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Liquid Crystals

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Ivan Cabrera^a; Helmut Ringsdorf^a; Martina Ebert^b; Joachim H. Wendorff^b

^a Institut für Organische Chemie, Universität Mainz, Mainz, F.R. Germany ^b Deutsches Kunststoff-Institut, Darmstadt, F.R. Germany

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Liquid crystal polymers from swallow-tailed mesogens

by IVAN CABRERA and HELMUT RINGSDORF

Institut für Organische Chemie, Universität Mainz,
Johann-Joachim-Becher-Weg 18-22, D-6500 Mainz, F.R. Germany

MARTINA EBERT and JOACHIM H. WENDORFF

Deutsches Kunststoff-Institut, Schloßgartenstrasse 6R, D-6100 Darmstadt,
F.R. Germany

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Swallow-tailed compounds containing an acetylenic unit have been synthesized. Only those compounds with a three ring structure exhibited liquid-crystalline phases. The platinum catalysed addition of these monomers to compounds containing Si-H groups was used to synthesize polymeric materials. Only those polymers with the tetramethyldisiloxane unit showed mesophases. The synthesis, characterization, and phase behaviour are described.

1. Introduction: molecular architecture of liquid crystals

A key issue in the development of advanced polymeric materials and a major question confronting materials scientists in general is how to obtain a more detailed understanding of the structure-property relationships in macromolecular systems. For this purpose, the molecular design of monomers and subsequent synthesis of differently built polymeric systems are very important. Indeed, by variation of the macromolecular architecture we can, on the one hand, determine how a particular property depends on the presence or absence of a chemical moiety, e.g. a change of the glass temperature (T_g) by variation of the chemical structure. On the other hand, sometimes the synthesis of novel chemical structures may permit the control of interesting processes, e.g. self-assembling of synthetic polymers during their formation [1] or may lead to materials with uncommon properties, e.g. biaxial nematic polymers [2].

In liquid crystal polymers the introduction of the spacer concept opened up the game of molecular design of these materials [3]. In the beginning, incorporation of rod-shaped mesogenic groups into macromolecules led to the already classical main chain and side chain liquid crystal polymers [4]. Later, the use of molecular discs led to macromolecules exhibiting discotic phases [5]. Further variations of the macromolecular architecture have included the different combinations of rod and disc shaped mesogens [6] as well as the combination of the structural principles of the two classical types of liquid crystal polymers, i.e. combined main chain/side group polymers [7]. Within this programme on molecular architecture of novel liquid-crystalline systems the incorporation of swallow-tailed mesogens into polymers was of interest.

Swallow-tailed mesogens are molecules with large branched substituents outside of the ring system [8–10]:



In contrast to the compounds which have lateral branches near to the centre of the molecule, they show broad liquid-crystalline phases [9, 10]. It was decided therefore to synthesize swallow-tailed mesogens with reactive end-groups at the two branches of the tail, use them as starting materials for the preparation of polymers, and determine whether such macromolecules exhibit mesophases.

2. Experimental

2.1. Materials

All of the solvents were dried and distilled before use. Malonic acid dichloride, 2-propin-1-ol, 4-hydroxybenzaldehyde (all from Merck); 1,1,3,3-tetramethyldisiloxane and *p*-bis(dimethylsilyl) benzene (both from Petrarch Systems) and hydride terminated polydimethylsiloxane (Wacker Chemie) were all used without further purification.

2.2. Monomer synthesis

The general reaction scheme for the preparation of the compounds is given in figure 1. The di-propin-malonate **1** was prepared by reacting malonic acid dichloride with the alcohol in dry THF. Triethylamine was used as a base and the compound was isolated by vacuum distillation (see table 1). Di-propin-4-hydroxybenzylidene malonate (**2**) was prepared by the piperidine acetate catalysed Knoevenagel condensation [11] of **1** with 4-hydroxybenzaldehyde in a toluene/THF mixture. The water was separated by passing the condensed solvent through a calcium hydride trap. The material was purified by flash chromatography with toluene-ethylacetate (3:1) as eluent. The monomeric swallow-tailed mesogens **3**, with the exception of **3a**, which was prepared from the acid chloride, were all synthesized using dicyclohexylcarbodiimide. The reactions were done in dry 1,2-dimethoxyethane and the materials were isolated by flash chromatography with toluene-ethylacetate (9:1) as eluent. The compounds were characterized by elemental analysis and ¹H NMR. The physical constants and yields are given in table 1.

Table 1. Properties of the low molecular weight compounds.

Compound	mp/°C/bp/°C	Yield/%
1	/106(0.2 mb)	37
2	101–103/	83
3a	71.6/	74
3b	97.4/	62
3c	74.7/	70
3d	101.3/	71

2.3. Polymer synthesis

The polymers were prepared from equimolar mixtures of the swallow-tailed monomers **3** and the Si-H containing compounds in the presence of dicyclopentadienyl-platinum(II) chloride. This catalyst was synthesized according to the procedure described in [12]. The components were dissolved in a minimum amount of dry and freshly distilled toluene. Into this and, under a constant stream of dry argon, a freshly prepared solution of the catalyst was added to give a ratio of Pt : alkyne of 1 : 10³. The sealed reaction vessel was kept for at least 3 days at 80°C. The reaction was monitored by the disappearance of the Si-H absorption at 2140 cm⁻¹. The polymers were isolated first by precipitation in methanol or methanol-aceto-nitrile mixtures and then by preparative gel permeation chromatography (GPC) using 10³-10⁴ Å columns (Polymer Laboratories) with CHCl₃ as eluent. The materials were dissolved in benzene, filtered through a millipore filter and freeze dried. After further drying under vacuum for at least 24 hours the yields ranged from 50 to 80 per cent. The polymers gave correct IR, ¹H NMR and elemental analyses. Typical molecular weights (*M_n*) are: **5b**, 10200; **5c**, 9000; **4b**, 7800.

2.4. Characterization methods

The ¹H NMR measurements were made with a Bruker FT-NMR spectrometer (Aspekt 2000). For the IR measurements a Nicolet FT-Spectrometer 5DXC was used. The differential scanning calorimeter measurement were performed with a Perkin-Elmer DSC-2C calorimeter; peak maxima were taken as the transition temperatures. The microscopic observations were made with a Leitz Ortholux Pol-BK II polarizing microscope equipped with a Mettler FB-52 hot stage. X-ray diffraction measurements were performed on oriented samples obtained by drawing a fibre from the melt. A flat camera combined with a heating cell and Cu-K_α radiation ($\lambda = 0.154$ nm) were used for this scattering studies. Analytical GPC (Waters 440 Chromatograph) in CHCl₃ with PL-Gel 10³-10⁴ Å columns (Polymer Laboratories) and narrow distribution polystyrene standards was used for the molecular weight determinations.

3. Results and discussion

The swallow-tailed monomeric compounds (**3**) synthesized are shown in figure 1. Only those compounds with a three-ring structure exhibit liquid-crystalline phases. The transition temperatures are listed in table 2. The nematic phases were assigned from their schlieren optical texture and high mobility when subjected to mechanical

Table 2. Phase transitions for the monomeric compounds.

Compound	Transitions temperatures/°C					
	Transition enthalpy/kJ mol ⁻¹					
3a			C	71.6	I	
				41		
3b	C	97.4	S _A	106.1	N	109.3 I
				1.04	0.25	
3c	C	74.7	S _A	98.9	N	113.1 I
				0.56	0.33	
3d			C	101.3	N	143.4 I
				0.57		

C = crystal; S_A = smectic A; I = isotropic.

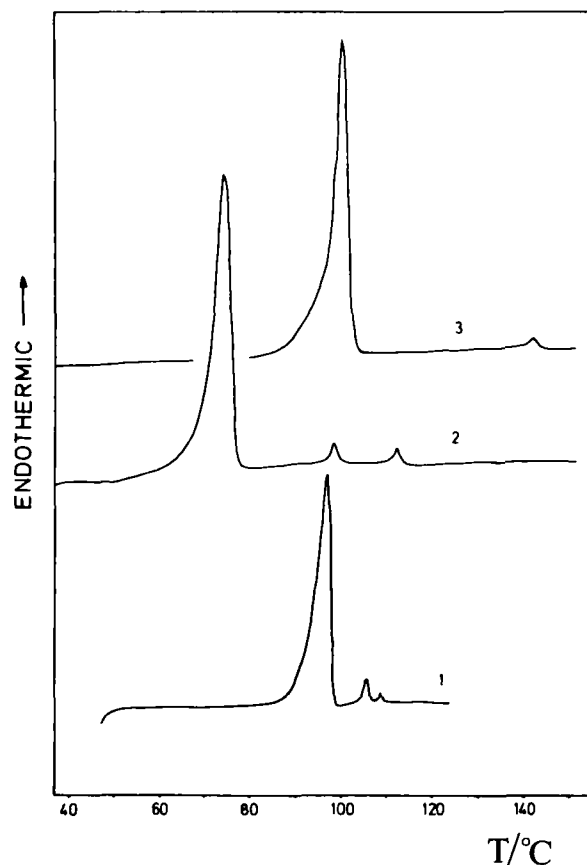


Figure 2. Heating curves for the mesogenic compounds **3**: **1**, **3b**, 2 K min^{-1} ; **2**, **3c**, 10 K min^{-1} ; **3**, **3d**, 10 K min^{-1} .

stress. The lower temperature phase gives regions of homeotropic and focal conic fan texture; it was, therefore, assigned as a smectic A phase. In the two ring compound (**3a**) the ratio of rigid core molecular length to swallow-tail breadth is, probably, not sufficient to give a significant molecular anisotropy and, therefore no mesophases are formed. In the three ring systems, those compounds with at least two phenyl rings form a smectic phase whereas the compound with the bicycloheyl moiety (**3d**) shows only a nematic phase. The DSC thermograms are given in figure 2.

The synthetic route chosen to incorporate these monomers into polymers is also shown in figure 1. In polymers, the formation of liquid crystal phases usually requires a certain degree of decoupling of the mesogenic groups from the backbone. Such decoupling should be of particular importance here because incorporation of compounds **3** into polymers leads to systems in which the rigid mesogenic core of the molecules is almost directly bound to the main chain. It was therefore expected that the flexibility of the addition reagent used would strongly influence the phase behaviour of the polymers.

To test these expectations three different compounds containing Si-H groups were used for the polyaddition reaction (see figure 1). The polymers synthesized and their transition temperatures are given in table 3. As can be seen in this table the thermal behaviour of the materials depends strongly on the type of silicon containing

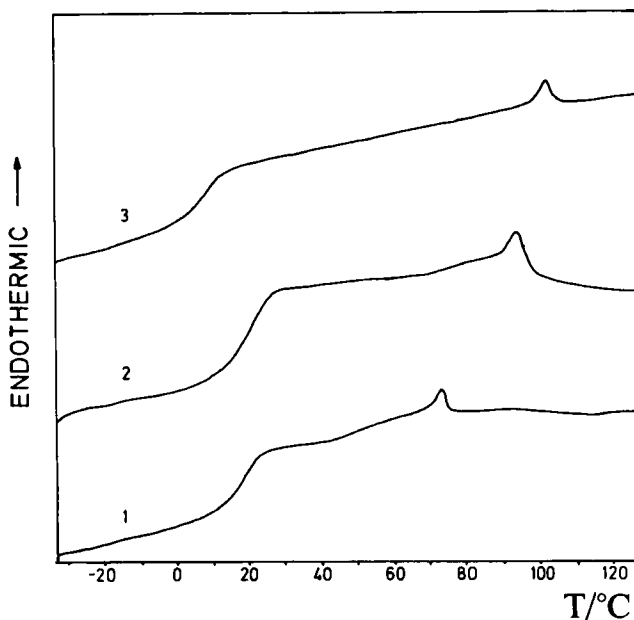


Figure 3. DSC thermograms measured at 10 K min^{-1} for the polymers **4**. 1, **4b**; 2, **4c**, 3, **4d**.

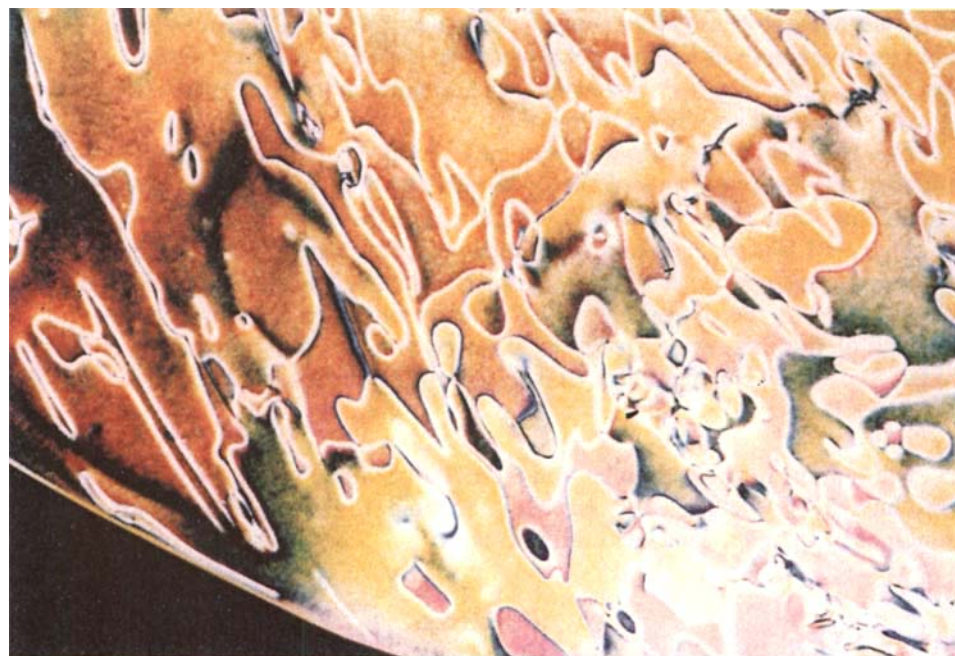
compound. Polymers **6** with the stiff bis-(silyl)-benzene unit have the higher T_g temperatures. As expected, polymers **5** with the highly flexible polydimethylsiloxane unit have much lower T_g s than polymers **4**, which contain only a disiloxane unit in the main chain.

The DSC measurements and microscopic observations indicate that only those polymers with the tetramethyldisiloxane compound (**4**) exhibit mesophases. The thermograms are given in figure 3. Compared to the corresponding swallow-tailed monomers (**3**) the polymers (**4**) show broader temperature ranges of the mesophases.

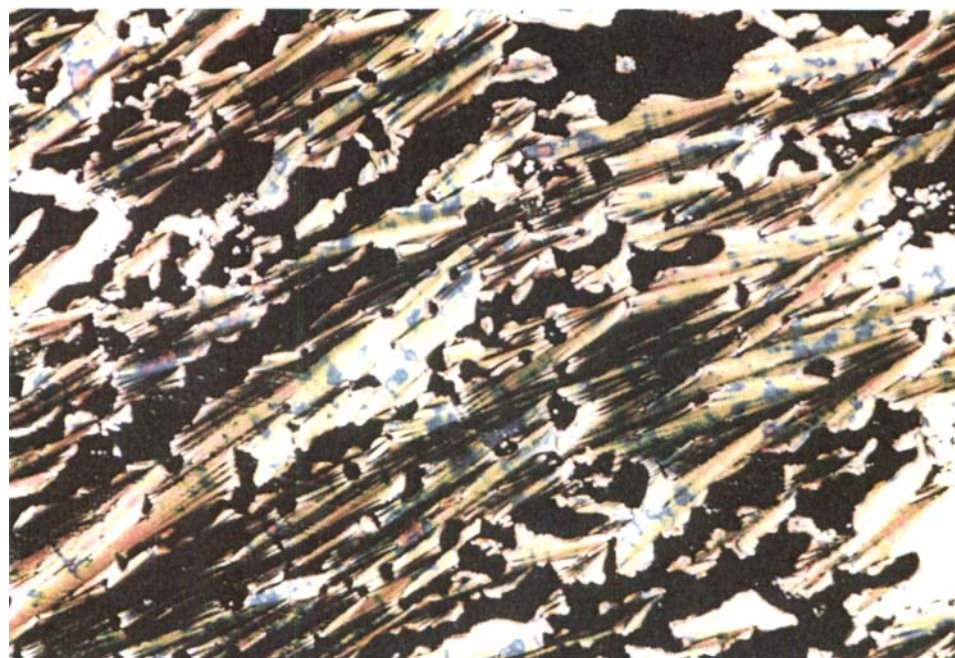
Table 3. Phase transitions for the polymers.

Polymer	Transitions temperatures/ $^{\circ}\text{C}$	
	Transition enthalpy/ J g^{-1}	
4a	g 17.1	I
4b	g 16.9	N 72.4 I
		0.50
4c	g 19.8	S_C 93.1 I
		0.71
4d	g 9.2	N 101.1 I
		0.46
5b	g -40.3	I
5c	g -52.1	I
5d	g -77.1	I
6c	g 44.5	I
6d	g 29.1	I

g = glass transition; N = nematic; S_C = smectic C; I = isotropic



(a)



(b)

Figure 4. A typical texture displayed by (a) polymer **4b** at 70°C; (b) polymer **4c** at 90°C.

The X-ray analysis of fibres drawn from the melt indicated that polymers **4b** and **4d** form a nematic phase with an average distance of 4.7–4.8 Å between the mesogens. The structural analysis for fibres of polymer **4c** revealed a S_C phase with an interlayer spacing, *d*, of 34.7 Å, which corresponds to a tilt angle of *c.* 30°. Typical textures given by these materials are shown in figure 4.

Why polymers **5** and **6** do not form mesophases can be ascribed probably to two different reasons. In polymers **6** the higher rigidity of the systems does not permit the decoupling of the mesogens, which is required for the formation of the mesophases. In polymers **5** it is the high dilution of the mesogenic units [13, 14], which is responsible for the disappearance of the phases. The fact that this dilution of the mesogenic groups leads to the disappearance of the mesophase hints at the side chain-type packing of the mesogenic groups in these polymers. Thus polymers **4** should be considered as side chain liquid crystal polymers with the spacer placed in the polymer backbone [15].

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