Synthesis and characterization of liquid crystal polymers with oligosiloxane spacers

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Diesters from 4-vinylbenzoic acid and biphenols with structural mesogenic characteristics were synthesized and interconnected by siloxane spacers with different lengths. Polymers were characterized by i.r., ^{1}H n.m.r. and elemental analysis. Thermal properties were studied by d.s.c. and polarized light microscopy.

(Keywords: synthesis; characterization; liquid crystalline polymer)

INTRODUCTION

It has been demonstrated by a number of investigations that polymers formed by rigid rod-like molecules, alternated with flexible spacers such as $-(CH_2)_n-$ or $-Si(CH_3)_2-O-_n$, produce liquid crystal polymers (LCPs) with low transition temperatures[1–3]. Many of these rigid molecules are esters which, with oligosiloxane spacers, form polymers with a wide mesophase range[4,5].

Jo *et al.*[6] have found that copolymers with siloxane spacer groups show glass transition temperatures (T_gs) and melting temperatures lower than copolymers with methylene spacers. This effect is attributed mainly to the flexibility and bulky structure of the siloxane units, which reduce the chain packing and interchain forces in the polymers more effectively than methylene spacers.

An extensive number of mesogenic esters derivatives from 4-alkyloxybenzoic acid have been prepared[7–9], having good thermal properties, such as low melting points and a wide mesophase range. Mesogenic structures derived from 4-vinylbenzoic acid have not been reported yet. These vinyl esters would be expected to have high melting points as the vinyl end groups make the molecules more rigid.

In this study, two esters with vinyl end groups have been synthesized and highly flexible oligosiloxane spacers have been inserted between them in order to reduce their transition temperatures. Main chain LCPs with low T_gs were expected to be obtained.

EXPERIMENTAL

All the chemicals and solvents were obtained from Aldrich and Merck. I.r. spectra were determined (in KBr pellets) using a Perkin-Elmer (model 567) spectrophotometer. ^{1}H n.m.r. spectra were obtained using a Varian XL-100 n.m.r. spectrophotometer. Elemental analyses were performed in a CH Heraeus Mikrostandart analyser. T_g values were determined using a Perkin-Elmer DSC-1B differential scanning calorimeter, with a heating rate of 16°C min^{-1} under N_2. For mesogenic properties, a Leitz Ortholux Pol BK II equipped with a Mettler hot stage was used. Thermogravimetric analyses were carried out with a Perkin-Elmer (model TGS-1) thermobalance with a Perkin-Elmer UU-1 programmer at a heating rate of 20°C min^{-1} under N_2. Viscosimetric measurements were made using a Desreux-Bischoff[10] viscosimeter at 25°C.

Synthesis of bis(p-vinylbenzoic acid) esters

p-Vinylbenzoyl chloride was obtained by stirring *p*-vinylbenzoic acid with $SOCl_2$ for 24 h at room temperature, according to a procedure described previously[11]. The product (yield 76%) was distilled at 66°C and 0.5 mm Hg pressure.

Hydroquinone or 4,4′-dihydroxybiphenyl (4.2 mmol) was dissolved in dry tetrahydrofuran (THF). *p*-Vinylbenzoyl chloride (8.8 mmol) in THF (1.6 ml) and triethylamine (TEA, 8.4 mmol) in THF (1.6 ml) were added to the solution stirred at 5°C. After stirring for 4–6 h, the reaction was left to stand for 20 h at room temperature. The mixture was poured into ethanol and filtered. Bis[1,4-phenylene (*p*-vinylbenzoate)] (yield 71%) was purified by recrystallization from $CHCl_3$/CH_3OH, and dried under vacuum. Bis[4,4′-biphenylene (*p*-vinylbenzoate)] (yield 83%) was recrystallized from *N*,*N*-dimethylformamide (DMF).

Synthesis of polymers

α-Dimethylsilanyl-ω-hydrogenoligodimethylsiloxane (0.5 mmol) in THF was added dropwise to bis[1,4-phenylene (*p*-vinylbenzoate)] or bis[4,4′-biphenylene

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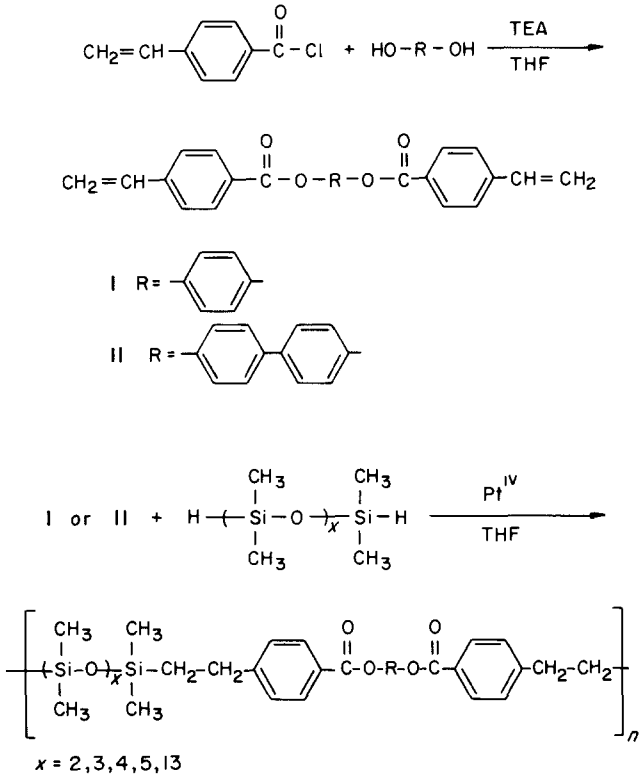
(*p*-vinylbenzoate)] (0.5 mmol) in dry THF at 60°C in N_2 with a catalyst based on H_2PtCl_6. The solution was stirred for 24 h. The polymer was precipitated in methanol and reprecipitated from THF/methanol, dried and characterized.

RESULTS AND DISCUSSION

Esters were synthesized (*Scheme 1*) by the reaction of *p*-vinylbenzoyl chloride with hydroquinone or 4,4'-dihydroxybiphenyl according to a procedure described previously[9], and characterized by i.r., ^1H n.m.r. and elemental analysis. The results are summarized in *Table 1* and are in good agreement with the structures proposed. Esters I and II do not melt but decompose at 230–240°C.

The spacers $H\text{-}[\text{-}Si(CH_3)_2\text{-}O\text{-}]_x Si(CH_3)_2\text{-}H$ with $x = 2$, 3, 4 and 5 were prepared according to Greber *et al.*[12]. A commercial siloxane with $x = 13$ was also used (Wacker oil, Wacker Chemie, Burghausen, Germany). The siloxane hydrides were purified by distillation under reduced pressure several times. Their purity was tested by gas chromatography and they were characterized by their boiling points, i.r. spectroscopy and quantitative elemental analysis.



Scheme 1

Polymers were synthesized (*Scheme 1*) by addition of esters I or II to α-dimethylsilanyl-ω-hydrogenoligodimethylsiloxane[9] catalysed by H_2PtCl_6 (Wacker oil; Wacker Chemie, Burghausen, Germany). Ten polymers were obtained from I or II and the oligodimethylsiloxanes (I_{2-5}, I_{13}, II_{2-5} and II_{13}). The elemental analyses are shown in *Table 2*. The reaction was carried out by dropping the Wacker oil catalyst/THF on the vinyl esters in THF. α-Dimethylsilanyl-ω-hydrogenoligodimethylsiloxane was also added dropwise. This order is in agreement with the mechanism suggested, which involves platinum–olefin complex formation before the reaction with the $-Si(CH_3)_2-H$ group[13]. By avoiding heating the siloxane in the presence of H_2PtCl_6 solely, the possibility of side reactions decreases[14]. These polymers were obtained with better yields and are whiter than those synthesized by adding H_2PtCl_6 over vinyl ester–siloxane functions. After 24 h, the i.r. absorption band at 2140 cm^{-1} of the Si–H group disappeared.

The i.r. spectra of the polymers are similar to those shown in *Figure 1* for I_{13}. Some of the absorption frequencies (cm^{-1}) are: 1710 (C=O), 1410 and 1250 ($Si-CH_3$) and a broad band at 1100–1000 (Si–O–Si).

All the polymers have similar ^1H n.m.r. spectra. The spectrum for polymer II_5 is shown in *Figure 2*.

Reproducible intrinsic viscosities were determined in $CHCl_3$ at 25°C for the unfractionated polymers. The following values were obtained: $I_5 = 0.15$ dl g^{-1}, $I_{13} = 0.15$ dl g^{-1}, $II_4 = 0.04$ dl g^{-1}, $II_5 = 0.05$ dl g^{-1} and $II_{13} = 0.05$ dl g^{-1}.

The remaining polymers are sparingly soluble in

Table 2 Elemental analyses of the polymers

Polymer	C (%)[a]	H (%)[a]
I_2[b]	66.00 (67.23)	6.20 (6.17)
I_3	58.89 (61.18)	6.74 (6.10)
I_4	56.19 (56.83)	6.88 (7.32)
I_5	53.99 (53.83)	6.99 (6.39)
I_{13}	44.49 (45.49)	7.41 (6.67)
II_2	66.06 (66.58)	6.42 (6.66)
II_3	62.63 (63.40)	6.58 (6.30)
II_4	59.84 (60.45)	6.72 (6.79)
II_5[b]	62.20 (61.04)	6.50 (6.20)
II_{13}	47.39 (48.21)	7.35 (8.31)

[a]Calculated (found)
[b]Values for trimer

Table 1 I.r., ^1H n.m.r. and elemental analyses of esters I and II

Ester	C (%)[a]	H (%)[a]	I.r. (cm^{-1})	^1H n.m.r. δ ($CDCl_3$)
I	77.72 (77.14)	4.89 (5.04)	3090 (CH_2=) 1730 (C=O) 1280 (C–O) 1090 (C–O)	7.34 (s, arom.) 7.90 (d, arom.) 6.84 (d, –CH=) 5.70 (d, CH_2=)
II	80.72 (80.62)	4.93 (5.21)	3060 (CH_2=) 1730 (C=O) 1290 (C–O) 1085 (C–O)	7.9 (d, arom.) 7.4–7.8 (m, arom.) 6.8 (d, CH=) 5.7 (d, CH_2=)

[a]Calculated (found)

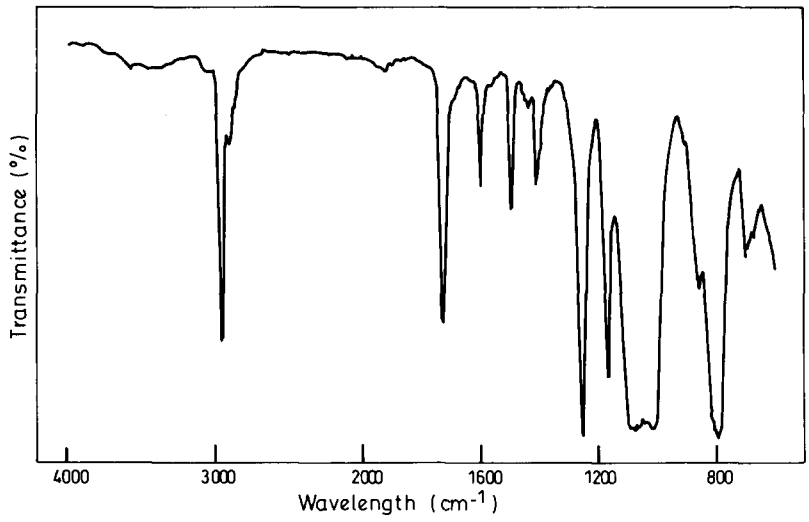


Figure 1 I.r. spectrum of I_{13}

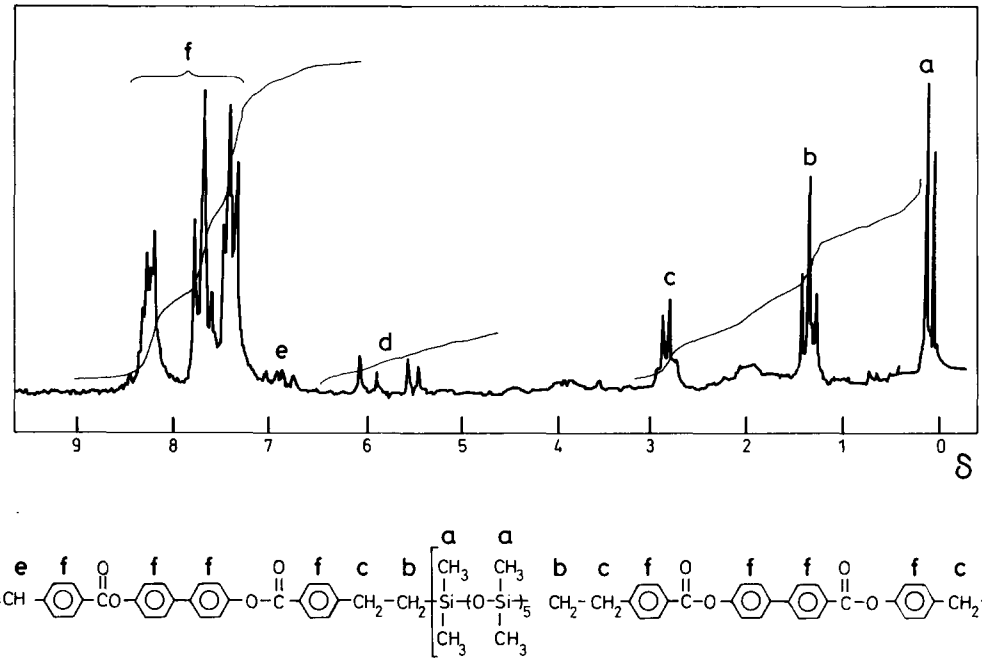


Figure 2 ^1H n.m.r. spectrum ($CDCl_3$) of II_5

solvents such as $CHCl_3$, CH_2Cl_2, 1,1,2,2-tetrachloroethane, DMF, toluene or ethyl acetate. Solubilities increase for the higher members of the series. Thus, good solubilities have been observed in THF and $CHCl_3$ for I_5, II_5, I_{13} and II_{13}.

The polymers were assumed to be of low molecular weight, judging by the low viscosity values obtained. Low molecular weights have been reported (M_n = 3000–7000)[9] for similar polymers, synthesized by the same experimental methods.

Thermogravimetric analyses of the two series of polymers are shown in *Figure 3*. The polymers showed good stabilities with normal thermal decomposition temperatures, which were considered to be the temperatures at which the polymers lost 3% of their weight. At this point the colour of the polymer changed from white to yellow. At the decomposition temperature, the polymers became brittle.

The thermal properties of the polymers are listed in *Table 3*. The T_g values were determined by d.s.c. from −70°C, and were taken during the second heating and are reproducible to within ±5°C from sample to sample. As expected, T_g values decrease with increase in length of the siloxane spacers. In series I, where the rigid unit is shorter, the T_g values are lower than those obtained for the homologous polymers in series II. The rigid unit in series II is longer than in series I, and higher transition temperatures are obtained for the same length of spacer, as shown in *Table 3*. Above the T_g, the polymers undergo a slow and continuous softening and do not show a melting peak in d.s.c.

The mesogenic properties were examined by polarizing microscopy. In series I, polymers do not show mesogenic properties. These compounds (except I_{13}) do not present any fluid phase below the decomposition temperature. In series II, only II_{13} presented liquid crystal behaviour

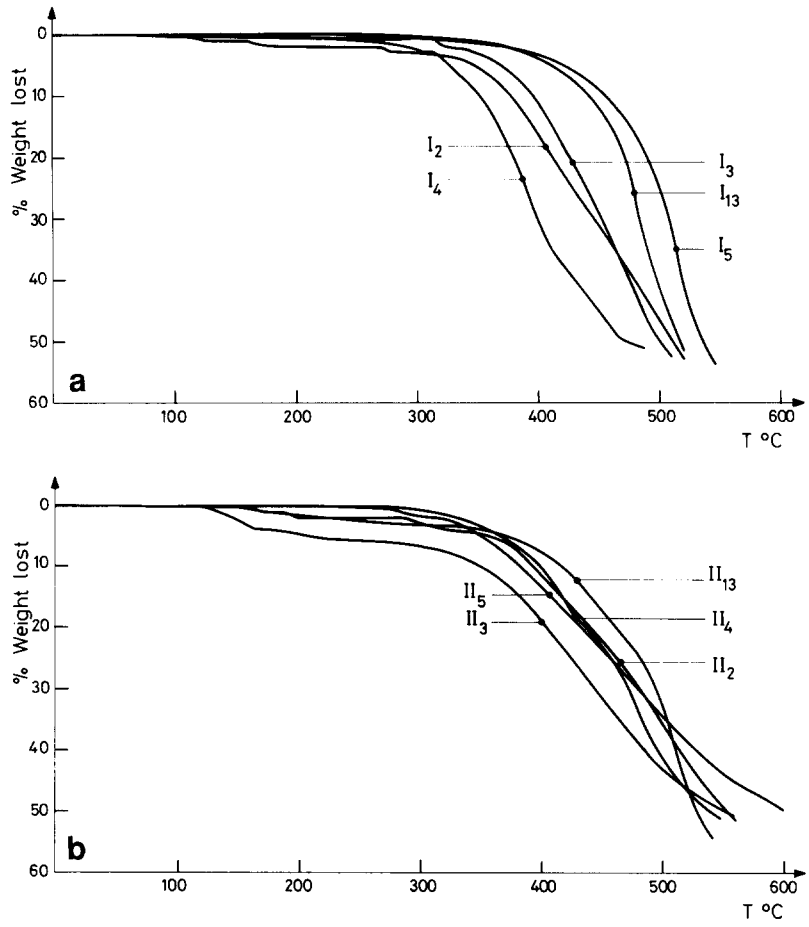


Figure 3 Thermogravimetric curves of (a) series I and (b) series II polymers

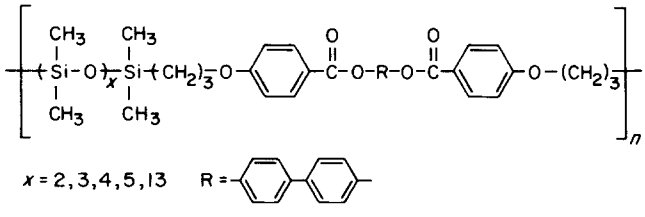
Table 3 Phase transitions of the polymers

Polymer	T (°C)[a]	Polymer	T (°C)[a]
I_2	g 47.8	II_2	g 55
I_3	g 27	II_3	g 22
I_4	g −20	II_4	g 3 b
I_5	g −30	II_5	g −12.5 b
I_{13}	g −45	II_{13}	g −* −40.4 s 260 d

[a] g, glassy; s, smectic; b, birefringent; d, decompose; *, phase transition

with a broad mesophase. Polymer II_{13} shows a smectic phase when the sample is observed under a polarizing microscope.

D.s.c. heating curves of II_{13} are presented in *Figure 4*. At −40.4°C an endotherm peak is observed which may be attributed to a phase transition. A melting transition is unlikely at such a low temperature for long siloxane spacers; this may be corroborated by similar polymers reported in the literature[9].



For $x = 13$, a glass transition is observed at −110°C and for $x = 2$ a melting transition is observed at 95°C. The

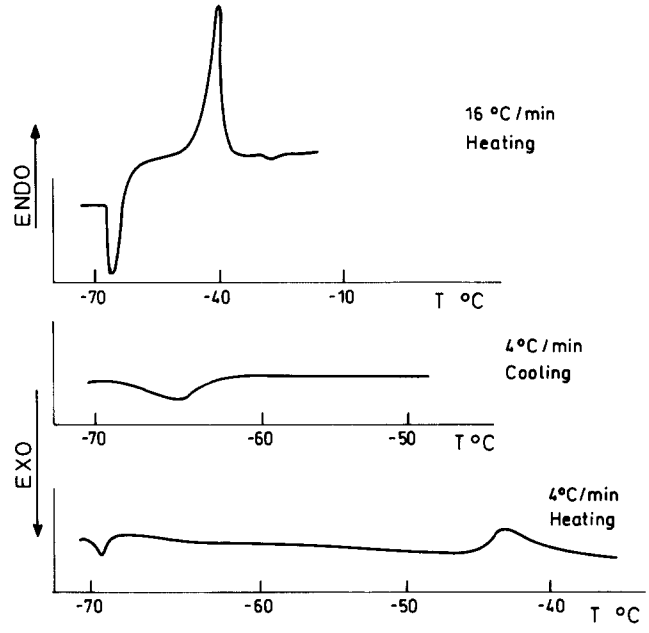
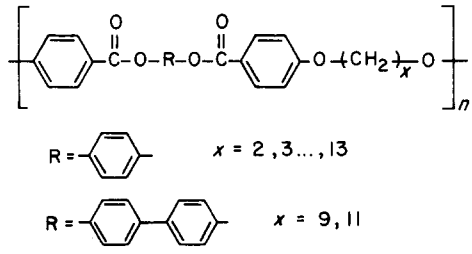


Figure 4 D.s.c. curves of the untreated polymer II_{13}

remaining polymers showed only T_g values between −110°C and 95°C. Other polymer series containing polysiloxane spacers synthesized by Ringsdorf and Schneller showed only glass transitions[15]. Analogous main chain polymers containing $-O-(CH_2)_x-O-$ as spacer groups were synthesized by van Luyen and



R = $x = 2, 3 \ldots, 13$

R = $x = 9, 11$

Strzelecki[16,17]. All these polymers showed a nematic phase at temperatures above 200°C. A smectic phase at temperatures above 200°C was observed when R = phenylene for $x = 10$ and 11. Both series of polymers reported exhibited melting transitions unlike the polymers containing polysiloxane spacers synthesized by us, which showed only glass transitions at low temperatures. It seems that the siloxane spacers reduce the interchain forces and the degree of crystallinity of the polymers because of their flexibility and the bulkiness of the $-CH_3$ groups.

The II_4 and II_5 polymers showed a clear birefringence at room temperature which remained until the decomposition temperature. A clear fluid phase was not observed. Shorter siloxane spacers do not increase the flexibility of the main chain sufficiently in these polymers making it impossible to attain melting before decomposition.

From these results it can be concluded that the vinyl esters I and II do not melt but decompose, and the compounds prepared interconnecting oligosiloxane spacers with the vinyl esters produce lower T_g values. Transition temperatures as low as −40.4°C were achieved in II_{13}, which shows liquid crystal behaviour over a wide range of smectic mesophase at low temperature.

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