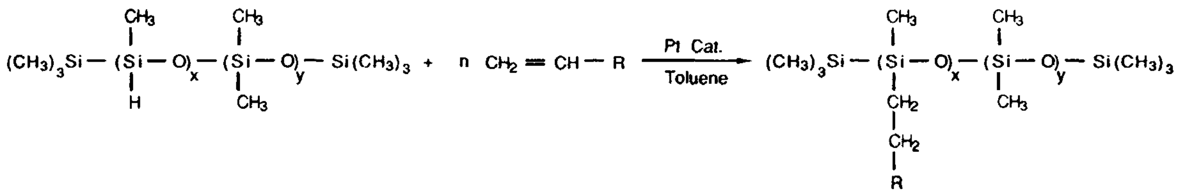
200 MHz ^{1}H-NMR spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ solution with TMS as internal standard. A Perkin-Elmer DSC-4 differential scanning calorimeter, equipped with a TADS 3600 data station , was used to determine the thermal transitions which were read at the maximum of their endothermic or exothermic peaks. In all cases, heating and cooling rates were 20°C/min. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity. Thermal transitions were collected from second or further heating and cooling scans. A Carl-Zeiss optical polarized microscope (magnification : 100 X) 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. 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. The measurements were made by using a UV detector, THF as solvent (1 ml/min; 40°C), a set of PL gel columns of 10^2, 5×10^2, 10^3, 10^4 and 10^5 Å and a calibration plot constructed with polystyrene standards. High pressure liquid chromatography (HPLC) determinations were performed with the same instrument.

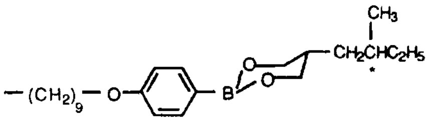
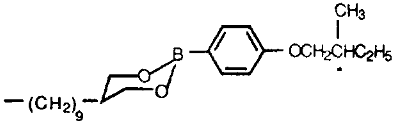
Synthesis of Monomer and Polymers

The synthesis of monomers and polymers is outlined in Schemes I and II.



Scheme I : Synthesis of 5-[S(-)-2-methyl-1-butyl]-2-[4-(10-undecen-1-yloxy)phenyl]-1, 3, 2-dioxaborinane monomer.



Polymers	x	y	R
16	43	0	
17	6	6	
18	43	0	
19	58[a]	45[a]	

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[a] calculated from theoretical value of M_n = 6900

Scheme II : Synthesis of poly(methylsiloxane)s and poly(methyl-co-dimethylsiloxane)s containing 5-[S(-)-2-methyl-1-butyl]-2-[4-(11-undecan-1-yloxy)phenyl]-1, 3, 2-dioxaborinane and 2-{4-[S(-)-2-methyl-1-butoxy]phenyl}-5-(11-undecan-1-yl)-1, 3, 2-dioxaborinane side groups.

10-Undecen-1-yl Tosylate (2)

2 was synthesized as described in a previous publication from our laboratory.[8]

p-(10-Undecen-1-yloxy)Phenyl Bromide (4)

10-Undecen-1-yl tosylate (42.2 g, 0.13 mol) was added to a solution containing 8.3 g (0.15 mol) of potassium hydroxide and 22.68 g (0.13 mmol) of p-bromophenol in 200 ml of 95 % ethanol. The reaction mixture was heated at reflux with stirring for 19 hours. The ethanol was removed on a rotavapor. The resulting product was mixed with 100 ml of water and extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether was evaporated on a rotavapor. The remaining product was distilled at 150-153°C / 10 mmHg to yield 32 g (75%) of a colorless liquid of 100% purity as determined by HPLC. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 1.2-2.1 (m, 16H, $-(C\underline{H}_2)_8-$), 3.7 (t, 2H, $-O-C\underline{H}_2-$), 5.0 and 5.8 (m, 3H, $C\underline{H}_2=C\underline{H}-$), 6.7 and 7.3 (2d, 4H, ArH)

Tri-n-Butyl Borate (7)

7 was synthesized as described in a previous publication.[8]

[p-(10-Undecen-1-yloxy)Phenyl]Boronic Acid (10)

To a dry ice - acetone bath cooled flask containing 200 ml of dry diethyl ether, 29.28 g (0.09 mol) of p-(10-undecen-1-yloxy)phenyl bromide were added under nitrogen. Then 10 ml (0.1 mol) of 10 M butyl lithium solution in hexane was added with a syringe and the reaction mixture was kept stirring in the dry ice - acetone bath for 2 hours. Then it was allowed to warm to room temperature where it stayed for 1/2 hour and then was cooled in a dry ice - acetone bath again, and 32 g (0.11 mol) of tri-n-butyl borate were added dropwise into the flask. The reaction mixture was warmed back to room temperature and kept stirring overnight. Cold H_2SO_4 (200 ml, 50%) was added to the resulting mixture. The mixture was then extracted with diethyl ether and washed with water 3 times. The diethyl ether was removed on a rotavapor. Some water was added to the resulting residue and the butanol was removed azeotropically on a rotavapor. The resulting white solid was dissolved in a solution of HCl/THF=1/10 (v/v) and the solution was stirred overnight. The solvent was removed on a rotavapor. The resulting solid was recrystallized from 95% EtOH to yield 8.0 g (31%) of white crystals.

S(-)-2-Methyl-1-Butyl Tosylate (11)

11 was synthesized as described previously.[8]

Diethyl 2-[S(-)-2-Methyl-1-Butyl]Malonate (13)

A solution of sodium ethoxide in ethanol was prepared by adding 3.3 g (0.14 mol) of freshly cut sodium to 200 ml of absolute ethanol. After sodium was completely dissolved, 22.8 g (0.14 mol) of diethyl malonate was added and the resulting solution was stirred for 5 hours. S(-)-2-Methyl-1-butyl tosylate (35 g, 0.144 mol) was added to the reaction mixture, which was then stirred at reflux temperature for 14 hours. The ethanol was removed on a rotavapor and 100 ml of water was added to the residue. The resulting mixture was extracted with diethyl ether. The ether layer was dried over anhydrous $MgSO_4$, filtered and the ether was evaporated on a rotavapor. The product was distilled under vacuum at 95-100° C / 10 mmHg to give 23 g (71%) of a colorless liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.8-2.0 (m, 17H, $-C\underline{H}_3$, $(C\underline{H}_2)_2C\underline{H}$), 3.4 (t, 1H, $(CO_2)_2C\underline{H}$), 4.2 (q, 4H, $-CO_2C\underline{H}_2$)

2-[S(-)-2-Methyl-1-Butyl]-1, 3-Propanediol (14)

A solution of diethyl 2-[S(-)-2-methyl-1-butyl]malonate (23.0 g, 0.1 mol) in 50 ml of dry diethyl ether was added dropwise to a suspension of $LiAlH_4$ (6.3 g, 0.17 mol) in 200 ml of dry diethyl ether cooled at 0°C with an ice-bath. The reaction mixture was heated at reflux temperature with stirring for 20 hours. Then it was cooled to room temperature, and the excess of $LiAlH_4$ was reacted with 50 ml of ethyl acetate. The resulting mixture was treated with 50 ml of hydrochloric acid and extracted with chloroform. The chloroform layer was washed with water, dried over anhydrous $MgSO_4$, filtered and the chloroform was evaporated. The resulting yellow liquid was distilled under vacuum (166-173°C/10 mmHg) to give 9.28 g (65%) of a colorless liquid. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.8-2.6 (m, 12H, $C_2\underline{H}_5$-$C\underline{H}(C\underline{H}_3)C\underline{H}_2C\underline{H}$), 3.6 and 3.8 (2m, 6H, $C\underline{H}_2O\underline{H}$)

5-[S(-)-2-Methyl-1-Butyl]-2-[4-(10-Undecen-1-yloxy)Phenyl]-1, 3, 2-Dioxaborinane (15)

A solution of 2-[S(-)-2-methyl-1-butyl]-1, 3-propanediol (1.00 g, 7 mmol), [p-(10-undecen-1-yloxy)phenyl]boronic acid (2.03 g, 7 mmol), and 100 ml of dry benzene was heated to reflux and the water formed was azeotropically removed with a Dean-Stark trap. After 18 hours at reflux, the remaining benzene was removed in a rotavapor and the borinane derivative 15 was crystallized from acetone at -70°C. Column chromatography (silica gel, chloroform as eluent) was used to complete the purification. Yield 1.73 g (61%) of white solid. m.p., 19.6°C. ^{1}H-NMR ($CDCl_3$, TMS, δ, ppm): 0.8-2.2 (m, 12H, $C_2\underline{H}_5(C\underline{H}_3)C\underline{H}C\underline{H}_2C\underline{H}$), 3.7 (t, 2H, $-OC\underline{H}_2$, axial), 4.0 (t, 2H, $-OC\underline{H}_2$), 4.1 (m, 2H, $-OC\underline{H}_2$, equatorial), 5.0 and 5.8 (m, 3H, $C\underline{H}_2=C\underline{H}$), 6.9 and 7.7 (2d, 4H, ArH)

Poly(methylsiloxane) and Poly(methyl-co-dimethylsiloxane)

The poly(methylsiloxane) and the poly(methyl-co-dimethylsiloxane) were synthesized by hydrosilation reaction of 5-[S(-)-2-methyl-1-butyl]-2-[4-(10-undecen-1-yloxy)phenyl]-1, 3, 2-dioxaborinane (15) with poly(methylhydrosiloxane) (M_n= 1,500, DP= 43) and poly[(56%)-methylhydro-co-(44%)-dimethylsiloxane] (M_n= 900-1,000, DP= 12) by following the general procedure described previously.[8, 9] An example for the preparation of the poly(methylsiloxane) is described below.

A solution of the dioxaborinane monomer (0.90 g, 20 mol % excess versus the Si-H groups present in poly(methylhydrosiloxane)) and the poly(methylhydrosiloxane) (0.11 g) in 10 ml of dry toluene was heated to reflux under nitrogen, and 100 ml of dicyclopentadienyl platinum (II) chloride catalyst[12] was then injected with a syringe as solution in methylene chloride (1 mg/ml). The reaction mixture was heated to reflux temperature under nitrogen until both IR and 200-MHz ^{1}H-NMR analyses showed that the hydrosilation reaction was complete. The resulting polymer was separated by precipitation into methanol and was then further purified by several reprecipitations from chloroform solution into methanol. The poly(methyl-co-dimethylsiloxane) was prepared from 0.65 g of dioxaborinane monomer and 0.16 g of poly[(56%)-methylhydro-co-(44%)-dimethylsiloxane] under the same reaction conditions as those used for the synthesis of the poly(methylsiloxane). Poly(methylsiloxane) and poly(methyl-co-dimethylsiloxane) 18 and 19 were synthesized as described in previous publications.[8, 9]

RESULTS AND DISCUSSION

Scheme I outlines the synthesis of 5-[S(-)-2-methyl-1-butyl]-2-[4-(10-undecen-1-yloxy)phenyl]-1, 3, 2-dioxaborinane (15). This procedure represents an almost mirror image of the method used for the synthesis of its constitutional isomer 2-{4-[S(-)-2-methyl-1-butoxy]phenyl}-5-(10-undecen-1-yl)-1, 3, 2-dioxaborinane.[8, 9] The melting temperature of 15 is 19.6°C while that of its constitutional isomer is 39°C.[8] The main difference between these mesogenic groups consists in the position at which the flexible spacer and the chiral group are attached. This can be observed from Scheme II which presents the synthesis and the structure of the corresponding poly(methylsiloxane)s and poly(methyl-co-dimethylsiloxane)s. The first and second DSC heating scans and the first cooling scan of the polymer 16 are presented in Figure 1. Subsequent heating and cooling DSC scans are identical to the second heating and first cooling scan. On the heating scan 16 presents only a melting from a crystalline into an isotropic phase. On cooling 16 presents a s_A phase followed by crystallization. Therefore, 16 exhibits only a monotropic s_A phase, which undergoes isotropization just above room temperature. The poly(methylsiloxane) 18 which contains the other constitutional isomeric mesogen presents an enantiotropic s_A mesophase which in the case of the polymer with a degree of polymerization of 43 undergoes isotropization at 99°C. In addition, the enthalpy change associated with the isotropization of 18 is 1.8 kcal/mru while the corresponding value of 16 is 0.16 kcal/mru. These data demonstrate that the attachment of the flexible spacer at the dioxaborinane unit generates a much better mesogenic moiety than that obtained by the attachment of the flexible spacer at the phenyl unit. The following explanation can be advanced for this behavior. The rigidity of the structural unit of 18 is higher than that of 16. Therefore, at a given molecular weight, the entropy of 18 is lower than that of 16 both in the isotropic and in the liquid crystalline phase. Consequently, in both phases the free energy of 18 is higher than that of 16. Inserting this trend into the plot of free energy versus transition temperature,[13, 14] leads to a higher isotropization temperature and enthalpy change of isotropization for 18. This result demonstrates that for a semiflexible mesogen the position of attachment of the flexible spacer can have a drastic effect on the temperature transitions and their associated enthalpies.

The effect observed for the polymers 16 and 18 is in agreement with the one observed previously for a different semiflexible mesogen, and can be explained in a similar way. The 2, 5-disubstituted 1, 3, 2-dioxaborinane based mesogen has two conformers which are in dynamic equilibrium. In the first one the two substituents

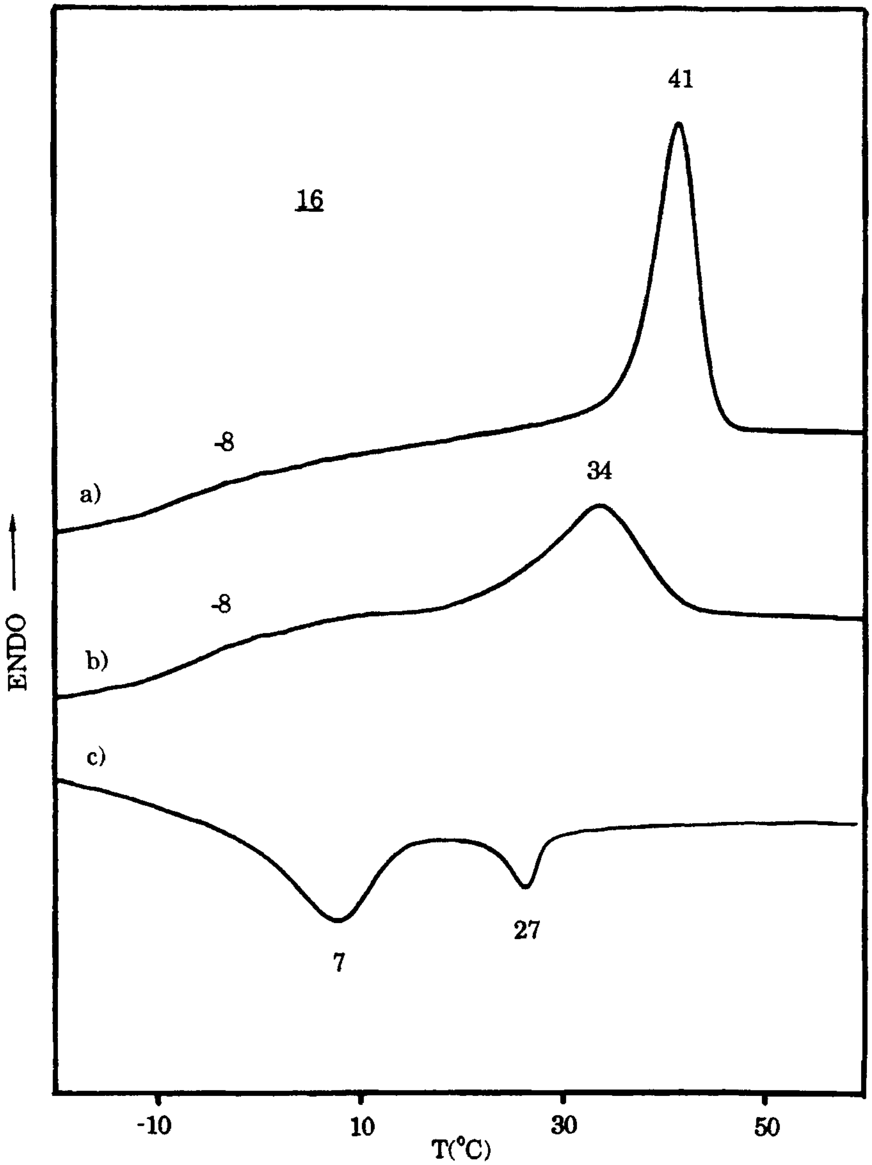

Figure 1 : First (a) and second (b) heating and cooling (c) DSC thermograms (20°C/min) of poly(methylsiloxane) containing 5-[S(-)-2-methyl-1-butyl]-2-[4-(11-undecan-1-yloxy)phenyl]-1, 3, 2-dioxaborinane side groups. (16)

Table I Thermal Transitions and Thermodynamic Parameters of the Liquid Crystalline Poly(methylsiloxane)s and Poly(methyl-co-dimethylsiloxane)s. Data on first line are from first heating and cooling and on second line from second heating and cooling scans

Polymer					Transition Temperatures (^{o}C) and Corresponding Enthalpy (Kcal/mru[a]) and Entropy (cal/^{o}K·mru) Changes	
No.	DP	Structural Units Containing Side Groups (mole % (NMR)	M_n	M_w/M_n	Heating	Cooling
			GPC			
16	43	100	5,200	2.09	g -8 k 41 (1.46/4.66) i g -8 k 34 (1.09/3.54) i	i 27 (0.16/0.55) s_A 7 (0.98/3.50) k i 27 (0.16/0.55) s_A 7 (0.97/3.45) k
17[b]	12	53	18,900	2.70	g -19 s_A 6 (0.17/0.58) i	i -2 (0.15/0.52) s_A
18[c]	43	100	16,400	1.60	g 10 k 21 (0.10/0.34) s_A 99(1.9/5.13) i	i 90 (1.8/5.00) s_A 15 (0.09/0.31) s_X[d]
19[c]	103[e]	56	25,900	2.17	g_1 -66 g_2 5 k 9 (0.23/0.82) s_A 75 (1.8/5.17) i	i 67 (1.8/5.29) s_A 2 (0.19/0.69) s_X[d]

[a] mru = mole repeat unit; [b] second DSC scan; [c] data from reference 9; [d] unidentified smectic phase;

[e] DP calculated from theoretical value of M_n = 6900.

are in axial positions while in the second one the same two substituents are in equatorial positions.[10] This difference should not provide a large difference between the phase behavior of these two monomeric conformers. However, once attached to a polymer backbone any of these two individual conformers exhibits a higher tendency toward mesomorphism (lower entropy) than any mixture of these two conformers (higher entropy). In the case of the structural unit of 18 we believe that the potential energy difference between these two conformers is higher than in the case of the structural unit of 16. Consequently, the concentration of a single conformer is higher in 18 than in 16. This is due to the easier conformational change of the monomeric unit of 16 versus that of 18. On going from 18 to the corresponding copolymer 19 we observe a decrease of the isotropization and melting transition temperatures (Table I). However, on going from 16 to the corresponding copolymer 17 the melting transition decreases more than the isotropization transition. As a consequence, 17 exhibits an enantiotropic s_A phase.

ACKNOWLEDGEMENT

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