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Preparation and thermal characterisation of some new liquid crystalline copolymers involving a spacer unit based on vinylacetic acid

Gary M. Day, W. Roy Jackson*, George P. Simon

Departments of Chemistry and Materials Engineering, Monash University, Clayton,
Victoria, Australia, 3168

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Summary

Three series of new liquid crystalline (LC) copolymers having a polysiloxane backbone and two different mesogenic pendant groups, one involving a vinylacetic acid moiety in the spacer, have been synthesised. Thermal characterisation of these polymers has allowed comparison of behaviour between a number of different copolymer systems. It was found that increasing amounts of the vinylacetic acid moiety lowered the clearing points (T_i) of the copolymers in an almost linear fashion whilst also inhibiting crystallinity in these polymers.

Introduction

In the liquid crystal field, mixtures containing several mesogenic components have been more useful for commercial applications than pure LC substances (1). By analogy, composite polymers may also be useful in side chain systems for application purposes (2). The liquid crystalline polymer (LCP) composites may be achieved by either blending side chain LCPs with other materials (3) or by synthesising copolymers (2, 4). The two most common types of side chain LC copolymers studied to date have been those with two different mesogenic pendant groups and those with a combination of mesogenic and non-mesogenic pendant groups (2, 4) ('dilution' copolymers). While many types of side chain LC copolymers have been investigated, the most intensely studied have been those with acrylate or siloxane backbones.

Side chain LC copolymers with an acrylate backbone have predominantly consisted of those polymers with two different mesogenic groups in the side chain (2, 4-6) although acrylate copolymers involving a non-mesogenic group have been prepared (7). Conversely, a majority of the LC siloxane copolymers have consisted of those with various proportions of mesogenic and non-mesogenic units in the side chain (8, 9). Siloxane copolymers with two different mesogenic units have also been prepared (4, 10-12) but are not as common as the siloxane 'dilution' copolymers.

In a continuing effort to synthesise materials for possible electro-optic applications we have produced three novel series of siloxane based copolymers with two different mesogenic pendant groups. One pendant group in each copolymer series has a flexible spacer involving a vinylacetic acid moiety which was recently developed by our group (13). The copolymers of general formulae **1**, **2** and **3** were prepared with the two pendant groups (R_1 and R_2) varying as shown in Figure 1.

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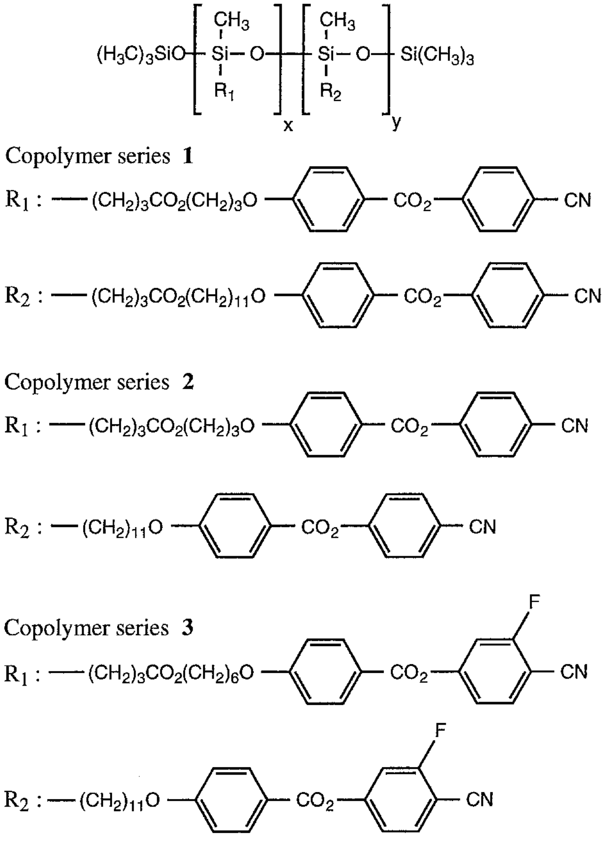
* Corresponding author



Key to copolymer series **1**, **2** and **3**.

Copolymer series **1**	x (R_1)	y (R_2)	Copolymer series **2**	x (R_1)	y (R_2)	Copolymer series **3**	x (R_1)	y (R_2)
1a	100	0	**2a**	50	50	**3a**	100	0
1b	75	25	**2b**	25	75	**3b**	50	50
1c	50	50	**2c**	0	100	**3c**	0	100
1d	25	75						
1e	0	100						

Fig. 1 Structures of the copolymers prepared in this work.

The homopolymers in these series have been shown to be smectic A in texture. It was of interest to see if a smectic A phase also existed for the copolymers in which different sized groups must be incorporated into layers.

Experimental

4-Cyanophenyl and 4-cyano-3-fluorophenyl 4-(ω-alkenyloxy)benzoates: These were prepared by standard literature methods (14, 15).

4-Cyanophenyl and 4-cyano-3-fluorophenyl 4-[ω-(but-3-enoyloxy)alkyloxy]benzoates: These were prepared by the general method used for the synthesis of acrylate esters (16). Full details of the preparation, spectroscopic and optical characterisation of these compounds have been reported elsewhere (17).

Copolymer synthesis: Based on a similar procedure (18), a typical reaction involved dissolving poly(hydrogenmethylsiloxane) (Petrarch PS120, $\overline{DP}$ 40 ± 3, 1 mol. equiv.) and one of the unsaturated esters (*ca.* 0.5 g) in dichloromethane (10-20 ml) followed by stirring at ambient temperature for a few minutes while under nitrogen. The platinum divinyltetramethyldisiloxane complex (Petrarch PC072, 3-3.5% in xylene, 10 μl) was addded and the mixture heated under reflux until the ester had reacted fully as shown by thin layer chromatography (*ca.* 24-36 h). The second unsaturated ester was then added [additional platinum catalyst (10 μl) was added every 12 h] and the reaction continued until no Si-H absorption was observed in the i.r. spectrum. The crude polymer was then dissolved in dichloromethane and precipitated with a five fold excess of methanol (5 times).

The grafted liquid crystalline polymers (LCPs) were identified as smectic A by texture using an Olympus Petrological Microscope fitted with a Mettler FP-80 hot stage.

DSC measurements were carried out under nitrogen using a Perkin Elmer DSC 7 instrument with a scanning rate of 10°C/min. All samples were heated to above the isotropic point to eliminate thermal history, cooled and then scanned a second time. All data reported in Table 1 refer to second heating runs.

Results and Discussion

All the LCPs exhibited a conical fan texture, indicative of a smectic A phase suggesting that there was no difficulty in accommodating the different sized groups into the requisite layer structure. The thermal data for phase transitions are listed in Table 1, including the transition temperatures for the corresponding homopolymers. Values of T_m and T_i are peak values determined using DSC. Values of T_i using optical microscopy for a limited number of samples were found to lie in the temperature range observed using DSC. All polymers were prepared using Petrarch poly(hydrogenmethylsiloxane) (PS120), having a $\overline{DP}$ of 40 (19).

In the copolymer series **1** and **2** (entries 1-8) the T_i values for the copolymers lie in between the T_i values for the two respective homopolymers for each copolymer series. Thus the values for polymers **1b**, **1c** and **1d** (entries 2, 3 and 4 respectively) lie between those of **1a** and **1e** (entries 1 and 5). Similarly the values for **2a** and **2b** (entries 6 and 7) lie between those of the homopolymers **1a** and **2c** (entries 1 and 8). It should be noted that polymer **1a** is a homopolymer for both the **1** and **2** polymer series. Figure 2 shows that for each copolymer series **1** and **2** the T_i values decrease incrementally in an almost linear fashion with respect to the amount of R_1 present.

In the case of the copolymer series **1** no crystallinity was observed, which is consistent with the lack of crystallinity for polymers containing a vinylacetic acid group in the flexible spacer (5). No glass transitions were observed for the copolymers **1b, 1c** (entries 2 and 3). A glass transition was observed for the copolymer **1d** (entry 4), but the value did not lie between the T_gs for the two homopolymers (entries 4 and 8) as would be expected.

Table 1 Thermal data for the phase transitions of the homo- and copolymers **1**, **2** and **3**.

Entry	Compd.	T_g (°C)	T_m (°C)	T_i (°C)	ΔP_w† (°C)	ΔH_m (J/g)	ΔS_m (10^{-3} J/gK)	ΔH_i (J/g)	ΔS_i (10^{-3} J/gK)
1	**1a**	-7	-	40	20	-	-	3.4	10.9
2	**1b**	*	-	52	22	-	-	4.6	13.4
3	**1c**	*	-	71	26	-	-	6.3	19.4
4	**1d**	-2	-	78	34	-	-	5.7	16.2
5	**1e**	-4	-	106	18	-	-	6.5	17.2
6	**2a**	*	-	120	36	-	-	1.7	4.3
7	**2b**	*	-	148	58	-	-	5.9	14.0
8	**2c**	*	56	189	10	8.0	24.3	5.7	12.3
9	**3a**	-9	-	58	15	-	-	2.4	7.3
10	**3b**	-12	-	106	29	-	-	3.7	9.8
11	**3c**	-7	39	173	18	12.0	38.5	4.3	9.6

* Glass transition not observed.

† Baseline peak width of clearing transition from DSC.

The copolymers **2a** and **2b** (entries 6 and 7) were not crystalline in character. This lack of crystallinity suggests that the introduction of a relatively small amount of the vinylacetic acid based pendant group caused sufficient disruption in packing to prevent crystallinity in these copolymers. Surprisingly, no glass transitions were observed by DSC for these copolymers **2a** and **2b** (entries 6 and 7).

The T_i for the copolymer **3b** (entry 10) lies almost halfway between the T_i values for the two corresponding homopolymers **3a** and **3c** (entries 9 and 11). The glass transition for the copolymer **3b** is considerably lower (-12°) than the T_gs for the two corresponding homopolymers [-9° for **3a** and -7° for **3c**]. This seems to indicate that changes in mesogenic packing may have an effect on the backbone mobility (i.e., there may be some sort of mesogen-backbone connectivity). Once again no crystallinity was observed for the copolymer **3b** due to the presence of a vinylacetic acid group in the spacer of one of the pendant groups.

All of the peak widths of isotropisation (ΔP_w) were broader for the copolymers than for the respective homopolymers. Peak width broadness (or biphasic region broadness) represents a range of structural (i.e., polymer composition) and physical environments (i.e., molecular packing). Since the possible molecular environments for copolymers effectively consist of two different homopolymer molecular environments, it is not surprising that the peak widths are broader for the copolymers. This type of behaviour has been exhibited previously in other polymer systems (7, 12, 13).

Perhaps surprisingly the entropy of isotropisation values (ΔS_i) were higher than would be expected based on simple proportionality. Thus a positive deviation from linearity is shown in Figure 3 for polymers **1a** to **1e**. Similarly the ΔS_i value for the copolymer **3b** is higher than the average value between the homopolymers **3a** and **3c**. An exception was the value of ΔS_i for the copolymer 2a which showed a negative deviation from linearity. A positive deviation implies that the copolymers are more ordered in the LC state or that the isotropic state is more disordered for the copolymers. Imrie *et al.* (5, 6) have shown both positive and negative deviations from average values for a series of 50:50 copolymers where one side chain spacer length was held constant and the other varied. Most of the deviations were negative in value in contrast to our work. The authors suggest specific unfavourable dipole interactions occurring for particular combinations of spacer lengths as an explanation for the negative deviations. It is possible that in our systems favourable dipolar interactions in the copolymers relative to the homopolymers exist.

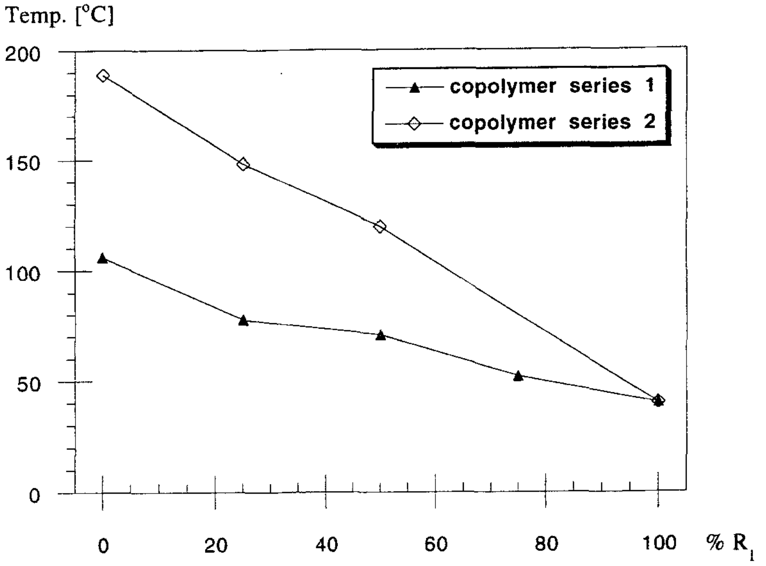


Fig. 2 Plot of isotropisation temperature (T_i) vs. % R_1 pendant group for copolymers **1** and **2**.

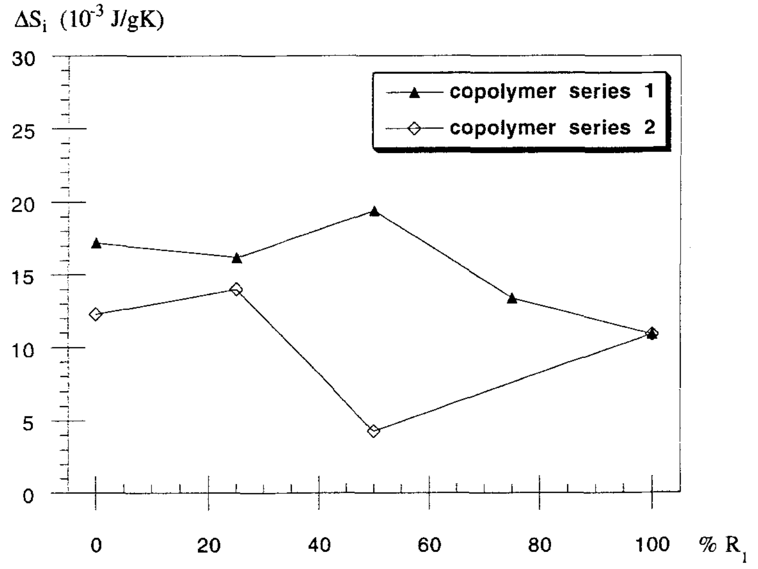


Fig. 3 Plot of isotropisation entropy (ΔS_i) vs. % R_1 pendant group for copolymers **1** and **2**.

Acknowledgements

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