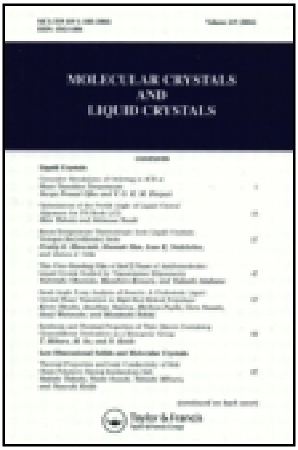

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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Synthesis and Properties of Some Liquid Crystalline Polysiloxanes

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SYNTHESIS AND PROPERTIES OF SOME LIQUID CRYSTALLINE POLYSILOXANES

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Abstract Series of side chain polymethylsiloxanes are synthesized by systematically varying the spacer length, the inter-ring linkage and the free tail in the mesogenic moieties. The mesomorphic properties are studied by optical microscopy, differential scanning calorimetry and X-ray scattering. General properties are established.

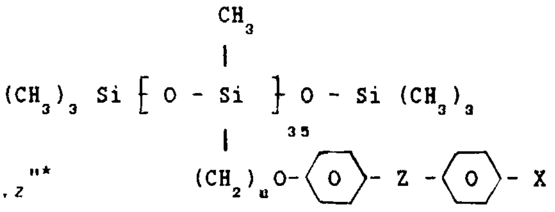
INTRODUCTION

A large number of polymers containing mesogenic side chains and polysiloxane backbone have been prepared and characterized [1-7]. In a previous paper[8] we report the synthesis of polymethylsiloxanes substituted with p-(polymethylen)oxy-phenyl p-substituted benzoates. In the side group, the length of the flexible spacer, the length and the polarity of the terminal group are systematically varied. Aimed toward a better understanding of the role of the chemical structure on the mesomorphic properties we present in this work the synthesis and characterization of polymers including a range of new central linkages and terminal groups*.

*Some compounds, previously studied by other authors[1,2] are synthesized again to be compared with our own products.

MATERIALS

The general formula of the studied polymers is :



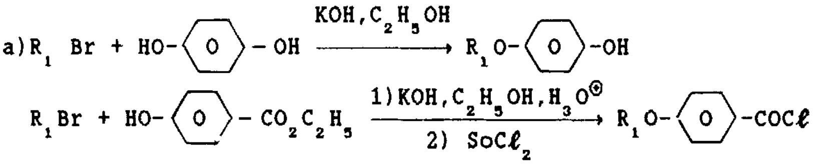
"$P_{n,X,Z}$"*

n = 3-11, Z = OCO, COO, OCH_2, X = H, CH_3, OCH_3, NO_2, CN

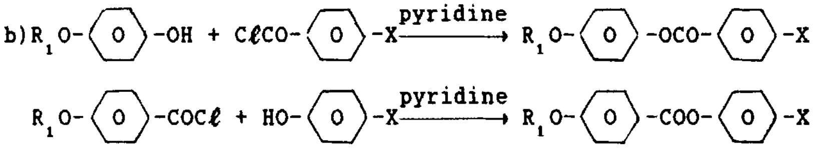
*In previous papers[8-10] the polymers are labelled "$P_{n,CN}$" or "$P_{n,m}$" corresponding to unspecified Z = OCO and X = CN or OC_mH_{2m+1}.

The mesogenic substituents are obtained by several classical steps :

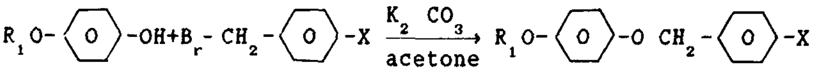
1) For benzoate series[11-13]



where R_1 : $CH_2 = CH-(CH_2)_{n-2}$



2) For benzyloxyphenyl series :



The commercial products are obtained from Aldrich and used without further purification.

Most of the synthesized compounds are purified on a silica chromatographic column, using various (ether/hexane) mixtures as eluent.

The vinyl moiety is attached to the polymer backbone (from Merck) following a standard hydrosilylation reaction as previously described [8]. The extent of completion is assessed by ^{1}H-NMR.

CHARACTERIZATION OF THE MESOPHASES

The mesogenic behaviour of the polymers was investigated by a Leitz-Dravert polarizing microscope equipped with a Mettler FP 52 hot stage. X-ray patterns for powder samples were obtained by a high temperature Guinier Camera (Hüber) using the CoKα_1 radiation. Cooling from the isotropic state the samples of polymers were analyzed throughout the stability range of their mesophases.

The glass transition and/or the melting temperatures were determined by DSC (Dupont 990); calorimetric data at the clearing points were also reported.

TABLE I Phase transition temperatures for the vinyl derivatives and the corresponding polymers

n	X	Z	Phase transition temperature °C											Polymer ΔH(Tcℓ' Jg^{-1}	Polymer index
			Vinyl Moiety					Polymer							
			K	S_C	S_A	N	I	T_g	T_m	S_C	S_A	N	I		
3	CN	OCO	.104			.[92.5]	.	36	100		.176		.	4.6	P_3,CN.OCO
	OCH$_3$		.105.5			.[75.5]	.	15	-		.123		.	2.0	P_3.OCH$_3$.OCO
	CH$_3$		. 72.5			.[42]	.	18	65				.		P_3.CH$_3$.OCO
	H		. 66				.	15	-				.		P_3.H.OCO
4	CN	OCO	. 88.9			.[61.3]	.	40	78		.174		.	5.0	P_4.CN.OCO
		COO	. 86.8			.[57.3]	.	15	-		.139		.	2.6	P_4.CN.COO
		OCH$_2$	. 69				.	10	78				.		P_4.CN.OCH$_2$
	NO$_2$	OCO	. 68.5				.	20	-		.165		.	2.7	P_4.NO$_2$,OCO
		OCH$_2$	. 48				.	-5	15				.		P_4.NO$_2$.OCH$_2$
	OCH$_3$	OCO	. 91.7			.[51.2]	.	7	-		. 74	.104	.	1.6	P_4.OCH$_3$,OCO
		COO	. 78			.[48.5]	.	15	-			. 95	.	2.4	P_4.OCH$_3$.COO
	CH$_3$	OCO	. 58.3				.	4	-			. 59	.	2.0	P_4.CH$_3$.OCO
5	CN	OCO	.103.7			.[91.8]	.	24	104		.184		.	5.6	P_5.CN,OCO
		OCH$_2$	. 54.5				.	5	106				.		P_5.CN.OCH$_2$
	NO$_2$	OCH$_2$	. 75				.	0	75				.		P_5.NO$_2$.OCH$_2$
	OCH$_3$	OCO	. 56			73.6	.	4	71		.122		.	3.0	P_5.OCH$_3$.OCO
	CH$_3$	OCO	. 46.5			.[40.2]	.	6	109				.		P_5.CH$_3$.OCO
	H	OCO	. 40				.	2	-				.		P_5.H.OCO

n	X	Z	Phase transition temperature °C											Polymer ΔH(Tcℓ) Jg^{-1}	Polymer index
			Vinyl Moiety					Polymer							
			K	S_C	S_A	N	I	T_g	T_m	S_C	S_A	N	I		
6	CN	OCO	. 81.8			.[76.5]	.	27	82		.190		.	6.0	P_6.CN.OCO
		COO	. 59.3			.[62.3]	.	16	44		.170		.	5.5	P_6.CN.COO
		OCH_2	. 41				.	0	45		. 86		.	8.0	P_6.CN.OCH_2
	NO_2	OCH_2	. 64				.	-8	-		. 73		.	4.8	P_6.NO_2.OCH_2
	OCH_3	OCO	. 54.9			. 56.4	.	-4	-		.110		.	3.4	P_6.OCH_3.OCO
		COO	. 62.7			.[58.4]	.	5	-	. 40		.105	.	1.7	P_6.OCH_3.COO
	CH_3	OCO	. 67.8			.[29]	.	0	58			. 67	.	1.5	P_6.CH_3.OCO
8	CN	OCO	. 72		.[65.6]	. 80.4	.	25			.190		.	8.5	P_8.CN.OCO
		OCH_2	. 55.5				.	-	50		.102		.	10.0	P_8.CN.OCH_2
	NO_2	OCH_2	. 67				.	-14	-		. 92		.	6.0	P_8.NO_2.OCH_2
	OCH_3	OCO	. 51			. 63	.	-5	45		.127		.	4.5	P_8.OCH_3.OCO
	CH_3	OCO	. 37.5			. 40.3	.	0	68		. 73	. 83	.	2.0	P_8.CH_3.OCO
	H	OCO	. 44.5				.	0	61				.		P_8.H.OCO
10	CN	OCO	. 56		. 82.6	. 83	.	18	108		.195		.	7	P_{10}.CN.OCO
	OCH_3	OCO	. 60.8			. 65.6	.	-5	42		.133		.	5.5	P_{10}.OCH_3.OCO
11	CN	OCO	. 60.8	.[47]	. 88		.	17	82	.119	.201		.	9.2	P_{11}.CN.OCO
	OCH_3	OCO	. 66.4			. 69.9	.	24	56	. 60	.134		.	6.1	P_{11}.OCH_3.OCO
	CH_3	OCO	. 61.5			.[50]	.	-	74	. 85	. 99		.	5.0	P_{11}.CH_3.OCO

[ ] : monotropic transition

RESULTS AND DISCUSSION

The chemical constitution and the polymorphism are reported in the Table :

The coupling of mesogenic molecules to the polymer backbone always increases their clearing temperature (Tcℓ) and tends to form higher ordered phases. Despite the fact that the vinyl moieties are mostly nematogens, only few polymers keep this character and their common feature is to exhibit a smectic A phase. If a non mesogenic moiety is linked (for example samples with $Z = OCH_2$) mesogenic polymers can be obtained.

The polymers are generally semi-crystalline materials and relatively low glass transition temperature ($Tg \leqslant 40°C$) is observed. Both glass transition and melting (Tm) temperatures increase with the polarity of the X end.

We successively discuss the influence on the polymer mesogenic efficiency of each parameter (spacer n, terminal substituent X, linking unit Z in the core structure) keeping the other ones constant :

* As the spacer length (n) increases we notice regular trends in the liquid-crystal behavior :

  - All the transition temperatures increase reaching a limiting value and an usual even-odd effect is observed on Tcℓ and Tm.
  - The nematic tendency disappears and the smectic properties are found to become more marked. Similarly in the case of low molecular weight mesogens, the extension of an aliphatic chain

gives direct smectic-isotropic transitions.

- A smectic C phase may occur.

* There is a strong influence of X on the polymorphism :

  - Without terminal substituent (X = H) the compounds do not exhibit mesomorphic properties, as is commonly found with low molecular weight liquid crystal material.
  - X = OCH_3 and more easily X = CH_3 often induce nematic phases for even n homologues.
  - Incorporation of strongly polar ends (X =NO_2, CN) only leads to smectic phases. It generally promote high T_{I-S_A} values which are almost the same for both terminal groups.
  - In fact, the clearing point is connected with the polarity of X and gradually increases when X is successively CH_3, O CH_3, a strong polar group (NO_2, CN).

* The nature of the central linkage Z is also of great importance :

  - A flexible linkage (Z = O CH_2) makes the transition temperature to drop or removes the mesomorphous character.
  - Replacement of Z = OCO by Z = COO gives more frequently nematic phases and diminishes the thermal stability of the liquid crystalline phases. The variation of the polarity due to this modification of Z could explain this result[14].
  - In addition, we observe that the direction of the central dipoles plays a more important role

than the Z flexibility on the tendency to give a partial "bilayer" structure in the smectic phases of cyano-substituted polysiloxanes, as illustrated on the Figure 1 :

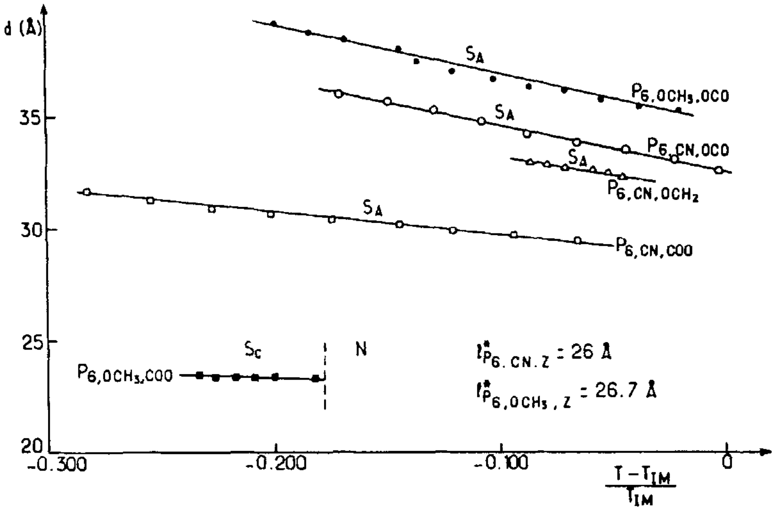


FIGURE 1. Variation of the layer spacing (d) with reduced temperature (T_{IM} : isotropic-mesophase transition temperature) for $P_{6,CN,Z}$ and $P_{6,OCH_3,Z}$ series.

ℓ^* : Molecular length of the side chain measured in the most extended conformation.

The central group partial "bilayer" smectic efficiency order is :

$$- OCO - > - OCH_2 - > - COO -$$

Such a consideration can be applied to polysiloxanes with a poorly polar terminal group OCH_3 in the pendant side chain : the replacement of Z = - OCO - by Z = - COO - leads to the loss of the bilayering arrangement. As a result, a monolayer S_C phase occurs with a small tilt angle (< 10°)[15] instead of a "partial bilayer" S_A phase [8].

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