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Preparation of thermotropic liquid crystalline polymers involving a novel spacer unit based on vinylacetic acid*

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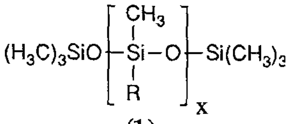
Summary

Liquid crystalline polymers (LCPs) involving a polysiloxane backbone and a novel vinylacetic acid unit in the spacer have been synthesised. These polymers all show dramatically lower clearing points (T_{cl}) than polymers with similar chain lengths but involving established polymethylene spacer groups.

Introduction

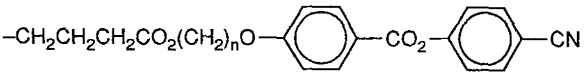
Side-chain liquid crystalline polymers are useful in electro-optic applications because of the ability of the mesogenic units to be switched under the direction of a.c. electrical fields. In an effort to synthesise materials which can be readily switched we have produced polymers which contain vinylacetic acid spacer units linking the siloxane backbone and mesogenic side-chain. These materials have been compared with more traditional polysiloxane LCPs. The polymers of general formula (1) were prepared with the group R varying as shown below:



$$(H_3C)_3SiO\left[\begin{array}{c}CH_3\\|\\Si-O\\|\\R\end{array}\right]_x Si(CH_3)_3$$

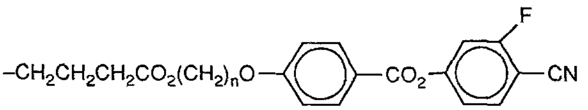
(1)

R: a,



n = 3,6,8,11.

b,



n = 6,8,11.

In addition, polymers with comparable chain lengths but using the established polymethylene spacer groups were prepared.[1,2]

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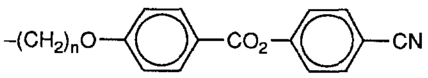
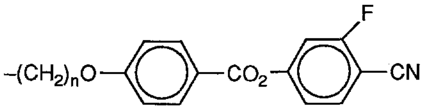
R: c,



n = 6,11.

d,



n = 3,6,11.

Other liquid crystalline side-chain polymers containing an additional ester grouping in the spacer unit have been reported, but this has been in the form of a carbonate unit.[3]

Experimental

4-(ω-Alkenyloxy)benzoic acid aryl esters: These compounds were prepared by standard literature methods.[4]

4-[ω-(But-3-enoyloxy)alkyloxy]benzoic acid aryl esters: These esters were prepared by the general method used for the synthesis of acrylate esters.[5] Full details of the preparation of these compounds, including their physical and optical properties will be reported elsewhere.[6]

Synthesis of the polymers: Based on similar methods,[1,2] the unsaturated esters (1-2 g scale) were reacted with poly(hydrogenmethylsiloxane) - either Petrarch PS120 ($\overline{DP}$ 40±3) or Merck ($\overline{DP}$ 47±3) - such that the alkene was in excess by *ca.* 10 mol%. Reactions were carried out in toluene (10-20 ml) and under nitrogen with 1 to 2 drops (Pasteur pipette) of platinum divinyltetramethyldisiloxane complex in xylene (Petrarch) at 60-70° until no Si-H was observed by i.r. (usually 24-72 hours). The crude polymer was dissolved in dichloromethane and precipitated with five times excess of methanol (3 or 10 times).

The grafted polymers were identified as smectic A by texture and enthalpy measurement and transition temperatures were confirmed 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^{-1}. All samples were heated to above the isotropic point to eliminate thermal history, cooled to ambient temperature and scanned a second time. All data reported in the Table refer to second heating runs.

Results and Discussion

Two commonly available polysiloxanes were used in this work. The Petrarch and Merck polymers were determined to have $\overline{DP}$s of 40 and 47 respectively. The two backbones were found to generally have little effect on the thermal properties of the grafted polymers (compare entries 5 and 6, 7 and 8). However, a significant drop in T_{cl} was observed in one case (compare entries 13 and 14). The literature suggests that a change in $\overline{DP}$ from 55 to 30 leads to a decrease in T_{cl} of *ca.* 8°.[7,8]

Thermal data for the phase transitions of the polymers (1)

Entry No.	Polymer	n	Backbone[a]	Number of precipitations	T_g	T_{cl}	
						Peak temp. (°C)	ΔH (Jg^{-1})
1	a	3	P	3	-7	40	3.4
2	a	6	P	3	-4	72	4.2
3	a	8	P	3	-8	96	5.1
4	a	11	P	3	-4	106	6.5
5	b	6	M	3	-9	60	2.6
6	b	6	P	3	-9	58	2.5
7	b	8	M	3	-12	64	3.6
8	b	8	P	3	-15	65	3.8
9	b	8	P	10	-14	66	3.7
10	b	11	P	3	-12	56	3.8
11	c	6	P	3	-	176	3.5
12	c	11	P	3	-	189	5.7
13	d	3	M	3	13	107	2.3
14	d	3	P	3	13	76	1.7
15	d	3	P	10	7	81	1.4
16	d	6	M	3	-4	144	3.0
17	d	6	P	10	-5	148	2.8
18	d	11	M	3	3	173	4.0
19	d	11	P	10	-7	171	5.5

[a] M = Merck, P = Petrarch

The effect of increasing the number of precipitations from 3 to 10 during purification of the grafted polymer was briefly examined (entries 8 and 9, 14 and 15). No unreacted alkene was detected by TLC for the polymers precipitated 3 times, which contrasts with previous work.[9] In addition, our results showed at most a 5° difference in transition temperatures resulting from the greater number of precipitations. Thus three precipitations were commonly adopted for polymer purification.

The effect of introduction of a vinylacetic acid moiety into the spacer unit can be estimated by comparison of these polymers with polymers containing only a polymethylene spacer. Spacers containing eleven atoms can be compared (entries 2 and 12, 5 and 18). The vinylacetic acid group caused a major decrease in T_{cl} (> 110°) and a decrease in T_g in one case of some 10°.

Two mesogenic units were incorporated into the vinylacetic acid based polymers. In agreement with published data[2] polymers involving a 3-fluoro-4-cyanophenol moiety had lower clearing points than polymers involving 4-cyanophenol. A drop in T_{cl} of 14° was observed for polymers with n=6 (entries 2 and 6) and the effect was even more marked for longer chains (ΔT_{cl} = 50° for n = 11, entries 4 and 10).

The polymers containing the vinylacetic acid moiety did not show crystalline structure, even with a long spacer group (entries 4 and 10). In contrast, some LCPs containing polymethylene spacers were crystalline. Thus the LCPs (entries 11 and 12) were crystalline with T_ms of 50° and 56° respectively. Similarly the LCPs containing the cyanofluoro mesogen and a long spacer group (entries 18 and 19) also showed crystalline properties, both with a T_m of 39°. In addition the LCPs containing the vinylacetic acid moiety generally showed lower transition temperatures than for polymers containing polymethylene spacers.

As previously reported,[10] increased spacer length in a homologous series resulted in the stabilisation of the smectic phase resulting in higher transition temperatures. Only one exception was noted involving a very long spacer unit (entry 10).

Several of the polymers with both the methylene and vinylacetic acid based spacer units showed biphasic behaviour of the type noted recently.[11] Results of such annealing studies with these materials are currently underway in our group.

Acknowledgements

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