Thermotropic liquid crystalline polymers with quasi-rigid chains: 2. Chain flexibility

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The melting points of polymers with quasi-rigid rod-like chains can be depressed below their decomposition temperatures by increasing their relative flexibility. However, v_{ni} is also depressed and the subtle balance between the axial ratio of the mesogenic segments and the flexibility of the macromolecule must be taken care of. A number of poly-esters, -amides, and -esteramides were prepared and their thermal behaviour investigated. One of the polyesters melts at 240°C–270°C to give a nematic phase. The solubility of the polymers also improved with increasing flexibility of the macromolecules.

(Keywords: quasi-rigid polymers; thermotropic nematic polymers; molecular flexibility; rod-like macromolecules)

INTRODUCTION

The motivation behind the search for thermotropic liquid crystalline polymers with quasi-rigid chains has been explained in part I of this series[1]. The recurring units of these polymers usually include rod-like mesogenic units (two cyclic moieties linked by a covalent bond or a diatomic linkage, e.g. –COO–, –CONH–). Therefore, such polymer chains possess high axial ratios and tend to align parallel to each other in their extended form. A large persistence length has been predicted for these types of polymers[2,3] thus indicating their rigidity. On melting mesogenic polymers, no major change in the chain configuration occurs as indicated by different studies[4,5]. In their molten state, the main motions are longitudinal translation, chain rotation and minor internal chain motions. Therefore, the entropy change (ΔS) at the melting point is expected to be relatively small. Since $T = \Delta H/\Delta S$, where ΔH is the melting enthalpy and T the melting temperature, it follows that ΔH has to be small in order to achieve relatively low melting temperatures. The flexibility of the macromolecules as well as their packing density (the molecular interaction energy strongly depends on the intermolecular distance) are known to be the major factors affecting ΔH of crystalline polymers[6]. In order to lower the melting point below the decomposition temperature, we tried to increase the flexibility of rod-like polymer chains by increasing the rotational freedom of their mesogenic units. The introduction of long aliphatic segments 'spacers' was avoided to retain the relative rigidity and high axial ratio of the macromolecules which seem to be necessary not only to stabilize the mesophase but also to obtain superior mechanical properties[7,8].

EXPERIMENTAL

Polymer characterization

The thermal behaviour of the polymers was investigated by differential thermal analysis and polarizing microscopy under N_2 using a PE-DSC2 and a Leitz Orthoplan microscope equipped with a Mettler FP5/52 heating stage. The phase transition temperatures were measured under the microscope at 2°C/min heating rate, while the thermal analysis was carried out at a rate of 10°C/min. The upper limit of the heating stage temperature range is 300°C. T.g.a. measurements were carried out in an airflow at 10°C/min on a Mettler TA 12.

General method of preparing the polyesters

A solution of the acid chloride (0.02 M) in sym-tetrachloroethane (TCE) 20 ml was added to a cooled solution (0–5°C) of the phenol or alcohol (0.02 M) in TCE 15 ml and pyridine 8 ml under N_2 with stirring. After 30 min, the temperature was left to rise to room temperature and kept there for another 30 min. The reaction mixture was then heated at 70°C for 4 h, after which it was diluted to 7% conc. and poured on methanol. The polymer obtained was filtered, washed with methanol, dried and dissolved in an appropriate solvent (*Table 1*) when possible. The polyester was reprecipitated in methanol, filtered, washed and dried at 70°C under reduced pressure.

General method of preparing the polyamides

A solvent mixture consisting of 1 part hexamethylphosphoramide, 2 parts 1-methyl-2-pyrrolidone and 1,5 parts *N,N*-dimethylacetamide was used in this reaction and will be designated PPA. A solution of the acid chloride (0.02 M) in dry PPA 20 ml was added to a cooled mixture of the diamine (0.02 M), PPA 20 ml, dry triethylamine 8 ml and lithium chloride 3 g under N_2 with stirring. After 30 min at 0°C–5°C, the temperature was left to rise to room temperature and kept there for 4 h. The reaction mixture was diluted with PPA to 7% conc., then poured on ethanol and the precipitated polymer filtered and washed with ethanol. When possible, the product was dissolved in an appropriate solvent (*Table 2*) and reprecipitated in ethanol, then filtered, washed and dried.

Monomers

The monomers were either commercially available or prepared according to methods described in the literature[1,10–13]. Their purity was checked by g.l.c. on a 1 m 3% OV17 column.

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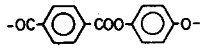
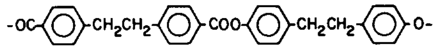
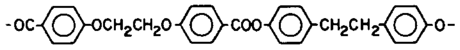
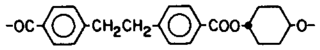
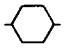
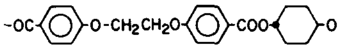
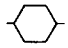
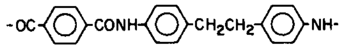
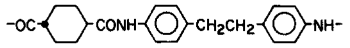
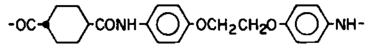
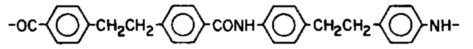
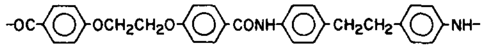
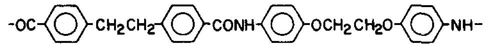
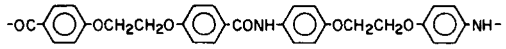
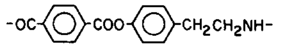
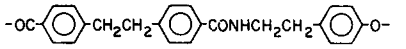
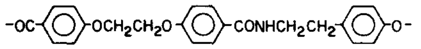
Table 1 Influence of chain flexibility on the thermal behaviour of quasi-rigid polyesters

Code	Recurring unit	Thermal behaviour	Remarks
P33		infusible	decomposes above 350°C
P28u		infusible	decomposes above 300°C, soluble in ClPh
P27u		infusible	decomposes above 350°C, soluble in ClPh
P53u		infusible	decomposes above 300°C, soluble in ClPh
P62u	*cis*/*trans* 1:1 	infusible	decomposes above 300°C, soluble in TCE
P55u		C240–260N 270–290	d.s.c., 2 broad endothermic peaks at 240°C, and 270°C miscible with the nematic phase of CBC33
P61u	*cis*/*trans* 1:1 	C225–270I	d.s.c., endothermic peak at 225°C, soluble in TCE

C = cyrstalline, N = nematic, I = isotropic, ClPh = 2-chlorophenol, TCE = 1,1,2,2-tetrachloroethane, DMF = dimethylformamide, THF = tetrahydrofuran. Temperatures are given in °C and the letter u in the synonyms denotes that the polymer was purified by reprecipitation. CBC 33 = 4,4'-bis-(4-*trans*-propylcyclohexyl)-biphenyl S 220 N 325 I

Table 2 Influence of chain flexibility on the thermal behaviour of quasi-rigid polyamides and polyesteramides

Code	Recurring unit	Thermal behaviour	Remarks
P19		influsible	no decomposition up to 450°C
P21		infusible	decomposes above 350°C
P73		infusible	decomposes above 350°C
P26		infusible	no decomposition up to 450°C
P25		infusible	decomposes above 350°C
P35		infusible	decomposes above 350°C
P36		infusible	decomposes above 350°C
P37		infusible	decomposes above 350°C, soluble in ClPh
P41u		infusible	decomposes above 350°C, soluble in THF
P42u		C245–260I	d.s.c. endothermic peak at 245°C, soluble in DMF

For symbols see *Table 1*

RESULTS AND DISCUSSION

The most common structure of mesogenic units yet built in polymer chains is two phenyl groups linked either by a covalent bond or a carboxyl group. A biatomic linkage (carboxyl group) between the cyclic moieties is expected to increase the flexibility of a mesogenic unit compared with that of the rigid biphenyl. However, the hydrogen bonding between the carbonyl group and the hydrogen atom in the ortho-position decreases the rotational freedom in phenyl benzoates. This partially hinders the expected molecular flexibility.

A mesogenic unit in which the phenyl groups are linked by an ethylene linkage instead of a carboxyl group has a higher degree of rotational freedom. The effect of increasing the flexibility of rod-like macromolecules, by incorporating such mesogenic units in their chains, on their thermal behaviour is shown in *Tables 1* and *2*. In P28u (*Table 1*), half of the carboxyl groups of the poly(1,4-phenylene terephthalate) molecule were replaced by ethylene linkages. Although the solubility was improved, the melting point remained too high and the polymer decomposed without melting. Replacing one of the ethylene groups by a longer and more flexible –OCH$_2$CH$_2$O– unit (P27u) also did not lead to the desired depression of the melting temperature. In P53u and P62u, the 4,4'-dihydroxy diphenylethane was replaced by 1,4-

cyclohexanediol to reduce the packing density and increase the flexibility[1]. This attempt was similarly unsuccessful. However, a combination of 1,4-*trans*-cyclohexanediol and the $-OCH_2CH_2O-$ linkage led to a thermotropic nematic polymer P55, whose melting temperature was 240°C–270°C.

The nematic phase was identified by its high fluidity and schlieren texture with $s=1/2$ singularities[9]. The complete miscibility of this mesophase with the nematic phase of 4,4'-bis- (4-*trans*-propylcyclohexyl)-biphenyl (CBC 33) confirmed the nematic assignment. The nematic isotropic transition temperature ν_{ni} of P55 is 270°C to 290°C. Partial decomposition of the polymer, however, occurs around this temperature and traces of the decomposition products lead to a homeotropic orientation. In the thermal analysis two broad endothermic peaks were observed on heating at 240°C and 270°C corresponding to ν_{cn} and ν_{ni}. On cooling, ν_{cn} was supercooled at 200°C while ν_{ni} was detected at 270°C. The temperature of 10% weight loss measured by thermal gravimetric analysis (t.g.a.) in an airflow, was found to be 335°C for this polymer. Replacing the *trans*-cyclohexyl unit by a 1:1 *cis–trans* mixture (P61u), lowered the melting point further but the mesophase was destabilized and no anisotropic behaviour could be observed. Attention must be drawn to the fact that the whole macromolecule in P28u and P53u can be considered as one mesogenic segment. In contrast, the molecules of P27u and P55u consist of several mesogenic segments attached together by $-OCH_2CH_2O-$ linkages. In P27u the mesogenic segments include two mesogenic units (four cyclic moieties linked by biatomic linkages) while those of P55 extend over three cyclic moieties only. In other words, these polymer chains consist of mesogenic segments with different lengths connected together by isotropic units. It is expected that mutual interactions between the mesogenic and isotropic parts of the molecules do exist. The ordered rigid mesogens restrict the rotational and conformational freedom of the isotropic units, and the restriction is more effective the longer the mesogenic segments (high axial ratio) and the shorter the flexible units. On the other hand, the isotropic units disturb the orientational order of the rod-like mesogens, and the effect is greater the shorter the mesogens and the longer the flexible units. Beside their effect on the melting point, these interactions strongly influence the stability of the mesophase. In the investigated polyesters the isotropic units are quite short and therefore are expected to be well oriented in the liquid crystalline matrix.

Similar attempts to lower the melting point of polyamides (P19, P21, P25, P26, P35, P73) failed to reach their goal (*Table 2*). This is probably due to the intermolecular hydrogen bonding which leads to high melting temperatures in these polymers. Not even two $-OCH_2CH_2O-$ groups per recurring unit (P36), which shortened the length of the mesogenic segment to a simple unit, were able to produce a fusible polyamide. The mixed polyesteramides (P37u, P41u and P42u), where the number of amide groups per molecule was reduced, had better solubilities. However, only P42u melted below its decomposition temperature to give an isotropic liquid. The mesogenic units of P42u are separated by long isotropic segments ($-OCH_2CH_2O-C_6H_4-CONHCH_2CH_2-$) which led to the disappearance of the mesophase. The mesogenic segments of P41u are longer than those of P42u (three cyclic units) and a higher ν_{ni} should be expected but the polymer is infusible.

In conclusion, it can be said that increasing the relative flexibility of quasi-rigid rod-like macromolecules decreases their melting points. However, ν_{ni} is also depressed and the subtle balance between the axial ratio of the mesogenic segments and the flexibility of the macromolecule must be taken care of.

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