Liquid crystalline side-chain polymers. 1. Polysiloxanes with a carbonate group in the spacer

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A series of new allyl and vinyl carbonates has been prepared by the reaction of allyl and vinyl chloroformates with 4-hydroxyphenyl esters of *p*-substituted benzoic acid, under phase-transfer catalysis conditions. These compounds, which exhibit nematic phases, have been bound onto a polysiloxane backbone by hydrosilylation. The side-chain polymers have been examined by ^1H and ^{13}C n.m.r. spectroscopy, g.p.c., differential scanning calorimetry and optical polarizing microscopy.

(Keywords: liquid crystals; polymethylhydrosiloxanes; hydrosilylation; carbonates; phenyl benzoates)

INTRODUCTION

The preparation of liquid crystalline side-chain polymers was first reported in 1978 by Shibaev and Platé[1] and Wendorff et al.[2] Since that time, several hundred such polymers have been made[3,4]. These polymers cause much interest because they combine the mechanical properties of polymers with the liquid crystalline behaviour of mesomorphic molecules. Among these polymers some side-chain polysiloxanes bearing phenyl benzoate moieties with *p*-alkoxy or cyano substituents have been prepared by reaction of polymethylhydrosiloxane with mesogenic molecules having a vinyl end group. The mesomorphic properties of these comb-like polymers have been examined as a function of the nature and the length of the terminal substituent as well as the nature of the spacer between the mesogenic group and the macromolecular backbone[5,6].

In most cases, the spacer is a flexible chain formed by 3–11 methylene groups connected to the mesogenic moiety through an ether linkage. We wanted to introduce a carbonate bond instead of an ether function into the spacer since it has been shown that polymers having a carbonate group in the side-chain are thermally stable: up to 250°C in the case of poly(vinyl phenyl carbonate)[7]. Therefore, the synthesis of a series of new unsaturated carbonates with a phenyl benzoate group has been effected by reacting vinyl or allyl chloroformate with 4-hydroxyphenyl esters of *p*-substituted benzoic acid derivatives and with 4(4′-methoxybenzoyloxy)benzyl alcohol. This has been performed under phase transfer catalysis conditions which have been successfully applied to the synthesis of other carbonates and carbamates[7]. These compounds have been subsequently hydrosilylated with polymethylhydrosiloxane.

The results concerning the preparation and the thermal behaviour of these new low molar mass mesogens and of the modified polysiloxanes are presented.

MATERIALS

Synthesis of unsaturated carbonates

Allyl and vinyl carbonates were prepared by the reaction of allyl or vinyl chloroformate with the following phenols and alcohol: $RC_6H_4COOC_6H_4OH$ (I) with $R{=}C_2H_5$, CH_3O, C_2H_5O, C_4H_9O, $C_6H_{13}O$ and CN, and $CH_3OC_6H_4COOC_6H_4CH_2OH$ (II).

Compounds (I) were synthesized according to the following reaction:

$$RC_6H_4COCl + HOC_6H_4OH \xrightarrow[\text{pyridine}]{-10^\circ C} RC_6H_4COOC_6H_4OH \tag{1}$$

In a typical experiment, *p*-substituted benzoyl chloride (10 mmol) was added dropwise to a solution of hydroquinone (30 mmol) in 100 ml of dry pyridine at −10°C. The mixture was stirred at −10°C for 15 min and then warmed up to room temperature. After the complete disappearance of the acid chloride checked by thin-layer chromatography, the mixture was poured into 1 litre of water. The formation of the monoester was favoured by using a three-fold excess of hydroquinone. It was recrystallized from 85% ethanol (yield: 70%). The melting points of the compounds (I) are in good agreement with the literature[8]. (The compound with R=CN is new: m.p. = 185°C.)

The synthesis of 4(4′-methoxybenzoyloxy)benzyl

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alcohol (II) was performed in two steps:

$$CH_3OC_6H_4COCl + HOC_6H_4CHO \xrightarrow[\text{dry pyridine}]{0°C} CH_3OC_6H_4COOC_6H_4CHO \quad (2)$$

$$CH_3OC_6H_4COOC_6H_4CHO \xrightarrow[NaOH]{NaBH_4} CH_3OC_6H_4COOC_6H_4CH_2OH \quad (3)$$

A solution of 4-hydroxybenzaldehyde (10 mmol) and *p*-anisoyl chloride (20 mmol) in dry pyridine (100 ml) was stirred at 0°C for 3 h. The mixture was then neutralized with diluted HCl, and the product was filtered and washed with water (yield of crude product = 60%). This aldehyde (10 mmol) was dissolved in 100 ml of ethanol at 0°C. An aqueous mixture (20 ml) of NaOH (20 mmol) and $NaBH_4$ (40 mmol) was slowly added. At the end of the reaction, the medium was neutralized with an aqueous HCl solution (1 M). The alcohol (II) was filtered, washed with water and recrystallized from a 30/70 mixture of water/ethanol (yield = 65%, m.p. = 88°C).

The allyl and vinyl carbonates were prepared by reaction of allyl or vinyl chloroformate with hydroxy compounds (I and II) under phase transfer catalysis conditions, according to a similar procedure described for the chemical modification of poly(vinyl chloroformate)[9]. Typically, allyl chloroformate (50 mmol) was added dropwise to a mixture of the hydroxy compound (12 mmol) and tetrabutylammonium hydrogen sulphate (1.2 mmol) in 20 ml of methylene chloride. The addition was carried out at −30°C under nitrogen. An aqueous NaOH solution (3 M, 12 ml) was then added sufficiently slowly to maintain the temperature below −20°C. At the end of the reaction, the mixture was washed several times with water, and the solvent was evaporated under reduced pressure. The product was recrystallized from 95% ethanol (yields = 70–80%). All these compounds were purified by chromatography on silica gel with chloroform or a 70/30 cyclohexane–ethyl acetate mixture as the eluent. Melting points and n.m.r. data for vinyl and allyl carbonates are given in *Tables 1* and *2*.

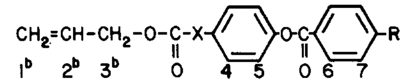
Synthesis of side-chain polysiloxanes

Polymethylhydrosiloxane (PMHS) and methylhydrodimethylsiloxane copolymer (Petrarch Systems) were purified by several dissolutions in toluene and precipitations in methanol[10]. A value of $\bar{M}_n$ determined by vapour pressure osmometry was found to be equal to 3600 and is in good agreement with that measured by ^1H n.m.r. The molar content of SiH groups was determined by i.r. for the copolymer (PS 123 = 31%) and its molecular weight, $\bar{M}_n$, is equal to 2500 (measured by vapour pressure osmometry).

In order to avoid any hydrolysis of the carbonate bond, hydrosilylation of allyl carbonates was catalysed by a divinyltetramethyldisiloxane platinum complex (Petrarch Systems). Hexachloroplatinic acid frequently used for this type of reaction generates HCl after reduction during the hydrosilylation process[11], and thus is not convenient in the present case. Several attempts at hydrosilylation of vinyl carbonates failed, and thus we focused our attention on the allyl derivatives.

In a typical experiment, allyl carbonate (5 mmol) in dry toluene (50 ml) was stirred with polymethylhydrosiloxane (4.5 milliequivalents of SiH) at 50°C under nitrogen, then the catalyst was added (10 μl of a 3.5% solution in xylene ≃ 3.5×10^{-4} mmol). The reaction was followed by monitoring the decreases of the SiH i.r. band at 2165 cm^{-1} and/or of the ^1H resonance at 4.8 ppm of the SiH. The polymer was recovered after precipitation in methanol and purified by several dissolutions in methylene chloride and precipitations in methanol. A further purification was done by chromatography on a silica gel column using a 30/70 mixture of chloroform/cyclohexane as the eluent. The product was then dried under high vacuum.

Table 1 Chemical shifts (δ, ppm) of the protons of allyl carbonates (200 MHz, $CDCl_3$, 25°C, reference: $CHCl_3$)[a]



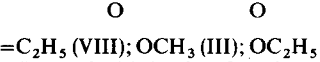
with X=O and R=$\underset{8}{OCH_3}$ (III); $\underset{9}{OCH_2}\underset{10}{CH_3}$ (IV); $\underset{11}{OCH_2}\underset{12}{CH_2}\underset{13}{(CH_2)_3}\underset{14}{CH_3}$ (V); CN (VI) and with X=$\underset{15}{OCH_2}$ and R=$\underset{8}{OCH_3}$ (VII)

Proton numbers	Compounds III	IV	V	VI	VII
4	7.2 (d)	7.2 (d)	7.0 (d)	7.2 (m)	7.2 (m)
5	7.2 (d)	7.2 (d)	7.0 (d)	7.2 (d)	7.5 (d)
6	8.1 (d)	8.1 (d)	8.1 (d)	8.1 (d)	8.1 (d)
7	6.9 (d)	7.0 (d)	6.9 (d)	7.0 (d)	7.0 (d)
8	3.9 (s)	–	–	–	3.9 (s)
9	–	4.1 (q)	–	–	–
10	–	1.5 (t)	–	–	–
11	–	–	4.0 (t)	–	–
12	–	–	1.9 (qi)	–	–
13	–	–	1.2–1.5 (m)	–	–
14	–	–	0.9 (t)	–	–
15	–	–	–	–	5.2 (s)

[a] With (s), singlet; (d), doublet; (t), triplet; (q), quadruplet; (qi), quintuplet; (m), multiplet

[b] A_2MNX system corresponding to the allyl group appears in all compounds at 4.8, 5.4 and 6.0 ppm

Table 2 Transition temperatures (°C) and enthalpies of transition at the clearing point (kJ mol^{-1}) for allyl and vinyl carbonates



$$R{-}C_6H_4{-}\underset{\underset{O}{\|}}{C}{-}O{-}C_6H_4{-}X{-}\underset{\underset{O}{\|}}{C}{-}O{-}Z$$

with X=O and R=C_2H_5 (VIII); OCH_3 (III); OC_2H_5 (IV); OC_4H_9 (IX); OC_6H_{13} (V); CN (VI) and with X=CH_2O and R=OCH_3 (VII)

Compounds	Z = allyl T_m	T_c	$\Delta H(T_c)$	Z = vinyl T_m	T_c	$\Delta H(T_c)$
VIII	66	[58][a]	0.41	86	92	0.66
III	93	[90][a]	0.42	110	132	0.41
IV	103	113	0.89	141	153	1.09
IX	88	110	–	–	–	–
V	81	89	0.84	69	129	1.07
VI	113	126	0.71	139	180	1.12
VII	59	–	–	75	–	–

[a] Metastable mesomorphic phase available only by supercooling

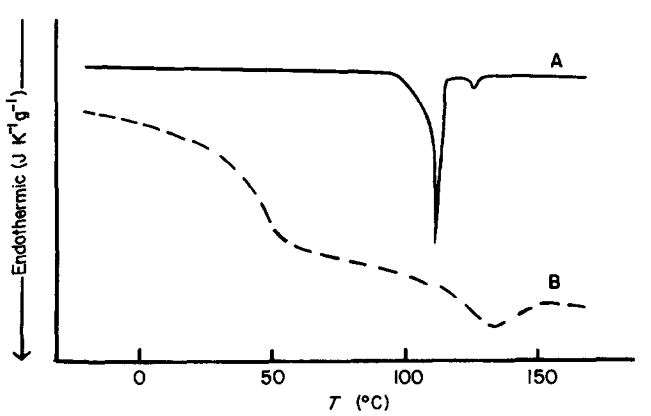


Figure 1 D.s.c. curves for low molar mass carbonate (VI) (A) and the corresponding modified polysiloxane (XII) (B)

Physicochemical characterizations

Allyl and vinyl carbonates were characterized by elemental analysis. The new compounds were examined by i.r. spectroscopy with a Perkin–Elmer 577 apparatus. The ^1H and ^{13}C n.m.r. spectra were recorded at 200 and 50.3 MHz, respectively, in $CDCl_3$ at 25°C, with a AM 200 SY Brucker apparatus. Molecular weights of PMHS and of methylhydrodimethylsiloxane copolymer were measured by vapour pressure osmometry in toluene at 45°C with 1,2-biphenyl-1,2-ethanedione standard using a Knauer apparatus. Those of the modified polymers were determined by g.p.c. in toluene at 25°C on a Waters apparatus equipped for refractive index detection using a polystyrene calibration curve. D.s.c. curves were recorded on a Perkin–Elmer d.s.c. 2 and on a du Pont 1090 apparatus. Glass transition temperatures were taken as the intersection of the extrapolation of the baseline with the extrapolation of the inflexion on curves obtained with a heating rate of 20°C min^{-1}. The structure of the mesophases was examined with a polarizing microscope (Leitz–Diavert) equipped with a hot stage (Mettler FP 52).

RESULTS AND DISCUSSION

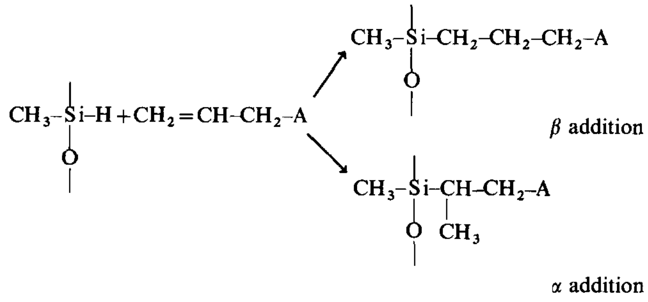
Allyl and vinyl carbonates

The ^1H n.m.r. chemical shifts of allyl carbonates are reported in *Table 1*. The carbonyl bands observed in the i.r. spectra of these compounds are located at 1740 cm^{-1} for the ester group, at 1765 cm^{-1} for the carbonate group close to the phenyl ring, and at 1730 cm^{-1} for the carbonate function in compound (VII).

Allyl and vinyl carbonates have been analysed by d.s.c. and by polarizing microscopy. The d.s.c. curve for the allyl carbonate (VI) is shown in *Figure 1* and typical mesomorphic textures were observed by microscopy. Upon cooling from the isotropic state, the nematic phase begins to separate in the form of typical droplets which after further cooling, grow, coalesce and reorganize their shape into a 'Schlieren' texture. The mesophases of all the other compounds have been identified as nematic, and the temperatures are given in *Table 2*. The temperatures follow the trends generally observed in a mesomorphic series. For a given rigid core, the thermal stability of the mesophase increases from the alkoxy (III, IV, IX, V) to the cyano (VI) substituted esters and also increases with the length of the alkoxy substituent up to four carbons (III–IX). The effect of the terminal cyano group (VI) is even stronger and is probably due to polar effects. Substituting the allyl group by a shorter and more rigid vinyl group leads to an increase in the transition temperatures together with an increase in the thermal stability of the mesophases. It should be noticed that the insertion of a methylene group between the carbonate bond and the aromatic ring (VII) leads to the absence of a mesophase. The enthalpies of transition $\Delta H(T_c)$ at the clearing point (isotropic to nematic) are listed in *Table 2*.

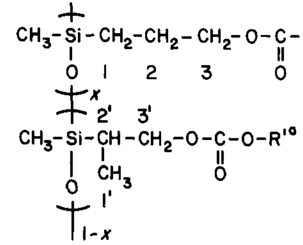
Side-chain polysiloxanes

All the polymers and copolymers modified by the allyl carbonates have been characterized by ^1H and ^{13}C n.m.r. The absence of the ^1H resonance at 4.8 ppm which corresponds to the SiH group shows that the chemical modification is complete within the experimental accuracy. The chemical shifts of the spacer are reported in *Table 3*. Two types of addition can occur during the hydrosilylation process according to the following scheme:



Hydrosilylation of most allyloxy derivatives by PMHS leads generally to quantitative β addition products[10,12]. However, in the case of carboallyloxy derivatives a ratio of β/α addition of about 80/20 has been found by ^1H n.m.r. analysis (*Table 3*).

Table 3 Chemical shifts (δ, ppm) of the protons and the carbons of the spacer of modified polysiloxanes X and XII (200 and 50.3 MHz, $CDCl_3$, 25°C, reference: $CHCl_3$)



with R′ being the mesogenic moieties of allylcarbonates III and VI described in *Tables 1* and *2*

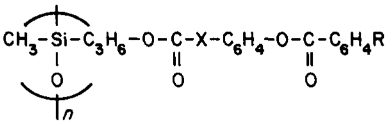
Protons	1	2	3	1′	2′	3′
δ (ppm)	0.6	1.7	4.1	1.2	0.6	4.1
Integrations	1.73	1.60	2.00	0.53	1.73	2.00

Carbons	1	2	3	1′	2′	3′
δ (ppm)	18.8	24.0	67.0[b] or 66.3	43.3	38.0	66.3[b] or 67.0

[a] The ^1H and ^{13}C chemical shifts of R′ are the same for the low molar mass compounds and for the corresponding modified polysiloxanes

[b] It was not possible to make a precise attribution for carbons 3 and 3′

Table 4 Molecular weights of polysiloxanes modified by allylcarbonates



Polymers	X	R	$\bar{M}_n$[a]	$\bar{M}_n$ (g.p.c.)	$\bar{M}_w$ (g.p.c.)	$\bar{M}_w/\bar{M}_n$
X	O	OCH_3	21 000	30 000	54 000	1.8
XI	O	OC_2H_5	22 000	32 000	60 000	1.9
XIII	O	OC_6H_{13}	25 000	36 000	72 000	2.0
XII	O	CN	21 000	35 000	66 000	1.9
XV	OCH_2	OCH_3	22 000	33 000	68 000	2.0

[a] Calculated from *n* of the polymethylhydrosiloxane determined by vapour pressure osmometry ($n = 57$, $\bar{M}_n = 3600$)

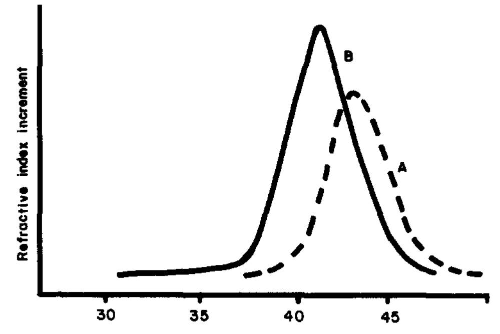


Figure 2 Gel permeation chromatograms of polymethylhydrosiloxane (A) and of the modified polysiloxane (XIII) (B)

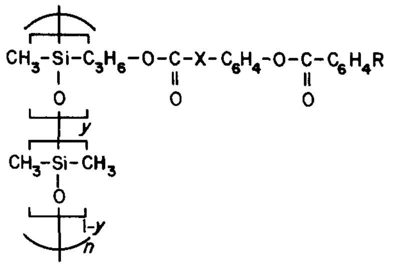
The molecular weights of polysiloxanes modified by allylcarbonates are listed in *Table 4*. The g.p.c. diagrams of PMHS and of the modified polysiloxane XIII are shown in *Figure 2*. An expected increase of the molecular weight of the modified polymer is observed.

The results of the d.s.c. analysis of these polymers are shown in *Table 5*. A typical d.s.c. curve (polymer XII) is shown in *Figure 1* together with that of the corresponding allyl compound (VI). All the polymers are amorphous and an increase in T_g is observed on increasing the proportion of the substituent as expected. The values of T_g for polydimethylsiloxane (PDMS), a copolymer containing 69% of dimethylsiloxane units (XVI) and the totally modified polymer (XIII) are −120, −40 and 6°C, respectively. The bulky mesogenic groups cause a severe hindrance to the motions of the main chain. It can be noticed that T_g does not vary much with the nature of the substituent for the homopolymers though a slight increase is observed with the CN terminal group (XII).

As observed for the allyl and vinyl carbonates (VII) (*Table 2*), the insertion of a methylene group between the carbonate bond and the aromatic ring destroys the mesophase for the corresponding modified polymer (XV). All the other polymers are mesomorphic and show only one type of transition (*Figure 1*) which is reproducible after several heatings and coolings. An increase in the clearing temperature, T_c, is noticed on increasing the length and the polarity of the terminal substituent on the mesogenic group (X→XIII) as already observed[6].

The T_c of a copolymer (XIV) prepared by cohydrosilylation of a mixture of two allyl carbonates (IV and V) differing by the length of the tail (in a molar ratio [IV]/[V] = 1.5) lies between the T_c values of the two homopolymers (XI and XIII). A copolymer containing 69% of dimethylsiloxane units and 31% of mesogenic groups (XVI) randomly distributed along the chain is still mesomorphic and exhibits a T_c slightly lower than that of the homopolymer (XIII). Ringsdorf *et al.*[13] examined the influence of the number of dimethylsiloxane units in the main chain and the number of methylene groups, *n*, as the spacer in the side chain on the phase transitions. They found that for $n = 5$ (which corresponds roughly to the length of our spacer) the mesophase still exists at

Table 5 Transition temperatures (°C) for polysiloxanes modified by allylcarbonates



Polymers	*y*	X	R	T_g	T_c
X	1	O	OCH_3	14	75
XI	1	O	OC_2H_5	14	106
XIII	1	O	OC_6H_{13}	6	119
XII	1	O	CN	39	133
XIV	1	O	OC_2H_5/OC_6H_{13}[a]	13	108
XV	1	OCH_2	OCH_3	9	–
XVI	0.31	O	OC_6H_{13}	−40	114

[a] Obtained by cohydrosilylation of a mixture of IV and V ([IV]/[V] = 1.5)

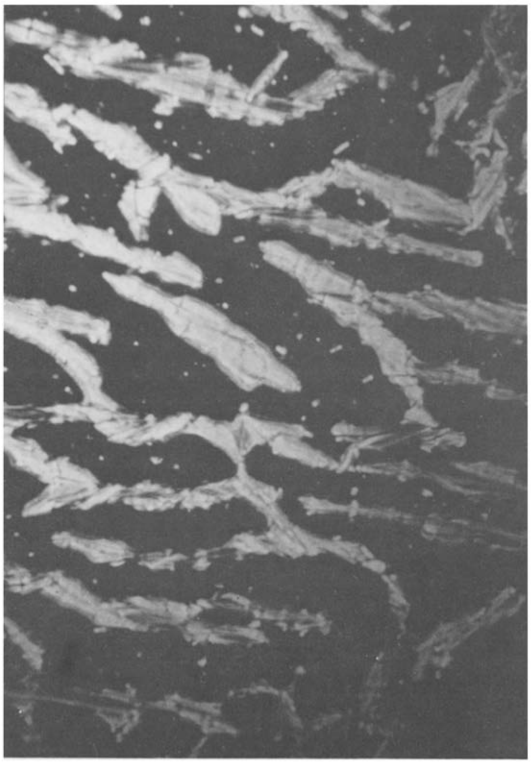


Figure 3 Photomicrograph of the polysiloxane (XII) modified by the allyl carbonate (VI) upon cooling from the isotropic state: focal conic texture (crossed polarizers)

17 mol% of mesogenic units whereas it disappears at higher 'dilution'.

Finally, Mauzac *et al.*[6] reported T_c values for side-chain polysiloxanes having the same mesogenic moieties as polymers X–XIII which are linked to the backbone through five methylene units and an ether group, instead of three methylene units and a carbonate function in our studies. The T_c values are around 50°C higher than our values whereas the T_g values are roughly the same. Therefore the domains of existence of the mesophases depend on the nature of the linkages in the spacer.

The mesophases have been examined by polarizing microscopy. A smectic phase has been identified in the case of polymer XII as shown in *Figure 3*. On cooling from the isotropic state, the smectic phase begins to separate in the form of typical bâtonnets which after further cooling grow, coalesce and reorganize into a focal conic texture. The detailed X-ray structural analysis of these polymers will be published separately.

CONCLUSION

In conclusion, a series of new allyl and vinyl carbonates has been prepared which exhibit nematic phases. After the binding of these mesogenic compounds onto a polysiloxane backbone, the stability range of the mesophases is enlarged (*Tables 2* and *5*) as already observed[4,5]. Further work is in progress concerning the study of the influence of a carbonate bond in the spacer upon the physical properties of this new class of side-chain liquid crystalline polymers.

ACKNOWLEDGEMENT

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