

Liquid Crystal Polymers

Thermotropic Liquid Crystalline Bimesogenic Molecules with Highly Flexible Oligosiloxane Spacer

C. Aquilera and L. Bernal

Department of Polymer Science, The University of Akron, Akron, Ohio 44325, USA

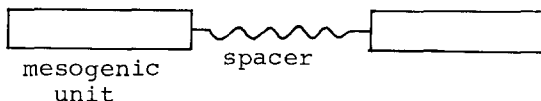
SUMMARY

A number of potentially mesomorphic ester derivatives of 4-allyloxybenzoic acid have been prepared. Bimesogenic molecules were synthesized by addition of the 4-allyloxymesogenic unit to α -dimethylsilanyl- ω -hydrogenooligodimethylsiloxane catalyzed by hexachloroplatinic acid. The thermal properties of this new series of thermotropic, liquid crystalline bimesogenic compounds were studied by differential scanning calorimetry (DSC) and polarized light microscopy. It was found that the length of the oligosiloxane spacer was the most important factor for the low transition temperature. The effects of structural changes on mesophase stability are also discussed.

INTRODUCTION

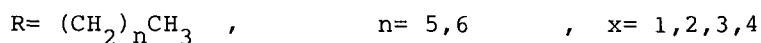
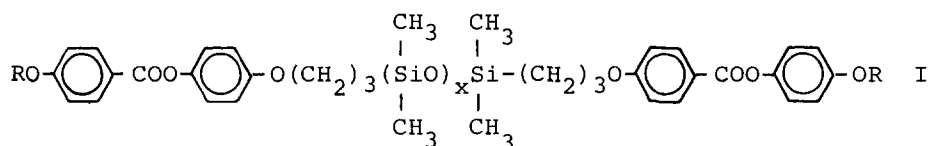
Many investigations have been carried out in order to understand the effects of symmetry and molecular structure in liquid crystals containing ester linkages. The majority of these investigations(1,2)have focused their attention on the synthesis of novel derivatives of 4-alkyloxybenzoic acid in an effort to prepare stable liquid crystals, which exhibit a wide mesophase range and low melting point for physical, chemical and technological applications (3). These studies indicated that esters with similar unsymmetrical structures would also be mesomorphic and have low crystals-to-liquid crystal transition temperatures. Benzoates with two phenylene rings depending on the length of the terminal groups, melting point as low as 40°C can be achieved. Benzoates with three phenylene rings generally have higher crystal-liquid crystal transition temperatures (4,5).

In order to reduce the transition temperature of mesogenic derivatives of 4-alkyloxybenzoic acid, a highly flexible spacer could be inserted between two rigid mesogenic units, as follows:



* To whom correspondence should be addressed.

In the present investigation, a study has been made of the influence of the length of a highly flexible oligosiloxane spacer on the liquid crystalline behaviour of this bimesogenic compound. It was expected that the siloxane group would contribute to the loss of crystalline stability and lead to low melting points. Thus a series of bimesogenic compounds, I, of the following structures were synthesized and characterized:



RESULTS AND DISCUSSION

Liquid crystalline 4-allyloxybenzoic acid esters 1

For the synthesis of liquid crystalline bimesogenic compound, mesogenic ester (**1a-1d**) derivatives of 4-allyloxybenzoic acid were used. The mesogenic unit was prepared by reaction of 4-allyloxybenzoic acid chloride with different 4-alkoxyphenolens. Table 1 shows phase transitions indicating the usual structure dependence for low molecular weight liquid crystals. The clearing temperatures of smectics in a homologous series generally rise initially with increasing chain length, reach a maximum at a moderate chain length, then decrease slightly and finally acquire a nearly constant value in long chains. Smectic phases are rarer with shorter lateral chains, but become most common with longer chains (6).

Table 1. Phase transition of liquid crystalline 4-allyloxybenzoic acid esters (1).

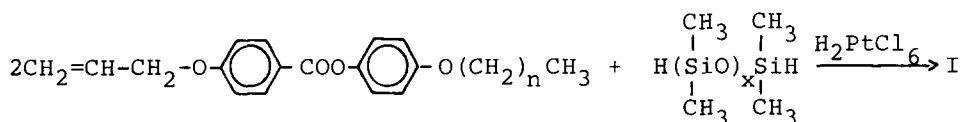
$$\text{CH}_2=\text{CH}-\text{CH}_2\text{O}-\text{C}_6\text{H}_4-\text{COO}-\text{C}_6\text{H}_4-\text{O}(\text{CH}_2)_n\text{CH}_3 \quad \text{1}$$

Ester	n	Phase transition ^{b)} temp. in °C.	Phase width temp. in °C.
1a	2	k 60 n 75 i	15
b	3	k 59 s 83 i	64
c	5	k 52 s 79 i	27
d	6	k 43 s 72 i	29

^{b)}k: crystalline, n: nematic, s: smectic, i: isotropic

Liquid crystalline bimesogenic compounds:

The liquid crystalline bimesogenic compounds were synthesized by addition of the 4-allyloxymesogenic unit to α -dimethylsilanyl- ω -hydrogenooligodimethylsiloxane(7,8) catalyzed by hexachloroplatinic acid.



The phase behaviour of the synthesized bimesogenic compound (I) shown in Table 2 indicates the characteristic differences caused by the specific properties of the highly flexible oligosiloxane spacer.

Table 2. Phase transitions of liquid crystalline bimesogenic compound I.

Bimesogenic compound	n	x	Phase transition temp. in °C.				Phase width temp. in °C.	
I a	5	1	k	9	s	45	i	36
b	5	2	k	1	s	50	i	51
c	6	1	k	20	n	52	i	32
d	6	2	k	12	s	48	i	36
e	6	3	k	-2	s	45	i	47
f	6	4	k	-7	s	39	i	46

In effect, the siloxane spacer greatly reduces the inter-chain interactions and the degree of crystallinity of the bimesogenic compound; apparently, the difference can be attributed to the effect of the bulky structure, flexibility and the irregular conformations of the oligo(dimethylsiloxane) spacer between the rigid mesogenic groups. The methyl groups in dimethylsiloxane units rotate with unusual ease around the Si-O bond even at temperatures as low as -195°C (9,10). This free rotation is one of the reasons for the weakened interchain attraction of the oligo(dimethylsiloxane).

Recently investigations (11,13) have been carried out in order to understand the effect of highly flexible oligosiloxane spacers on the thermotropic, liquid crystalline main chain polyesters. The incorporation of a relatively short oligosiloxane spacer resulted in a considerable decrease in the transition temperatures of the polyesters showed liquid crystal behaviour even at room temperature. Again, highly flexible oligosiloxane spacers can be used to prepare bimesogenic compounds with very low melting points for practical applications.

The melts of all bimesogenic compounds (I) below their clearing temperatures were clearly birefringent and showed nematic or smectic texture when observed on the hot stage of a polarizing microscope. By direct visual observation they showed stir-opalescence. The bimesogenic compound with oligosiloxane, when examined by DSC, showed a broad and weak melting transition and completely reversible mesophase-to-isotropic transition. However, the crystal-to-mesophase transition temperatures were observed to be lower during a cooling cycle, owing to supercooling of the liquid crystalline phase. For example, at the same heating and cooling rate of $20^\circ\text{C min}^{-1}$, the crystallization exotherm in the cooling curve of the compound I_e (x=3) occurred 60°C below the melting endotherm. Those reported

are for the heating cycle. (See Table 2)

The effect of the size of the spacer group on melting as well as on clearing temperature are shown in Figure 1 as a function of the number of the siloxane units (x). Inspection of Figure 1 indicates clearly that the phase transition temperature decreases slightly with increasing spacer length of the siloxane group.

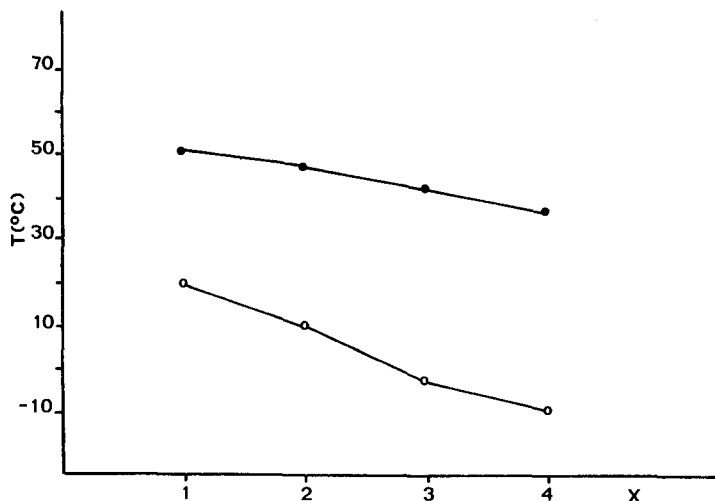


Fig.1 Influence of the length of the siloxane spacer on the transition temperatures of the liquid crystalline bimesogenic esters $I_C - I_f$, \bullet = Clearing point; \circ = melting point; x = number of oxydimethylsilanediyl (siloxane) units.

It is reasonable to expect that longer flexible spacers should be increasingly effective in increasing the molecular mobility in the melt of the bimesogenic compound. This increased mobility should result in a lower clearing temperature and lower melting point. Another interesting observation was that the temperature range, over which the mesophase existed, was consistently broader for the bimesogenic compounds (I) as compared to 4-allyloxy-mesogenic ester (1) as shown in Table 1. These results can be attributed to the ability of the siloxane spacer to have a greater decreasing effect on the melting transition or to the increase in anisotropic molecular polarizability. The bimesogenic compound has four polarizing aromatic rings.

A complete systematic analysis of the behaviour of bimesogenic molecules with highly flexible oligosiloxane spacers will require many more studies; our research in this area is directed at a systematic variation of mesogenic units and siloxane spacers for a better characterization of the structure and properties of mesogenic phases.

EXPERIMENTAL PART

4-allyloxybenzoic acid ester (1a - 1d):

0,02 mole p-alkyloxyphenol (e.g p-propyloxy, p-butyloxy- or p-hexyloxyphenol) is dissolved in dry tetrahydrofuran (THF). The stirred solution is cooled to 5°C. 0,22 mole of 4-allyloxybenzoyl chloride in 10 ml of THF and 0,03 mole of triethylamine in 20 ml of THF are added dropwise and simultaneously. After 8 h stirring at room temperature the solvent is evaporated. The residue is dissolved in methylene chloride, washed several times with cold water and dried over Na_2SO_4 . The methylene chloride is evaporated and the product is purified by recrystallization from dioxane and ethanol. Yield 75-90%. Elemental analyses are shown in Table 3.

Table 3. Elemental analyses the 4-allyloxybenzoic acid esters 1 (See Table 1).

p-allyloxybenzoate of:	Empirical formula (Mol. weight).	C		H	
		Calc.	found.	Calc.	found
4-Propyloxyphenylene (1a)	$\text{C}_{19} \text{H}_{20} \text{O}_4$ (312,2)	73,03	72,92	6,46	6,49
4-Butyloxyphenylene (1b)	$\text{C}_{20} \text{H}_{22} \text{O}_4$ (326,2)	73,57	73,97	6,80	6,59
4-Hexyloxyphenylene (1c)	$\text{C}_{22} \text{H}_{26} \text{O}_4$ (354,2)	74,53	74,49	7,40	7,27
4-Heptyloxyphenylene (1d)	$\text{C}_{23} \text{H}_{28} \text{O}_4$ (368,2)	74,96	74,55	7,67	7,68

Bimesogenic molecules I:

Addition of the 4-allyloxybenzoic acid ester 1a-1d to the α -dimethylsilyl- ω -hydrogenooligosimethylsiloxane (mole ratio 2:1) is carried out with stirring in a nitrogen atmosphere in dry THF at 60 C with a Wacker-Oil catalyst based on H_2PtCl_6 . Concentrated solutions of both components in THF have to be used. After complete addition (18-20 h; disappearance of the Si-H absorption at 2140-cm^{-1}), most of the THF is evaporated. The compound is precipitated from methanol and reprecipitated several times from ethanol/methanol.

All substances give correct IR and ^1H -RMN-Spectra; transition temperatures was measured on a Perkin-Elmer DSC-2. For polarizing microscopy a Leitz Ortholux Pol BK II was used.

ACKNOWLEDGEMENTS

This work was supported by the Deutscher Gessellschaft für Zusammenarbeit (GTZ) and by the Dirección de Investigación, Universidad de Concepción. The authours are indebted to Wacker Chemie, Burghausen, for the donation of the catalyst (Wacker-Oil).

REFERENCES

1. Steinsträsser R., Z. Naturforsch. 276, 774 (1972).
2. Young, W.R., Haller I., Green D.C., J.Org.Chem.37,3707(1972)

3. Meier G., Sackmann E., Grabmaier J.G., Applications of Liquid Crystals, Springer Verlag, N.York 1975.
4. Dewar M.J.S., Golberg R.S., J.Org.Chem.35, 2711 (1970).
5. Demus D., Demus H. Zschke H., Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1974.
6. Gray G.W., Winsor P.A., Liquid Crystals and Plastic Crystals Vol.1, John Wiley & Sons, Inc. London, New York 1974.
7. Patnode W., Wilcock D.F., J.Am.Chem.Soc. 68, 358 (1946).
8. Greber G., Metzinger L., Makromol.Chem. 39, 167 (1960).
9. Rochow E.G., Model F.S., Plaste Kaut. 15, 466 (1968).
10. Jon L.K., Robert U., Macromolecules 2,525 (1969).
11. Aguilera C., Ringsdorf H., Schneller A., Zentel R., IUPAC International Symposium on Macromolecules , 1980 Florence, Italy. Preprints, Vol.3 p. 306.
12. Jo B.W., Jin J.I., Lenz R.W., Eur.Polym.J. 18,233 (1982).
13. Aguilera C., Bartulín J., Hisgen B., Ringsdorf H., Makromol. 184, 253 (1983).

Accepted September 25, 1984