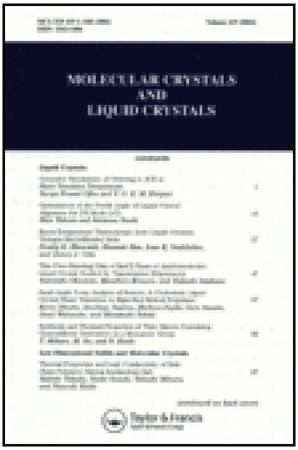

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SYNTHESIS AND PROPERTIES OF NEW LIQUID CRYSTALLINE SIDE-CHAIN POLYSILOXANES

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Abstract. The synthesis of new mesomorphic side-chain polymethylsiloxanes with spacers derived from ω-alkenoic acids is described.These liquid crystalline polymers exhibit nematic and(or) smectic A and(or) smectic C phases, depending of spacer and terminal tail lengths.

INTRODUCTION

Thermotropic liquid crystalline polymers with mesogenic side-groups have been the subject of much research in recent years[1,2].Such materials which combine the properties of thermotropic liquid crystals and polymers are of interest not only from an academic point of view but also because of possible applications in electrooptical devices[3,4], nonlinear optics[5,6] and so on.

However, while several thousands of low molecular liquid crystals have been described in the litterature[7] which could be considered as potential side-groups for the liquid crystalline side-chain polymers, only a few kinds of mesomorphic polymers have been synthesized and characterized so far.

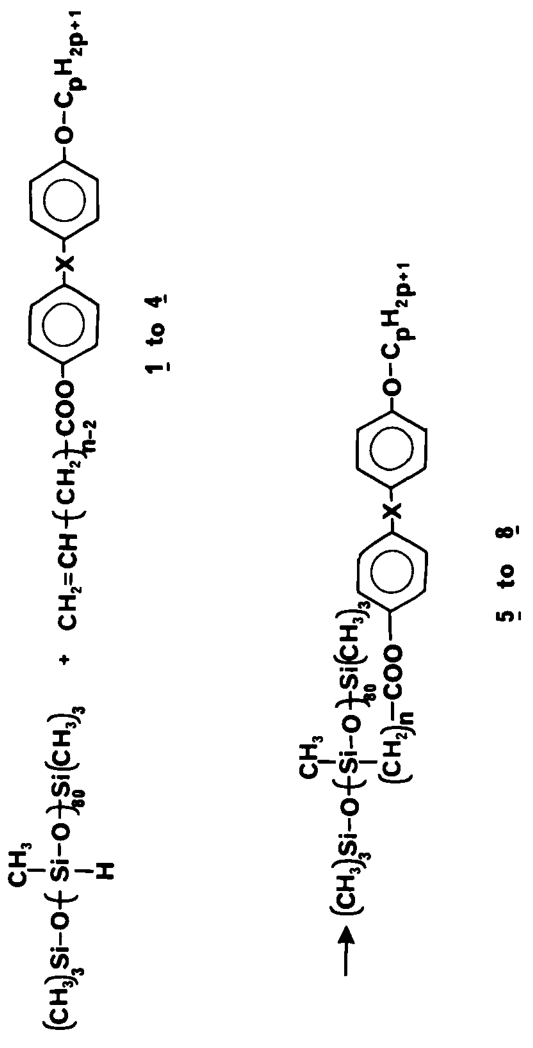
Thus, there is a need for new series of liquid crystalline side-chain polymers in order to diversify the structures of the compounds available. We present in this work the synthesis and the phase behaviour of a new series of liquid crystalline polymers with a polymethylsiloxane backbone.

RESULTS AND DISCUSSION

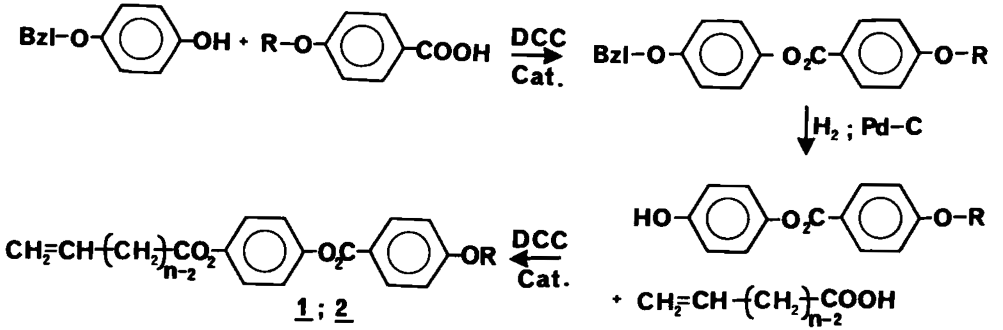
Liquid crystalline polymethylsiloxanes (5 to 8) are prepared by polyhydrosilylation reactions of poly(hydrogenmethylsiloxane) with mesogenic monomers (1 to 4) containing a terminal vinyl group in the presence of a platinum catalyst[8-13](Scheme 1).

Mesogenic monomers, 4-(ω-alkenoyloxy)phenyl 4-alkyloxybenzoates (1 and 2) and 4-alkyloxyphenyl 4-(ω-alkenoyloxy)benzoates (3 and 4), are prepared by two distincts synthetic ways described in Schemes 2 and 3 respectively.

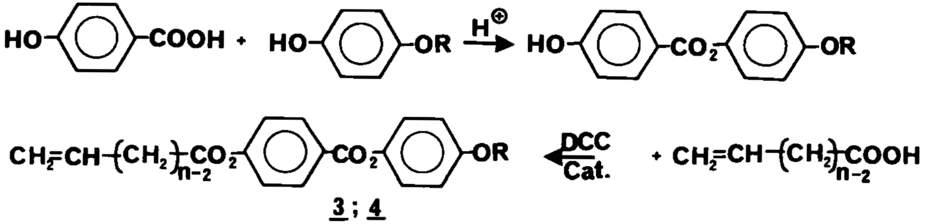
Of the wide range of platinum based catalysts able to effect hydrosilylation[14,15], we have selectioned the platinum complexe proposed by



Scheme 1



Scheme 2



Scheme 3

Apfel and coworkers[10]: dicyclopentadienyl platinum(II) chloride. With this active catalyst, liquid crystalline polysiloxanes were obtained as white (or cream-like) polymers and no crosslinking side reaction or "aging" of the catalyst solution[12] were detected.

Liquid crystalline polysiloxanes were obtained by heating(80°C) under argon for 48h a benzene solution of poly(hydrogenmethylsiloxane) of commercial source, a mesogenic monomer and a known amount of platinum catalyst. The mesomorphic polysiloxanes were isolated from benzene solutions by precipitation with methanol as non-solvent (see Experimental part).

Completion of the alkylation was monitored by IR spectroscopy (disappearance of the Si-H absorption band at 2140 cm^{-1}) and confirmed by elemental analysis.

The melting and transition points for the mesomorphic polysiloxanes are listed in Tables 1 and 2. The phase behaviour was studied by polarization microscopy and DSC measurements.

Identification of the mesophases was done by examination of the textures[16] exhibited by thin samples sandwiched between two glass slides.

From the results reported in Tables 1 and 2, the following remarks can be drown: 1.The mesomorphism of polysiloxanes 5-8 is strongly influenced by the chemical structure of the central core: reversing the sense of the ester link between the two phenyl rings result in a change in the mesomorphism from mainly a smectic A phase (polymer 5) to mainly a nematic phase (polymer 7). (This behaviour is also found when comparing polysiloxanes series described by Finkelmann[1] with the one synthesized by Mauzac and coworkers[11] but might not be generalized (see for example ref.17)). 2.Lengthening of the spacer promote the apparition of a smectic C phase in both series of polymers (6 and 8) as previously found in other polysiloxane series[11]. 3.Purely amorphous side-chain polymers are obtained only for two compounds (5a and 7d), the others being mainly crystalline.

Table 1. Transition temperatures for mesomorphic polysiloxanes (5) and (6).

Polymer	n	p	Phase Transitions[a]
5a	4	1	g 42 SA 124 N 128 I
5b	4	2	K 72 SA 136 I
5c	4	3	K 62 SA 159 I
5d	4	4	K 97 SA 176 I
5e	4	5	K 82 SA 127 I
5f	4	6	K 112 SA 173 I
5g	4	7	K 129 SA 174 I
5h	4	8	K 130 SA 165 I
6a	10	5	K 82 SC 103 SA 125 I
6b	10	6	K 79 SC 95.5 SA 164 I
6c	10	7	K 72 SC 109 SA 167 I
6d	10	8	K 73 SC 94 SA 169 I

[a]) T in C; g=glass;SA=smecticA;SC=smecticC;N=nematic;I=isotropic.

Table 2. Transition temperatures for mesomorphic polysiloxanes (7) and (8).

Polymer	n	p	Phase transitions[a]
7a	4	1	K 75 N 125 I
7b	4	2	K 98 N 141 I
7c	4	3	K 78 N 122 I
7d	4	4	g 50 SC 115 N 127 I
8a	10	1	K 92 SC 127 N 140 I
8b	10	2	K 101 SC 142 N 157 I
8c	10	3	K 92 SC 142 N 155 I
8d	10	4	K 82 SC 151 I

[a]) see note [a]) in Table 1.

CONCLUSION

The synthesis of new series of liquid crystalline polysiloxanes with spacers derived from ω-alkenoïc acids, allowed us to find new materials with nematic and(or) smectic A and (or) smectic C depending of the spacer and terminal tail lengths. The existence of a smectic C phase in the polysiloxanes with relatively long spacers give us the opportunity to prepare new ferroelectric liquid crystalline polysiloxanes by replacing the non-chiral terminal tail with a chiral one. Such polymers might possibly be employed in differents forms of applications.

Also, a copolymer prepared with 50% in mole of monomer (1,n=1) and 50% in mole of monomer (3,n=1) exhibit a nematic phase between 35 and 131°C and might be useful as host for nonlinear optic experiments.

Further works are in progress on these subjects and results will be forthcoming.

EXPERIMENTAL SECTION

Thermal properties of the compounds were studied by optical microscopy using a polarizing microscope (Leitz Ortholux Pol BK) fitted with a Mettler FP 82 heating stage and FP 80 control unit. They were checked by DSC (Mettler FP 85 TA cell and FP 80 control unit).

Infrared spectra were determined with a Shimadzu IR-408 instrument.

Materials. The poly(hydrogenmethylsiloxane) used in the preparation of mesomorphic polymers was purchased commercially (Petrarch Systems; MW=4500-5000) and was used as received. The side chain alkenes (1 to 4) used in this study were prepared by standard methods adapted from literature[18-20]. The catalyst used for all grafting reactions, dicyclopentadienyl platinum(II) chloride, was synthesized according to[10] and was used as a solution in dichloromethane ($1 mg.cm^{-3}$). Other compounds and solvents were from commercial sources.

Mesomorphic polysiloxane(Polymer 7a). Typical procedure:Into a 25ml tree necked round-bottomed flask equipped with a reflux condenser (fitted out with a bubbler (to close off the reaction vessel from the atmosphere)), two rubber septa and a stir bar were placed 0.1g ($1.66x10^{-3}$mol.) of poly(hydrogenmethylsiloxane) and 0.65g ($2x10^{-3}$mol.) of 4-methoxyphe-enyl 4-(4-pentenoyloxy)benzoate (3;m=1) dissolved in 15ml of dry benzene.

The flask was flushed with argon for 10mn, then plunged in an oil bath preheated to 80°C. The catalyst solution (200μl;$5x10^{-7}$mol. of Pt complexe) was then injected with a syringue through the septa and the resulting reaction mixture was stirred and heated at 80° C for 48h.. The solution was then cooled and poured into 50ml of methanol. The precipitate was collected by filtration. The polymer was dissolved in chloroform (2ml), following which it was reprecipitated with methanol and collected once more by filtration. The polymer was dried in a vacuum oven at 50 °C for 24h.(Yield:0.5g).

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