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Thermal properties of liquid crystalline siloxane copolymers and homopolymer blends

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Side-chain liquid crystalline polymers (SCLCPs) with differing spacer groups have been prepared as copolymers or as blends of the individual homopolymers. The resulting materials have been examined by thermal and optical methods. The copolymers showed intermediate properties between those of the homopolymers. In contrast, blends of SCLCPs with either chemically distinct or similar side-chain spacer units showed two clearing points (both of which are lower than those of each homopolymer) and one major melting point. We interpret the latter results in terms of partial contamination of each phase by a small amount of the other phase.

(Keywords: liquid crystalline polymers; dielectric relaxation; copolymers)

INTRODUCTION

Since the first side-chain liquid crystalline polymers (SCLCPs) were reported[1], many different structures have been synthesized which vary both in the chemical structure of longitudinal mesogenic units[2] and, more recently, in laterally attached units and longitudinal/lateral combinations[3-6]. Much structure and property work has been done using polysiloxane SCLCPs and this has been summarized by Gray et al.[3].

One method for altering the chemical structure of polysiloxane SCLCPs involves polyhydrosilylation of two types of mesogenic monomers onto a single siloxane backbone to produce siloxane SCLCP copolymers[7]. Very few studies have been reported in which the properties of the materials resulting from a systematic variation of the molar ratio of two side chains within a siloxane copolymer are compared with each other or with the properties of the two homopolymer materials. Some work reported by Gemmel et al.[8] and Nestor et al.[9] indicates that the type of mesophase can be altered by copolymerization of two side-chain units with varying molar ratios. The two mesogenic units differed only slightly in that one of them was laterally substituted by a methyl group on one phenyl ring. A recent paper on acrylate SCLCPs with a smectic texture indicates that copolymers show transition temperatures which are the mean of the two homopolymers[10] whilst essentially maintaining the smectic phase and showing negative deviations of isotropization entropies from a simple weighted mean. This has been explained by the presence of reduced order in the copolymer system in comparison to that of the homopolymers.

Another potential method of altering mesophase properties (such as side-chain mobility) involves blending of SCLCP materials. Blending of thermoplastics by melt

and solution techniques is the source of much interest both academically and industrially[11]. Whilst main-chain thermotropic LCP systems have been blended with thermoplastics[12] or with other main-chain thermotropic LCPs[13], little work has been done with SCLCP blends. A recent paper, however, described attempts to blend an acrylate SCLCP with an amorphous thermoplastic[14]. No work on SCLCP blends with other SCLCP materials has, to our knowledge, been reported in the literature previously.

In this work we present preliminary results detailing the synthesis and properties (thermal and optical) of SCLCP copolymers and blends based on a polysiloxane backbone and their characterization using thermal methods, optical measurements and dielectric spectroscopy.

Homopolymers, blends and copolymers with varying molar ratios of 1 and 2 were prepared by established methods detailed in the Experimental section. Homopolymers of 1 and 2 were made as were copolymers 3a to 3c with the molar ratios shown in Table 1. Blends with molar ratios of homopolymers 1 and 2 were made as shown in Table 2 (structures 4a to 4c).
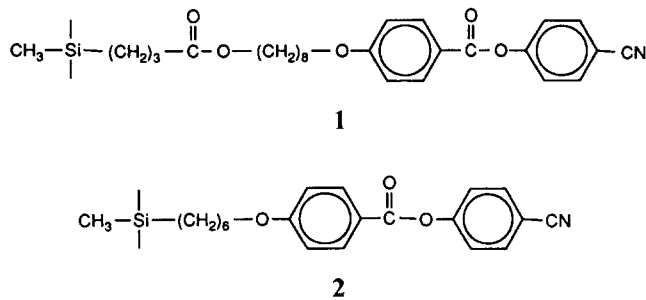
The structures 1 and 2 have spacer units that are fundamentally different (a novel vinylacetic acid

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group[15,16] and a straight alkyl chain, respectively). In order to evaluate the importance of this change in spacer functionality, we also examined blend systems of homopolymers both containing alkyl chain spacers (structures 2 and 5) but of different length.

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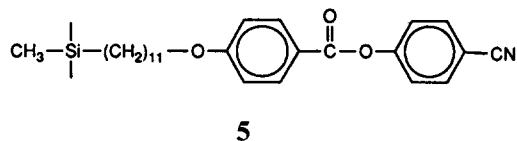
Homopolymers 2 to 5 were mixed in various molar ratios (*Table 3*) and the blends labelled 6a to 6c.

The side-chain groups attached to the homopolymer structures 1, 2 and 5 will be known as side-chains 1, 2 and 5, respectively, and refer to the total side chain (spacer group and mesogenic unit).

EXPERIMENTAL

Materials

Homopolymer materials (1, 2, 5) were synthesized and characterized using techniques described in detail elsewhere[15,16]. The poly(hydrogenmethylsiloxane) used was Petrach 120, $DP = 40 \pm 3$ (determined by ^1H, ^{19}Si

n.m.r.). The monomers were added in the desired stoichiometric ratio of 1:1 with Si–H unit. When the reaction was about 98% complete (i.r. spectroscopy), excess of 1-octene was added to ensure complete reaction of Si–H. Materials were purified by six precipitations using dichloromethane and methanol.

Characterization

Thermal analysis was performed using differential scanning calorimetry (d.s.c.) with a Perkin–Elmer DSC-7 scanning at 10°C min^{-1}. Hot-stage optical microscopy was performed with a microscope fitted with a hot stage.

RESULTS AND DISCUSSION

Polysiloxane copolymers and blends of the homopolymers (1, 2) containing different functionalities in the spacers

Copolymers of side chains 1 and 2. Figures 1A and B show the d.s.c. clearing point region of homopolymers 2 and 1, respectively. Figures 1F–H show similar data for the copolymers 3c, 3b and 3a. It can be seen that the copolymer clearing point endotherms lie intermediate between those of the homopolymers with similar broadness (width at half height).

Table 1 D.s.c. data of homopolymers and copolymers

Polymer number	Copolymer molar ratio, 1:2	$T_g{}^a$ (°C)	$T_m{}^b$ (°C)	$\Delta H_m{}^b$ (J g^{-1})	T_{cl} (°C)	ΔH_{cl} (J g^{-1})	ΔS_{cl} (J g^{-1} K^{-1})
1	1.0:0	−8	*	*	96	5.1	0.014
3a	0.5:0.5	+	*	*	103	2.6	0.007
3b	0.3:0.7	+	*	*	122	4.1	0.010
3c	0.1:0.9	+	37.5	2.69	156	3.7	0.009
2	0:1.0	+	50	11.5	176	3.5	0.008

^{a} +, Glass transition not observed
^{b} *, Melting transition not observed

Table 2 D.s.c. data for blends of homopolymers 1 and 2 with different molar ratios

Polymer number	Blend molar ratio, 1:2	$T_m{}^a$ (°C)	T_{cl_1} (°C)	ΔH_1 (J g^{-1})	T_{cl_2} (°C)	ΔH_2 (J g^{-1})
1	1.0:0	50	–	–	170.6	3.5
4a	0.5:0.5	42.6	80.2	3.4	166.6	1.9
4b	0.3:0.7	42.3	82.8	4.2	166.6	2.3
4c	0.1:0.9	39.9	82.8	1.6	170.4	3.6
2	0:1.0	*	96	5.1	–	–

^{a} *, Melting transition not observed

Table 3 D.s.c. data for blends of homopolymers 2 and 5 with different molar ratios

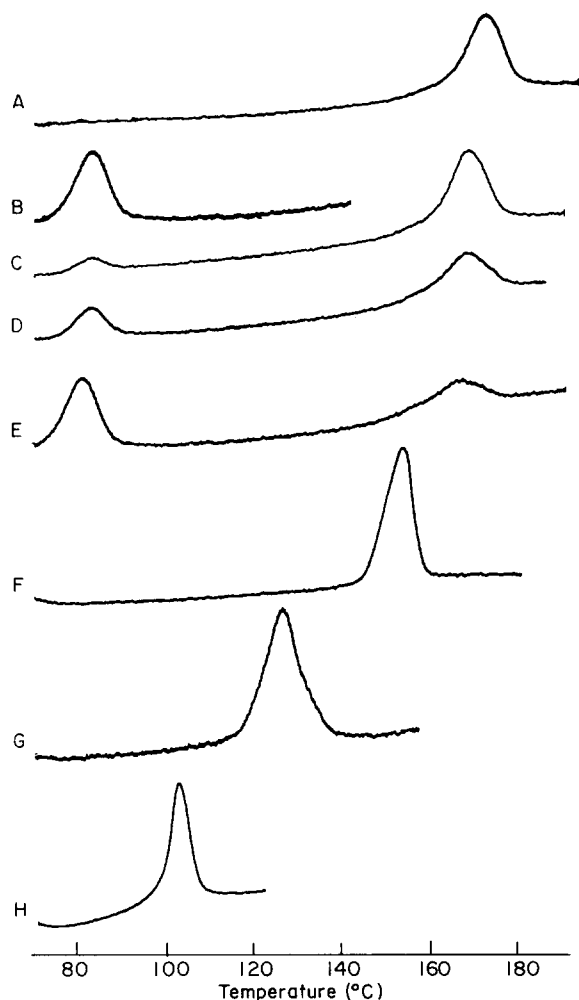| Polymer number	Blend molar ratio, 2:5	T_{m_2} (°C)	ΔH_{m_2} (J g^{-1})	T_{m_5} (°C)	ΔH_{m_5} (J g^{-1})	T_{cl_2} (°C)	ΔH_{cl_2} (J g^{-1})	T_{cl_5} (°C)	ΔH_{cl_5} (J g^{-1})
2	1.0:0	50	11.5	–	–	176	3.5	–	–
6a	0.9:0.1	45.7	11.7	54.4	0.63	167.7	3.6	181.1	2.9
6b	0.7:0.3	42.7	12.1	55.4	1.4	169.2	3.7	183.2	5.0
6c	0.5:0.5	45.1	10.6	55.5	1.9	170.1	4.6	184.4	8.2
5	0:1.0	–	–	56.0	8.0	–	–	189	5.7

Figure 1 D.s.c. thermograms of the homopolymers, copolymers and blends of side chains 1 and 2. The curves refer to the following materials: A, homopolymer 2; B, homopolymer 1; C, blend of molar ratio homopolymer 1:homopolymer 2 = 0.1:0.9; D, blend of molar ratio homopolymer 1:homopolymer 2 = 0.3:0.7; E, blend of molar ratio homopolymer 1:homopolymer 2 = 0.5:0.5; F, copolymer 3c; G, copolymer 3b; H, copolymer 3a

different alkyl and vinylacetic acid groups. This chemical dissimilarity of the spacer units would be expected to frustrate packing in our copolymer system to a much larger degree. The values of ΔH_{cl} for the copolymers 3 were intermediate to those of the homopolymers 1 and 2.

Only the homopolymer 2 shows crystallinity; whilst small amounts of comonomer 1 (10%) such as in copolymer 3c still show some degree of crystallinity, further amounts of side chain 1 result in no crystallinity. Clearly, the addition of the flexible vinylacetic acid spacer group (side chain 1), which is highly mobile, leads to the absence of crystallinity in its homopolymer and a low clearing point when compared to homopolymer 2, and inclusion of even small amounts of side chain 1 with its increased mobility in a copolymer is sufficient to disrupt the three-dimensional crystalline order observed in homopolymer 2. In addition, at the clearing point, the greater mobility of the vinylacetic acid units of side chain 1 is able to lower the isotropization temperature of the copolymers. Copolymerization of mesogens with different spacer units to a common siloxane backbone results in intimate intermixing on a molecular level, as seen by the monotonic decrease of copolymer clearing temperatures. Also apparent is the disproportionate dominance of the very flexible vinylacetic acid spacer in side chain 1 which, even when included in only a 0.5 molar fraction copolymer with chain 2 (copolymer 3a), leads to thermal properties similar to those seen in homopolymer 1. Glass transitions were not observed by d.s.c. in these materials.

Optical microscopy of homopolymers and copolymers indicated that all materials were smectic A (fine conical fan texture).

Table 1 summarizes the d.s.c. results for copolymers with the thermal data for the corresponding two homopolymers also presented. The thermal properties included are the glass transition (T_g), melting point (T_m), the clearing point (T_{cl}; liquid crystal to isotropic), the enthalpy of isotropization (ΔH_{cl}) and the entropy of isotropization, $\Delta S = (\Delta H_{cl}/T(K))$. Whilst the clearing points of the copolymers lie between the clearing points of the two homopolymers, their value is less than a weighted mean of the homopolymer clearing point values. This indicates that the structural order of the copolymers is somewhat lower than that expected by simple averaging of the homopolymer values according to comonomer feed ratio. Analysis of the results of Imrie et al.[10], who synthesized only 1:1 copolymers and homopolymers of acrylate SCLCPs, also showed clearing transitions to be slightly less than that of the weighted homopolymer mean. In both this work and that of Imrie et al.[10], the addition of dissimilar comonomer units would be expected to interfere with the efficiency of packing (and hence lower T_{cl}). The work of Imrie et al.[10] considered copolymers of units with very similar spacer units, whilst ours consists of spacer units containing quite

Blends of homopolymers 1 and 2. Given the miscibility of the different side-chain units observed in the copolymer, it was of interest to determine whether physical blending of the different constituent homopolymers would also result in a miscible blend with intermediate transition temperatures. Such blends were prepared by mixing solutions of the two homopolymers, 1 and 2, in dichloromethane and removing the solvent under reduced pressure. Various molar ratios were combined; their d.s.c. blend thermograms are shown in *Figure 1C–E* and resultant thermal properties are given in *Table 2*. It was found that each of the blends showed two clearing points. That is, unlike the copolymers where only one intermediate clearing point was observed, a high and a low isotropization transition temperature similar to that of homopolymers 1 and 2 (denoted T_{cl_1} and T_{cl_2}, respectively, in *Table 2*) can be seen.

The positions of T_{cl_1} and T_{cl_2} in the blends are seen to be relatively invariant to the molar fractions of the blend components. Whilst the two peaks are clearly associated with either homopolymer peak temperature, they are slightly lower than the position of the corresponding homopolymer peaks. There appears to be some blend interaction, as indicated by T_{cl_1} of the blends which are some 16°C lower than T_{cl} of homopolymer 1. Likewise, T_{cl_2} is some 6°C lower than T_{cl} homopolymer 2. Whilst the appearance of two clearing points is indicative of a gross phase separation of the phases, some sort of interpenetration of the two phases, sufficient to result in concentration-independent values of T_{cl_1} and T_{cl_2}, must have occurred. It may be indicative of some partial miscibility.
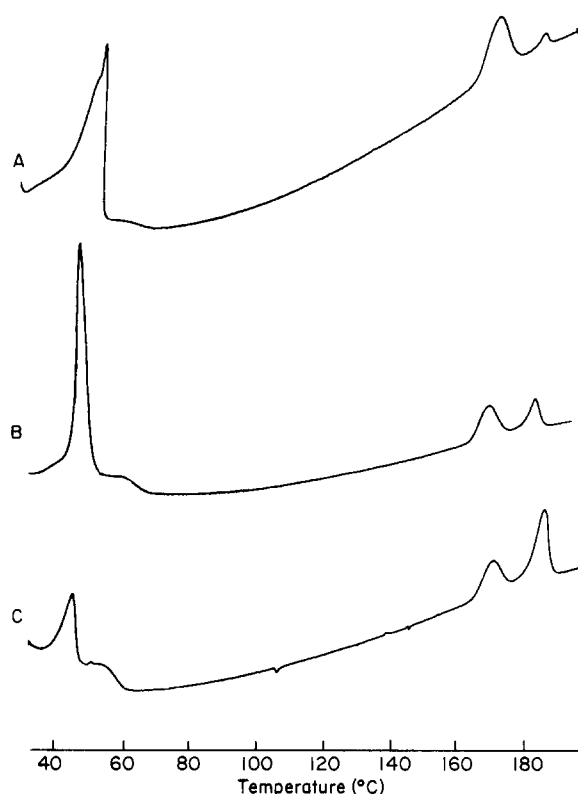
Figure 2 D.s.c. thermograms of blends of homopolymers **2** and **5**. The curves refer to the following materials: A, blend of molar ratio homopolymer **2**:homopolymer **5**=0.9:0.1; B, blend of molar ratio homopolymer **2**:homopolymer **5**=0.7:0.3; C, blend of molar ratio homopolymer **2**:homopolymer **5**=0.5:0.5

The predominantly two-phase behaviour was confirmed by optical microscopy, where two phases could be observed through crossed polars if the temperature was raised above T_{cl_1} and hence rendered black due to that phase being in the isotropic state. It was impossible to distinguish between the two phases at room temperature in optical micrographs when both phases were in the liquid crystal state.

Blends of homopolymers 2 and 5 differing only in the length of the spacer unit

In the blends and copolymers described so far, the spacer groups of homopolymers **1** and **2** attaching the mesogenic unit to the siloxane chain have been different (vinylacetic acid and alkyl chain spacer units, respectively). We have seen that with these chemically distinct spacer moieties in copolymers, a single liquid crystal phase with one clearing temperature is obtained, whilst the blended system is predominantly biphasic. It is thus of interest to determine whether a blend of homopolymers with even greater structural similarity (such as almost the same alkyl chain spacers) would show increased blend miscibility. To this end, we physically blended homopolymers of structure **2** and **5** in varying molar ratios and measured the thermal transitions by d.s.c. These homopolymers differ only in the length of their spacer units. The results are shown in *Figure 2* and summarized in *Table 3*.

The results are similar to the previous blend in that two discrete phases (indicated by two clearing temperatures, T_{cl_2} and T_{cl_5}) are observed in these blends. Likewise

the clearing temperatures are lower than the values for the homopolymer and are independent of blend concentration. No glass transitions could be observed by d.s.c.

In this blend system, because both homopolymers **2** and **5** possessed straight alkyl chain spacer units, both of the homopolymers possessed semicrystalline structure and the resultant blends were also semicrystalline. As with the clearing points, two crystalline melting points were seen in blends of homopolymers **2** and **5** and each occurred below the melting points of the constituent homopolymers. Interestingly, the melting point of homopolymer **2** dominates the magnitude of endotherm ΔH_{m2}, even up to a molar ratio of 0.5:0.5 (sample **6c**).

CONCLUSION

Both side-chain liquid crystal homo- and copolymers with differing spacer groups, as well as physical blends of these materials, have been prepared and examined by thermal and optical methods. The copolymers of side-chain units with very different spacer groups tended to show clearing points intermediate between those of the homopolymers. One of the homopolymer side-chain units was able to form a semicrystalline material and the other homopolymer, containing a rather flexible spacer, was not. Crystallinity in the copolymers seemed to be disrupted due to the influence of the flexible mesogenic side-chain unit and thus most of the copolymers were not crystalline.

Physical blends of SCLCPs with either very different chemical structures or similar side-chain spacer units proved largely immiscible. This was surprising given the overall chemical similarity of the components, particularly in the case of homopolymers **1** and **5**. It might have been expected that such materials would be miscible and show single transition temperatures (T_m, T_{cl}). However, despite two distinct clearing points (and two crystalline melting points in the case of blends of SCLCPs with chemically similar alkyl spacers of different lengths), the values of these transitions were slightly reduced compared to those in the homopolymer. We propose that this is due to slight contamination of each phase by a small amount of the other phase or partial miscibility, which leads to increased disorder and thus lower clearing points. Such gross two-phase behaviour was also observed in the optical microscope. The copolymer units are coupled together by the siloxane backbone leading to a greater forced connectivity and intermediate transition temperatures are seen whilst the different side chains in the blended materials move rather more independently and a two-phase mixture occurs. We were not able to observe glass transition temperatures in the blends by d.s.c. and hence we cannot say whether the polysiloxane backbones were miscible or whether the immiscibility of the anisotropic liquid crystalline phase was sufficient to force immiscibility between the polymer chains.

It is clear from this work that the influence of the spacer unit and the siloxane chain is sufficient to cause immiscibility when homopolymers are physically blended, but that the connectivity of these side chains within a copolymer results in single-phase materials with intermediate transition temperatures. Therefore, copolymerization seems to be a better way of tailoring SCLCP properties.

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