

Synthesis and characterization of biphasic liquid crystalline polysiloxanes containing 4-undecanyloxy-4'-cyanobiphenyl side-groups

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SUMMARY

The synthesis and characterization of liquid crystalline polysiloxanes and copolysiloxanes containing 4-undecanyloxy-4'-cyanobiphenyl side-groups is presented. The polysiloxane presents a single glass transition temperature followed by a S_C and a S_A mesophase. Copolysiloxanes presenting around 50% weight fraction of side-groups exhibit two glass transition temperatures i.e., one due to the independent motion of the main chain and the other due to the cooperative but independent motion of the side groups, and in addition to the S_C and S_A phases exhibited by the homopolymer, present also side-chain crystallization.

INTRODUCTION

In several previous papers from our laboratory we have presented the first examples of biphasic i.e., micro-phase separated side-chain liquid crystalline polymers (LCP) (1-3). These polymers exhibit two glass transition temperatures i.e., one due to the independent motion of the main-chain, and the other due to the cooperative but independent motion of the side groups. These side-chain LCP might represent the first examples of highly decoupled side-chain LCP. These structures were predicted by the spacer concept advanced by Finkelmann and Ringsdorf (4, 5) but were never previously accomplished although Ringsdorf and Schneller have synthesized some side-chain LC copolysiloxanes exhibiting two glass transition temperatures (6, 7). According to recent unpublished data from our laboratory (8), it is not only the spacer length which controls the degree of decoupling, but also the miscibility between the side-chains and the polymer backbone.

The goal of this paper is to present some additional experimental results which support this last assumption. These results are based on the thermal behavior of a series of polysiloxanes and copolysiloxanes containing 4-undecanyloxy-4'-cyanobiphenyl side-groups.

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EXPERIMENTAL

Materials

Poly(methylhydrosiloxane) ($\bar{M}_n=4500-5000$) and poly[(30-35%)- or (15-18%)-hydrogenmethyl-(65-70%)- or (82-85%)-dimethylsiloxane]s ($\bar{M}_n=2000-2100$) were obtained from Petrarch Systems Inc., and were used as received. 4-Cyano-4'-hydroxybiphenyl and the 10-undecylenylether of 4-cyano-4'-hydroxybiphenyl were synthesized as previously reported (9).

Techniques

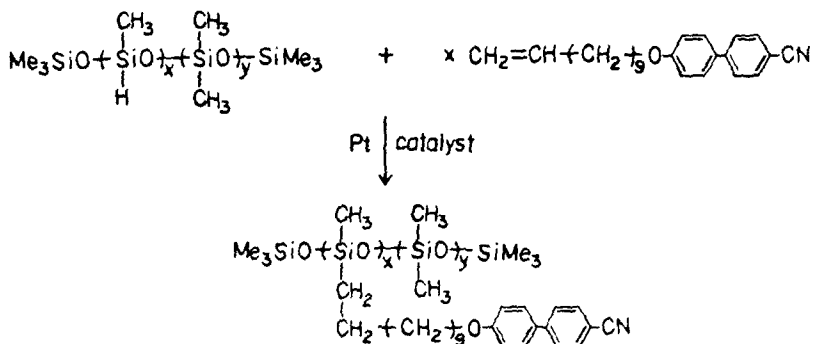
Experimental techniques used in the characterization of intermediary compounds and of polymers are identical to those previously reported (10, 11).

Synthesis of Polymers and Copolymers

The synthesis of LC polysiloxanes and copolysiloxanes is outlined in Scheme 1. The detailed procedure used to accomplish a quantitative hydrosilation reaction is in press elsewhere (1, 3).

RESULTS AND DISCUSSION

The nature of the polymer backbone apparently plays a more important role than previously considered in achieving a highly decoupled side-chain LCP. It has been already accepted that for the same mesogenic unit and spacer length, a more flexible backbone gives rise to a broader range of thermal stability of the mesophase (8, 10, 12, 13). Recently, we have shown that for the same mesogenic unit and spacer length, the number of transitions exhibited by the polymer increases in going from a polymethacrylate to a polyacrylate and subsequently to a polysiloxane backbone (8). This result has been associated with an increase in the degree of freedom of the side-groups, and this is certainly related not only to the mobility of the polymer backbone but also to its miscibility with the side groups. This statement can be more clearly understood if we make a comparison between side-chain LCP and graft copolymers. When the graft and the backbone are miscible, the overall properties of the graft copolymer are weight averaged. When the graft and the backbone are nonmiscible, the graft copolymer exhibits a micro-phase separated biphasic morphology and presents synergistic properties exhibited by the individual graft and backbone segments (14). The micro-phase separated morphology of a graft copolymer when transplanted to a side-chain LCP, in our opinion, should give rise to a highly decoupled side-chain LCP. It is certain that the same parameters governing the miscibility in blends and/or graft



Scheme 1: Synthesis of LC Polysiloxanes

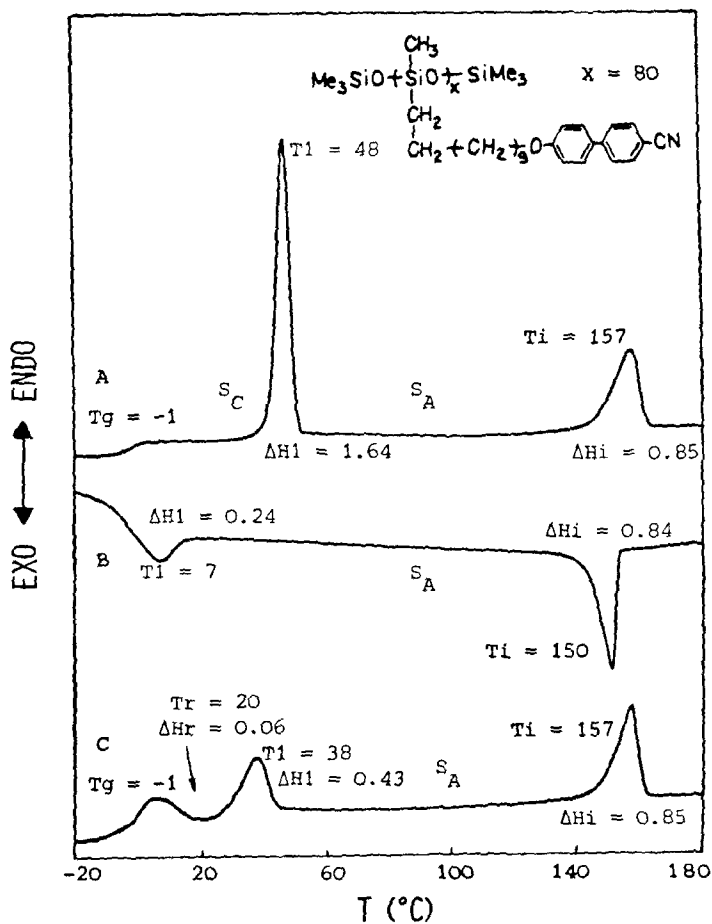


Figure 1: Normalized DSC thermograms (20°/min) of LC polysiloxane (x=80): A) first heating scan; B) cooling scan; C) second heating scan

copolymers would have to be considered in achieving microphase separated side-chain LCP. One of the simplest parameters which dictate the domains size of a phase separated system is the weight ratio of the two systems. This is because a very small weight fraction of a polymer is at least partially miscible with the other polymer. Therefore, large domain sizes are expected at about a 50/50 weight ratio.

This paper will discuss the influence of the weight ratio between the backbone and side-groups in the LC polysiloxanes presented in Scheme 1. Previously, we have shown (9) that this homopolymer exhibits a S_A and a S_C phase as shown in Figure 1 (curve A). This result is in agreement with the mesomorphic behavior of the homologous polyacrylate (15). Since the T_g is quite close to the transition from S_C to S_A , on the cooling scan T_1 is supercooled and overlaps the T_g (curve B). This gives rise to a reorganization transition (T_r) on the next heating scan (curve C) i.e., a transition which transforms the S_A phase into the S_C phase. Nevertheless, since the process is again very slow due to its proximity to T_g , T_1 on this second scan appears at a lower temperature than in the first scan. If the sample is allowed to "anneal" at room temperature for several hours, the next heating scan is identical to that in curve A (Fig. 1). This polymer exhibits only one T_g , and this is not unexpected since the weight fraction of the polymer backbone represents only 18% from the overall polymer weight. Even if this polymer would exhibit a biphasic morphology, its composition is at the borderline where two T_g 's could be detected by DSC.

Figure 2 presents representative DSC scans for the copolysiloxane: $x=10$, $y=20$. The first heating scan (curve A) shows an additional endotherm which was assigned to a melting transition (T_m3), followed by a S_C phase, T_1 , a S_A phase and T_i . The melting transition (T_m3) is preceded by a crystallization exotherm (T_c2). The cooling scan (curve B, Fig. 2) is similar to the same scan (curve B, Fig.1) for the homopolymer, except that this time ΔH_1 from the cooling scan is larger than ΔH_1 from the heating scan. This means that it contains part of ΔH_c2 . The second heating scan (curve C, Fig.2) is quite similar to the first one, except that T_m3 and T_1 are overlapped. Annealing the sample at room temperature, leads to a new heating scan identical to the first one (curve A, Fig.2). Curve D presents the DSC trace of the low temperature range. It demonstrates a biphasic system, since it presents two glass transition temperatures i.e., T_{g1} due to the independent motion of the polymer backbone and T_{g2} due to the cooperative but independent motion of the side groups. The heat capacity change at T_{g1} is proportional to the weight fraction of the backbone

(39.8%), while the heat capacity change at Tg2 is proportional to the weight fraction of the side groups (60.2%). It is clear that this micro-phase separated system allows a high degree of freedom for the side groups and therefore they can undergo side-chain crystallization. The present case represents a happy situation where the side-groups exhibit Tg2, Tc2 and Tm3. Tg2 can be observed only because Tc2 is above Tg2.

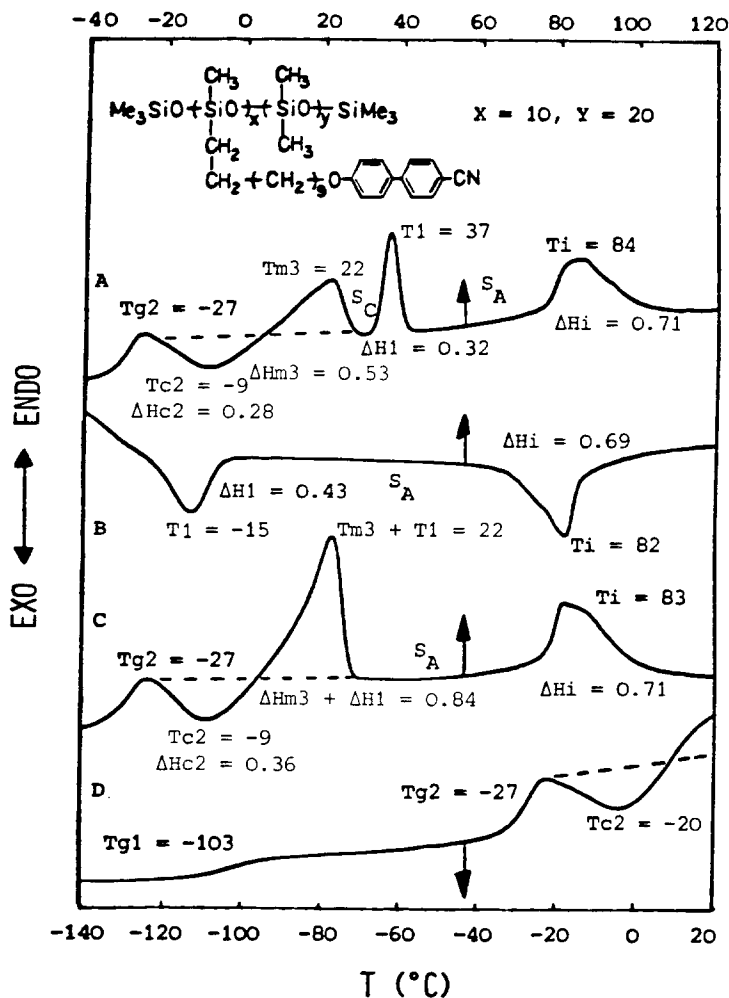


Figure 2: Normalized DSC thermograms (20°C/min) of LC polysiloxane ($x=10, y=20$): a) first heating scan; B) cooling scan; C) second heating scan; D) heating scan for the low range of temperatures

Figure 3 presents representative DSC scans for the copolysiloxane: $x=5, y=25$. This figure is self-explanatory. It resembles the behavior of the previous copolysiloxane from

Fig.2 except that T_{m3} , T_1 and T_{c2} are overlapped on the heating scan. Evidence for this is that $\Delta H_i + \Delta H_1$ (both from curve B) + ΔH_{c2} (from curve C) is equal to $\Delta H_{m3} + \Delta H_1 + \Delta H_i$ from curve C of Fig.3. This LC copolymer exhibits also two glass transition temperatures and their heat capacity changes are proportional to the weight fraction of the side groups (43.0%, T_{g2}) and main chain (57%, T_{g1}).

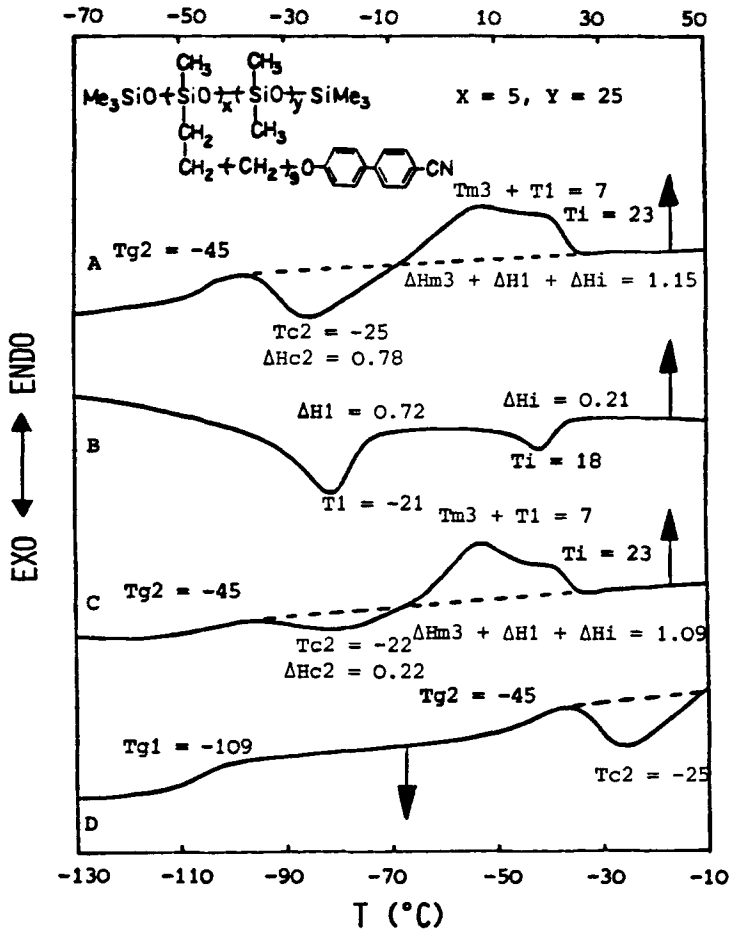


Figure 3: Normalized DSC thermograms (20°C/min) of LC copolysiloxane ($x=5, y=25$): A) first heating scan; B) cooling scan; C) second heating scan; D) heating scan for the low range of temperatures

Table I summarizes all the thermal transitions and the thermodynamic parameters of some of the starting materials, a poly(dimethylsiloxane) and of the LC polysiloxane and copolysiloxanes.

TABLE 1: THERMAL TRANSITIONS AND THERMODYNAMIC PARAMETERS OF POLYSILOXANES

POLYMERS		THERMAL TRANSITIONS, (°C) AND THERMODYNAMIC PARAMETERS, ΔH (KCAL/MRU), ^A ΔS (CAL/MRU.°K) ^A										
No.	x	y ^B	HEATING						COOLING			
			Tg1	Tc1	Tm1	Tm2	Tg2	Tc2	Tm3	T1	T1	T1
			$\Delta H_2/\Delta S_2$		$\Delta H_{M3}/\Delta S_{M3}$		$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$		
1	0	80	-123	-79	-40	-26	--	--	--	--	--	--
2 ^C	10	20	-126	--	--	--	--	--	--	--	--	--
3 ^C	5	25	-127	--	--	--	--	--	--	--	--	--
4	80	0	--	--	--	-1	--	--	48	157	150	7
			$\Delta H_2/\Delta S_2$		$\Delta H_{M3}/\Delta S_{M3}$		$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$		
			--/--		--/--		1.64/5.10	0.85/1.97	0.84/1.99	0.24/0.86		
5	10	20	-103	--	--	-27	-9	22	37	84	82	15
			$\Delta H_2/\Delta S_2$		$\Delta H_{M3}/\Delta S_{M3}$		$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$		
			0.28/1.06		0.53/1.80		0.32/1.03	0.71/1.99	0.69/1.94	0.43/1.49		
6	5	25	-109	--	--	-45	-25	7	--	23	18	-21
			$\Delta H_2/\Delta S_2$		$\Delta H_{M3}/\Delta S_{M3}$		$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$	$\Delta H_1/\Delta S_1$		
			0.78/3.14		--/--		--/--	1.15/-- ^D	--/--	1.15/-- ^D		

A) MRU = MOLE OF REPEAT UNITS, CONSISTING OF MESOGENIC UNIT AND TEN METHYLENIC UNITS.

B) X AND Y ACCORDING TO SCHEME 1. C) POLY(X-HYDROGENMETHYL-Y-DIMETHYLSILOXANE)

D) OVERLAPPED TRANSITIONS, $\Delta H_1 = \Delta H_i + \Delta H_m$

The overall conclusion obtained from these experiments is that the synthesis of micro-phase separated LCP requires not only highly nonmiscible polymer backbones and side-groups, but also a proper weight ratio between the backbone and the side-groups. A higher degree of freedom of the mesogens is provided by a micro-phase separated system, and this is supported by the fact that while the LCP presenting a single T_g exhibits only two thermal transitions, the LC copolymers presenting two T_g's exhibit three thermal transitions.

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