

## Transition temperature control of liquid crystalline poly(heptene sulphone)s

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### Summary

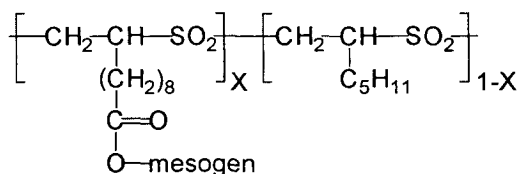
Liquid crystalline poly(heptene sulphone)s containing cholesteryl undecylenic ester and cholestanyl undecylenic ester were synthesized. The polymers displayed cholesteric mesophases during thermal transition. The clearing temperatures were from 114 to 172 °C depending on the molar ratio of mesogenic esters in the polymers.

### Introduction

Thermotropic side chain liquid crystalline polymers (LCPs) are hybrid materials, which like polymers, have good mechanical and film forming properties, while also exhibiting the remarkable thermo-optical property. The polymers are promising for optical storage applications. Side chain LCPs are prepared by incorporating the low molecular weight mesogen in the pendant side group. Systems based on poly(acrylic acid), poly(methyl-alkylsiloxane)s and poly(methyl methacrylate) have been widely studied (1), however, the work on liquid crystalline polysulphones is limited (2-5).

Simple alternating poly(olefin sulphone)s form readily from many olefins and sulphur dioxide by a free radical reaction (6). Thus, mesogenic olefins can react with sulphur dioxide to form liquid crystalline polysulphones. The nature of the polymer can be modified by including other comonomers in the polymerisation. If a non-mesogenic monomer is employed in the copolymerisation with a mesogenic monomer, the concentration of mesogenic units in the polymer is diluted. Subsequently, the copolymer loses its mesomorphic behaviour below a minimum mesogen concentration, which depends on the nature of both monomers. Moreover, the mesophase transitions may also be affected.

The polymers we studied have the general formula:



where  $x$  is the mole fraction of residues from mesogenic olefins in the chain, and the mesogen is either from cholesterol or from cholestanol.

## Experimental

### Materials

$3\beta$ -Cholesterol (Aldrich) and dihydrocholesterol (Aldrich) were crystallised from ethanol until constant mp were obtained.

Undecylenic acid (Aldrich) was crystallised from its melt.

Hept-1-ene (Aldrich) was refluxed over potassium-sodium amalgam for 24 h and then fractionally distilled.

Tertiary butyl hydroperoxide (Sigma), dicyclohexylcarbodiimide (Aldrich) were used as supplied.

Ether and dichloromethane were refluxed over sodium metal for 24 h and then fractionally distilled.

### Preparation of cholesteryl undecylenic ester and cholestanyl undecylenic ester

Cholesteryl undecylenic ester and cholestanyl undecylenic ester were synthesized by using dicyclohexylcarbodiimide to link the alcohol to the acid as reported before (3,5). The mp were  $79.0^\circ\text{C}$  and  $68.5^\circ\text{C}$  respectively.

### Preparation of liquid crystalline poly(heptene sulphone)s

Liquid crystalline poly(heptene sulphone)s were obtained by the following typical reaction: cholesteryl 10-undecylenate (0.552 g, 0.0010 mol) and hept-1-ene (0.098 g, 0.0010 mol) were dissolved in dichloromethane (10 ml), cooled to  $-35^\circ\text{C}$ , and added to 2.5 ml of sulphur dioxide at  $-35^\circ\text{C}$  in a reaction tube. 0.25 ml of tertiary butyl hydroperoxide was

**Table 1:** Experimental conditions for preparation of liquid crystalline poly(heptene sulphone)s

Sample <sup>a</sup>	Liquid crystalline olefin (g)	Hept-1-ene (g)	Mole fraction of mesogen in feed (%)	Yield (g/%)
TPHS1	0.552	0.196	33.00	0.43/45.7
TPHS2	0.552	0.098	50.00	0.39/50.1
TPHS3	0.552	0.049	66.67	0.37/53.1
TPHS4	0.552	0.025	80.00	0.42/63.9
CPCES <sup>b</sup>	1.656	-	100	1.42/76.8
TPHS5	0.554	0.196	33.00	0.77/81.7
TPHS6	0.554	0.098	50.00	0.67/85.9
TPHS7	0.554	0.049	66.67	0.61/87.3
TPHS8	0.554	0.025	80.00	0.56/85.0
CPCAS <sup>b</sup>	1.662	-	100	1.52/82.2

<sup>a</sup> The upper group (TPHS1-CPCES) was prepared from the cholesteryl ester, and the lower group (TPHS5-CPCAS) was prepared from the cholestanyl ester

<sup>b</sup> The data are from previous work (5)

added over 3 h and the polymer was precipitated after 12 h by pouring the solution into acidified methanol. The polymer was purified by reprecipitating it three times from dichloromethane solution into methanol. It was finally collected on a scintered glass disc and dried in a vacuum oven at 50°C overnight. The yield was 0.39 g (50.1 %). For other similar copolymerisations, yields between 45.7 % and 76.8 % were obtained, as summarised in Table 1. The experiment was repeated with cholestanyl 10-undecylenate. The liquid crystalline monomer was routinely recovered from the methanol solutions by evaporating off the volatile materials, sulphur dioxide, methanol and the normal olefin, and it was then reperfired.

#### Characterization of the monomers and polymers

The molecular weights of the polymers were measured in THF with a PLgel 10 $\mu$  mixed-B column GPC system (Waters 510 HPLC pump, Waters 410 differential refractometer) that had been calibrated with polystyrene standards. The infra-red spectra of the samples were measured by KBr disc method with a Nicolet Magna-IR spectrometer 750. The compositions of the polymers were measured by elemental analysis and confirmed by NMR. The thermal transitions of the monomers and polymers were measured with a Mettler FP 82 hot stage and a polarising microscope.

## Results and discussion

The two olefinic esters exhibited liquid crystal behaviours. Our samples had the following transition temperatures. Cholesteryl 10-undecenate: mp 79.0°C, to cholesteric phase (oily streaks and mosaics), clearing temperature 85.0°C to 85.5°C. Cholestanyl 10-undecenate melted at 68.5°C, but became anisotropic upon clearing, and crystals formed on further cooling between 50°C and 28°C (3,5).

The molecular weights and the compositions of the liquid crystal polymers are summarised in Table 2. In general, the molecular weights were above 10,000 except the two 100% mesogenic polysulphones.

**Table 2:** Mole fractions of mesogen in polymer, molecular weights and thermal transition temperatures of liquid crystalline poly(heptene sulphone)

Sample	Mole fraction of mesogen in polymer x (%) <sup>b</sup>	Molecular weight, Mn	Melting temperature (°C)	Clearing temperature (°C)
TPHS1	24.03	6800	98.0	114.0
TPHS2	31.55	14600	126.0	149.0
TPHS3	46.97	15500	133.0	154.0
TPHS4	54.62	12500	142.0	168.0
CPCES <sup>a</sup>	100	1000	163.5	179.5
TPHS5	29.47	12500	97.0	112.0
TPHS6	42.83	12500	115.0	138.0
TPHS7	54.75	13000	130.0	160.0
TPHS8	67.32	12000	138.0	169.0
CPCAS <sup>a</sup>	100	1700	160.0	180.0

<sup>a</sup> The data are from previous work (5)

<sup>b</sup> The data were derived from elemental analysis

All the IR spectra of the polymers had absorption peaks at 1734s cm<sup>-1</sup> (C=O stretching), 1308s cm<sup>-1</sup> (S=O antisymmetric stretching), 1130s cm<sup>-1</sup> (S=O symmetric stretching), and 729-715m cm<sup>-1</sup> (C-S stretching), indicating the presence of the liquid crystalline mesogens in the polymers. Moreover, the NMR spectra of the polymers, had no peak at the chemical shift of 5.80 and 4.95 ppm (due to the olefinic hydrogens in the undecylenic unit of the liquid crystal monomers), further proved the incorporation of the mesogens into the polysulphones.

After precipitation and vacuum drying, the polymers were white brittle solids at room temperature. The thermal transitions of the polymers were observed on a hot stage

microscope. The sample initially showed green and red patches. On warming the samples, these colours eventually disappeared, and the samples all showed a transition to clear isotropic liquids. Linking hept-1-ene in the polymer chain affected the melting and clearing temperatures greatly. The thermal transition data of the polymers are summarised in Table 2.

As the amounts of hept-1-ene in the polymers increased, the mp and clearing temperatures of the polymers decreased. Similar results were observed in other liquid crystalline polymers (3,5,7). It is probable that hept-1-ene is not mesogenic, thus it produced a diluting effect to the polymer chain; the degree of structural order would decrease with increasing concentration of the nonmesogenic comonomer, thus the mp and clearing temperatures of the polymers decreased as more hept-1-ene sulphone residues were in the polymers. Also, the mp and clearing temperatures of the polymers were lower than those of the liquid crystalline poly(hexene sulphone)s (3). This may be due to the additional methylene group in the liquid crystalline poly(heptene sulphone)s. Since the methylene group is flexible and it increased the distance between the polymer chains, thus the thermal transition of the polymers was lowered.

## Conclusion

In conclusion, a series of the liquid crystalline poly(heptene sulphone)s with a wide range of clearing temperatures from 114 °C to 172 °C was synthesized. This feature is particularly important because it means the clearing temperature can be tailor-made by varying the amounts of mesogenic groups in the polymer chain. This property is highly desirable in the optical storage and liquid crystal display applications at different temperatures. Also, the polymers can be economically synthesized.

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