

Alkoxy-substituted liquid-crystalline aromatic copolyesters

4. Synthesis and properties of main chain copolyesters derived from 2,5-bis(pentyloxy)terephthaloyl dichloride and *trans*-1,4-dihydroxycyclohexane

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Summary

Rigid rod copolyesters derived from 2,5-bis(pentyloxy)terephthaloyl dichloride (**3**), 4,4'-dihydroxybiphenyl (**4**) and *trans*-1,4-dihydroxycyclohexane (**5**) were synthesized and their thermal behavior analysed. The structures were characterized by ¹H-NMR, GPC and elemental analyses; their thermal behavior was studied by DSC measurements, microscopy under polarized light and thermogravimetric analyses. The composition of the copolyesters with 30, 50 and 70 mol % **5** was not as expected, due to the differing reactivities of the diols **4** and **5** during the polycondensation. This led to the existence of two species of polyesters from one reaction mixture. The higher the content of **5** in the polymer, the lower the molecular weight. By increasing the amount of **5**, the thermal stabilities and melting points decrease drastically, whereas the solubility increases. The copolyesters **6a-g** show only a low ability to form fibres which are brittle and break very easily.

Introduction

In order to overcome serious problems such as melting points which are higher than the thermal decomposition points or extremely low solubilities of liquid crystalline polyesters, in previous work¹⁻³ we attempted to influence these physical properties by disturbing the symmetry and linearity of the structure by modifying poly(4,4'-biphenyldiyl)terephthalate by several diols. We discovered that these changes in structure reduce the melting points and clearing points. The influence on the melting points is greater than on the clearing points, thus broadening the liquid crystalline range. The solubilities of these polyesters increase.

This paper reports on the disruption of the planarity of the polymeric chain by incorporating *trans*-1,4-dihydroxycyclohexane (**5**) as a diol.

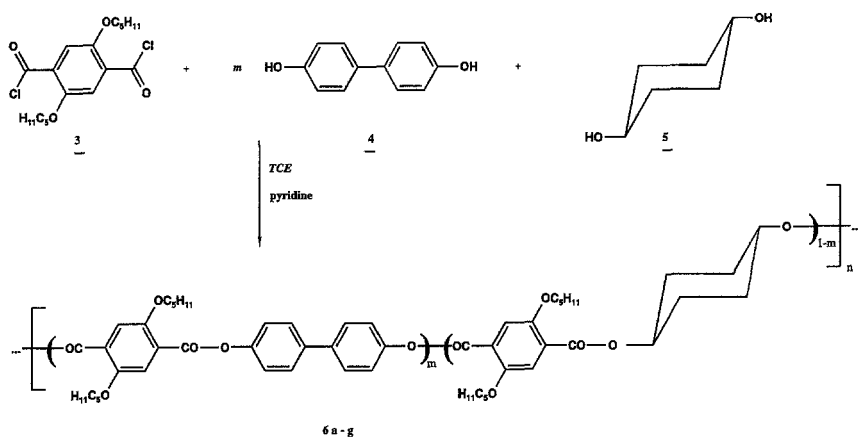
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Experimental part

The synthetic route to the substituted terephthalates starts with diethyl 2,5-dihydroxyterephthalate being refluxed with 1-bromopentane to form diethyl 2,5-bis(pentyloxy)terephthalate (**1**). Saponification with 5 wt.% aqueous potassium hydroxide yielded 2,5-bis(pentyloxy)terephthalic acid (**2**), which was converted to 2,5-bis(pentyloxy)terephthaloyl dichloride (**3**) by the action of thionyl chloride as described previously¹). The copolyesters **6a-g** were prepared in 1,1,2,2-tetrachloroethane (TCE) as solvent following the method of Dicke and Lenz⁴) (see scheme 1).

Measurements

The molecular weight was measured by GPC; the elemental analyses are performed with a Perkin-Elmer 240 Elemental Analyser; IR spectra with a Perkin-Elmer 580 B; ¹H NMR spectra with a Bruker AL 250, 250 MHz; MS with a Finnigan 112 S, EI, 80 eV; TGA measurements with a Heraeus TGA 500; DSC-measurements with a Heraeus TA 500S and the ¹³C NMR spectra with a Bruker AL 250, 250 MHz.



SCHEME 1

TABLE 1: Composition of the reaction mixtures (**3** and diols **4** and **5**) and elemental analyses of the copolyesters **6a-g**

polyester	4	5	C in %	H in %
			calc/found	calc/found
6a	100	-	73.75/73.57	6.60/6.57
6b	95	5	73.54/72.71	6.67/6.56
6c	90	10	73.33/71.77	6.74/6.57
6d	70	30	72.44/71.01	7.03/6.84
6e	50	50	71.50/69.45	7.33/7.08
6f	30	70	70.50/68.91	7.66/7.45
6g	-	100	68.58/67.47	8.19/8.14

Results and discussion

Compositions of the copolyesters 6a-6f

The compositions of the copolyesters **6a-6f** were characterized by ^1H NMR, TGA, polarized microscopy and ^{13}C NMR. When the content of **5** of the reaction mixture is raised, signals of endgroups in the ^1H NMR spectra appear, meaning that the length of the polymer chains decreases when the amount of **5** is increased. The integrals of the signals indicate the desired composition, but the results acquired via polarized light microscopy show a different result. After melting and under polarized light microscope, the existence of two different species of polyesters is perceivable in the copolyester **6f**. Apart from liquid crystalline areas, isotropic areas also exist. These two phases combine during the first heating cycle and therefore no liquid crystalline areas were observed during the second heating cycle. The outcome of the TGA measurements verify these phenomena, the TGA traces showing two decomposition temperatures, one of which represents the decomposition temperature of the polyester derived from **3** and **4**, the other, the decomposition temperature of the polyester derived from **3** and **5**. This signifies that one polymer species is built up mainly of **3** and **4** and the other species mainly of **3** and **5**. The polymer species showing a liquid crystalline phase chiefly consists of **3** and **4**, as the pure polyesters from **3** and **4** possess liquid crystalline characteristics. The other polymer species which shows an isotropic melt is built up of **3** and **5**, as here the pure polyester from **3** and **5** is incapable of forming liquid crystalline phases. The existence of these two polymeric species is a result of the varying reactivities of the diols **4** and **5** during polycondensation.

TABLE 2: Yield and properties of the copolyesters 6a-g

copolymer	yield	M_w	$T_m/^\circ\text{C}$	$T_i/^\circ\text{C}$	$T_d/^\circ\text{C}^{\text{b}}$
<u>6a</u>	92%	-	305	335-337	400
<u>6b</u>	75%	-	245	335-345	395
<u>6c</u>	75%	-	240	325-340	380
<u>6d</u>	70%	-	220	300-315	310
<u>6e</u>	65%	31000 ^{a)}	1st run:168 2nd run:175	265-285 265-285	300
<u>6f</u>	65%	11000 ^{a)}	1st run:120 2nd run:190	245 -	300
<u>6g</u>	60%	-	170	-	300

a) measured by GPC

b) measured by TGA

M_w = average molecular weight

T_m = melting point

T_i = clearing point

T_d = decomposition point

Thermal behavior of the copolyesters 6a-g

As seen in Tab.2, the introduction of 5 mol % of 5 leads to a drastic reduction of the melting temperature (70°C), and an increase of 5 leads to a further reduction of the melting temperature. Copolyesters containing 50 mol % and more of 5 induce a reduction of the clearing points. The liquid crystalline ranges broadened, and the melting and clearing temperatures were below their decomposition temperatures. This demonstrates how unproblematic it is to handle these copolyesters.. The copolyesters 6a-e form mesomorphic melts, and their textures are typical for nematic phases. Copolyester 6f behaves differently, showing two species of polymer (see above). The disturbance of 5 in the structure of polyester 6g is so extreme that the polyester is no longer capable of forming liquid crystalline phases.

The TGA traces of samples 6d, 6e and 6f - copolyesters with approximately the same amount of the two different diols 4 and 5 - show the existence of two differing polymer species depicted as two steps in the trace. The existence of these polymers in sample 6f is verified by polarized light microscopy. In contrast to sample 6f, this phenomenon is not visible by polarized light microscopy for the samples 6d and 6e, which only show liquid crystalline phases. The isotropic areas are so minute that they are not visible.

Solubility, molecular weight and ability to form fibres

Solubility

The influence of the disturbance in sequence of the polymer chain through introduction of 5 on the solubility is high. The solubility is already increased when small amounts of 5 are introduced into the polymer chain (see Tab.3).

TABLE 3: Solubilities of the copolyesters 4a-g:

+++ = spontaneously soluble, ++ = soluble, + = partially soluble, - = insoluble, DCB = 1,2-dichlorobenzene, DCM = dichloromethane, Pen = pentane, Hex = hexane, DIGL = diglyme, DIO = dioxane, TRI = trifluoro acetic acid, Py = pyridine, EtOH = ethanol, MeOH = methanol, THF = tetrahydrofuran

solvent	copolyesters						
	<u>6a</u>	<u>6b</u>	<u>6c</u>	<u>6d</u>	<u>6e</u>	<u>6f</u>	<u>6g</u>
CHCl ₃	-(+)	++	++	+	+++	+++	+++
DCB	-	+	+	+	+++	++	+++
Pen	-	-	-	-	-	-	-
Py	-	-	-	-(+)	+++	++	++
Hex	-	-	-	-	-	-	-
DMF	-	-	-	-	-	-	+
EtOH	-	-	-	-	-	-	-
DCM	-	+	+	++	+++	+++	+++
MeOH	-	-	-	-	-	-	-
THF	-	-	-	-	++	++	++
DIGL	-	-	-	-	-	-	-(+)
DMSO	-	-	-	-	-	-	-(+)
DIO	-	-	-	-	+	+	++
DCM	++	+++	+++	+++	+++	+++	+++
TRI							

Molecular weight

The molecular weight of the samples 6e and 6f was measured by GPC. With regards to the GPC measurements, the reference was polystyrene, whereas the investigated polymers are rigid. The average molecular weight of sample 6e is 31,000 and of 6f 11,000. This verifies that the chain length decreases when the amount of 5 is raised.

*Ability to form fibres***TABLE 4: Ability of the copolyesters 6a-g to form fibres**

polymer	length of fibre
6a	2-3 cm
6b	2-3 cm
6c	<10 cm
6d	2-3 cm
6e	<10 cm
6f	2-3 cm
6g	none

The copolyesters 6a-g form only short, brittle fibres (see Tab. 4) which break easily during handling. This behaviour is in contrast to copolyesters with only aromatic units arising from 3 and aromatic diols^{2,3}) having less voluminous units and therefore a higher solid state order with more intense aromatic-aromatic interactions.

A correlation between the quantity of 5 (instead of 4) in the polymer chain and the ability to form fibres does not exist.

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