Polymer Bulletin 33, 497–504 (1994)

Polymer Bulletin

Alkyloxy-substituted liquid-crystalline aromatic copolyesters

3. Synthesis and properties of main chain copolyesters derived from 2,5-bis-(pentyloxy)-terephthaloyl dichloride and aromatic diols

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Summary

The synthesis and characterization of main chain liquid crystalline polyesters arising from 2,5-bispentyloxy substituted terephthalic acid (3) and aromatic diols are described. 3 was prepared from diethyl 2,5-dihydroxyterephthalate and 1-bromopentane. The polyesters were prepared from 4,4'-dihydroxybiphenyl (5), hydroquinone (6), 2,5-dimethyl hydroquinone (8) and the substituted terephthaloyl dichloride (4) in 1,1,2,2-terachloroethane. Their structures were characterized by ^{1}H-NMR, GPC and elemental analyses; their thermal behavior was studied by DSC measurements, microscopy under polarized light, and thermogravimetric analyses. The melting points are in the range of 130-280°C. All of them except of those with a high amount of 2,5-dimethyl hydroquinone (8) form a nematic phase above their melting point.

Introduction

Rigid rod liquid cyristalline polymers are insoluble in common organic solvents and decompose before melting$^{1)}$. Because of their potential use for materials such as high-modulus fibers the structure of the polymers must be modified to make them soluble and meltable. Investigations by Goodman et al.$^{2)}$, Krigbaum et al.$^{3)}$, Lenz et al.$^{4)}$ and Ballauff et al.$^{12)}$ have shown that the melting point can be shifted to lower values and the solubility can be increased by appending flexible substituents to the rigid backbone of the polymers. M. Ballauff et al.$^{6)}$ showed, based on the lattice model of Flory et al.$^{13)}$ for nematic liquids, that the substituents act like "chemical bonded solvents".

In order to obtain liquid crystalline aromatic polyesters with desirable properties such as additives for polyethylene terephthalate-fibers to raise the tensile strength we studied the influence of the correlation of the structure of liquid crystalline main chain polyesters and their thermal behavior. The "basic polyester" in our aim to design liquid crystalline polyesters with interesting properties is poly (4,4'-biphenyldiyl terephthalate) with a melting range of > 650°C. To depress the melting point two pentyloxy substituents were introduced to the terephthalic acid component at the 2 and 5 position. In addition to this we report about two series of polymers

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obtained by direct polycondenzation of 2,5-bis(pentyloxy)terephthaloyl dichloride (4) with 4,4'-dihydroxybiphenyl (5) and hydroquinone (6) (the polymer chain is disturbed in its sequence) and 2,5-bis(pentyloxy)terephthaloyl dichloride (4) with hydroquinone (6) and 2,5-dimethyl-hydroquinone (8) (the polymer chain is disturbed by additional substituents).

To prepare the substituted terephthalic acid diethyl 2,5-dihydroxyterephthalate (1) was refluxed with 1-bromopentane using the method of Claisen[14)]. The obtained diethyl 2,5-bis(pentyloxy)terephthalate (2) was saponified with 5 wt.-% aqueous potassium hydroxide to yield 2,5-bis(pentyloxy)terephthalic acid (3).
The corresponding polyesters were prepared by the solution polycondenzation method described by Dicke and Lenz[15)] as described previously[11)].

Experimental part

Materials

Diethyl 2,5-dihydroxyterephthalate (1) was purified by recrystallization from ethanol; pyridine was dried by distillation over sodium hydroxide; cyclopentanone was dried by distillation over calcium chloride; thionyl chloride was distilled before use; the pentyl bromide was used without further purification. The phenols were purified by recrystallization from aqueous acetic acid (50% by weight); 1,1,2,2-tetrachloroethane was dried by distillation over phosphorus (V) oxide.

Measurements

The molecular weight was measured with a Knauer vapor measure osmometer and by GPC from Waters; 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; mass spectra with a Finnigan 112 S, EI, 80 eV; TGA measurements with a Heraeus TGA 500; DSC-measurements with a Heraeus TA 500S and the ^{13}C NMR spectra with a Bruker AL 250, 250 MHz.

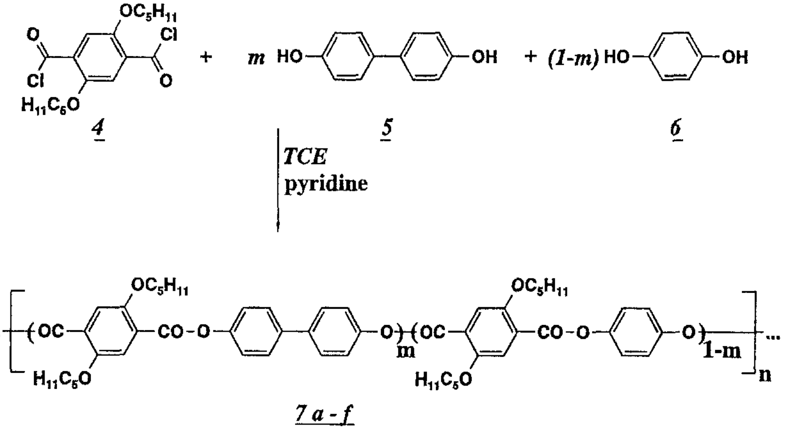
Synthesesis of the monomer (see scheme 1)

2,5-Bis(pentyloxy)terephthalic acid (3):
The synthesis method of 2,5-bis(pentyloxy)terephthalic acid from diethyl 2,5-dihydroxy terephthalate and bromopentane in the presence of potassium carbonate is similar to the methods described in previous papers[11, 16)]. A solution of 25,4 g (0,1 mol) diethyl 2,5-dihydroxyterephthalate, 30,0 g (0,3 mol) potassium carbonate, 1,0 g (0,006 mol) of KI and 31,5g (0,2 mol) 1-bromopentane were refluxed for at least 24 h in cyclopentanone. The yellow color changed to orange color. For forming the ether groups the reaction mixture was refluxed until no diethyl 2,5-dihydroxyterephthalate was left (control by thin-layer chromatography with ethanol/methylene dichloride, 1:10). Then the potassium bromide was filtered

off and washed twice with hot methylene dichloride. The combined filtrates were concentrated and the obtained oil was refluxed with 20 ml ethanol and an excess of 5 wt. % aqueous potassium hydroxide until no educt was seen by thin-layer chromatography (~24 h). Then the water was removed partially in vacuo. The precipitate was filtered off, dissolved in water and the acid was precipitated by acidifying the solution. The acid was purified by recrystallization from methylene dichloride. The sodium salt of the acid which remained in the filtrate was precipitated by adding acetone to the solution. The precipitate was treated as described above. The purity was checked by HPLC to be higher than 99 %.

The 2,5-bis (pentyloxy)terephthalic acid is identical with the product described by Schleeh et al[11].

mp: 157°C (152°C[11])
Yield: 23,7 g (70%)
IR, MS, ^1H NMR:[11]
^{13}C NMR ($CDCl_3$) δ in ppm: 14 (-CH_2-$\underline{C}H_3$); 22 (-CH_2-$\underline{C}H_2$-CH_3); 28 (-CH_2-$\underline{C}H_2$-CH_2-); 29 (-O-CH_2-$\underline{C}H_2$-CH_2-); 71(-O-$\underline{C}H_2$-CH_2-); 118 (-$\underline{C}$=C-); 123 (HOOC-$\underline{C}$=C-); 152 (-RCO-$\underline{C}$=C-); 164 (-$\underline{C}$OOH)

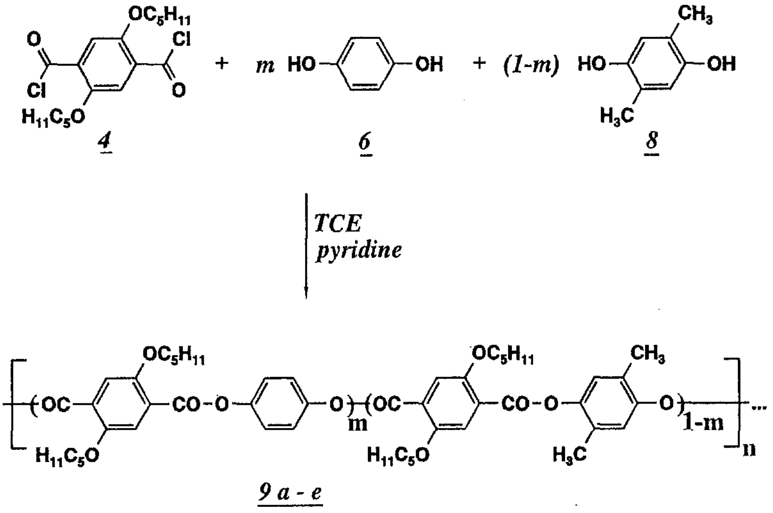


Scheme 1

Synthesis of the polyesters (see scheme 2)

The polyesters 7a-f arising from 2,5-bis(pentyloxy)terephthalic acid (3), 4,4'-dihydroxybiphenyl (5) and hydroquinone (6) and the polyesters 8a-e arising from 2,5-bis(pentyloxy)terephthalic acid (3), 2,5-dimethyl hydroquinone (8) and hydroquinone (6) were prepared as follows:

0,8450 g (2,5 mmol) of 2,5-bis(pentyloxy)terephthalic acid (3) was refluxed 24 h with an excess of freshly distilled thionyl chloride and pyridine. The remaining thionyl chloride was removed by vacuum distillation. 2,5-bis(pentyloxy)-terephthaloyl dichloride (4) was dissolved without further purification8) (in order to prevent hydrolysis) in 8 ml 1,1,2,2-terachloroethane under an argon atmosphere. While stirring 2,5 mmol of the diol or the diol mixture was added at once. Afterwards absol. pyridine was added forming a clear solution. The mixture was stirred and heated up to 100°C for 24 h. If the mixture got to viscous a small amount of 1,1,2,2-terachloroethane was added (~3 ml). The mixture was diluted with methylene dichloride and the polyester was precipitated by pouring the reaction solution into 400 ml of a mixture of methanol/conc. hydrochloric acid (95:5). The polyester was filtrated, washed with methanol and water several times and finally dried over posphorus (V) oxide in vacuo at 80°C. Experimental data see Tab. 1 and Tab. 2.



Scheme 2

TABLE 1: Composition of the reaction mixtures (4 and diol 5, 6 or 8) and elemental analyses of the polyesters 7a-f and 9a-e

polyester	5	6	8	C in %	H in %
				calc/found	calc/found
7a	100	-	-	73.75/70.75	6.60/6.49
7b	80	20	-	73.08/70.91	6.64/6.62
7c	60	40	-	72.36/70.64	6.69/6.22
7d	40	60	-	71.59/69.99	6.74/6.24
7e	20	80	-	70.77/68.59	6.79/6.09
7f	-	100	-	69.89/68.40	6.84/6.78
9a	-	80	20	70.99/69.24	7.78/7.38
9b	-	60	40	70.96/69.01	7.64/7.13
9c	-	40	60	70.93/68.82	7.52/6.89
9d	-	20	80	70.91/69.03	7.41/7.16
9e	-	-	100	70.89/69.50	7.32/7.38

Results and discussion

Thermal behavior

The melting point of the "basic polyester" poly(4,4'-biphenyldiyl terephthalate) decreases as expected when two pentyloxy substituents were introduced to each terephthaloyl unit of the polymer chain. A melting point of the resulting polyester of 212°C is observed in contrast to the melting point for the unsubstituted polyester of higher than 650°C. The additional disturbance in the sequence of the polymer chain by the introduction of hydroquinone (6) causes a further reduction of the melting point up to a content of 60 % 6. By increasing the amount of 6 the melting point raises again. The melting points of the copolyesters 7b-e are below their decomposition points (see Tab.2). The copolyesters 7c and 7d even have their clearing point (transition from the liquid crystaline phase to the isotropic melt) below their decomposition temperature. The polyester 7a decomposes right after it's melting point. The polyester 7f decomposes before melting. The polyesters 7a-f show a mesomorphic melt (transition solid →liquid crystalline phase). They exhibit a nemetic phase and show a threaded texture. The range of the liquid crystalline phase (temperature range of the liquid crystalline phase up to 150°C) increases when 6 is introduced into the polymer chain up to a content of 40% . By further increasing the amount of 6 the temperature range of the liquid crystalline phase decreases again. The endotherms and the exotherms in the DSC traces are very broad and weak due to the polydispersion; no transtion enthalpy were measured. The weak endotherms gradually disappeared upon repeated heating and cooling.

TABLE 2: Yield and properties of the polyesters 7a-f and 9a-e

polymer	yield	M_W	T_m/°C	T_i/°C	T_d/°C[c]
7a	86%	2000[a]	212	330	215
7b	66%	2050[a]	140	240	215
7c	61%	2800[a]	106	260	290
7d	61%	2300[a]	96	245	250
7e	86%	6300[a]	144	260	210
7f	76%	2500[a]	206	230	190
9a	70%	3000[b]	205	275	275
9b	65%	2500[b]	185	235	250
9c	73%	6500[b]	180	-	250
9d	70%	8800[b]	206-235	-	300
9e	71%	12600[b]	230-270	-	300

a) measured by vapor pressure osmometry
b) measured by GPC
c) measured by TGA

M_W = average molecular weight
T_m = melting point
T_i = clearing point
T_d = decompostion point

The polyesters **9a** and **9b** show a mesomorphic melt. If the content of 2,5-dimethyl hydroquinone (**8**) is higher than 40% the polymers do not form mesomorphic melts. The copolyester with a given compositon of 40% **8** and 60 % **6** shows an existence of two species of polymers due to the different reactivities of the two diols. By polarized light mikroscopy anisotropic areas are seen besides of isotropic areas. Up to an amount of 40% **8** the copolyesters exibit a liquid crystalline phase. Higher amounts lead to copolyesters with isotropic melts. The disturbance of the polymer chain by the two additional substituents in the diol component is to large to enable the polymer to form a liquid crystalline phase. The DSC traces behave in the same manner as of the polyesters **7a-f**.

Solubility and molecular weight

The influence of the disturbance in the sequence of the polymer chain by introducing **6** on the solubility is not very high. The introduction of two additional substituents in the diol component (**8**) is much higher. These copolyesters (**9a-e**) are soluble in methylene chloride, chloroform, toluene and 1,2-dichlorobenzene (see Tab.3).

Tab.3: Solubility of the polyesters 7a-f and 9a-e

polyester	CH_2Cl_2	$CHCl_3$	toluene	1,2-dichlorobenzene
7a	++	++	-	-
7b	++	+	-	-
7c	++	+	-	-
7d	++	+	+	-
7e	++	+	+	-
7f	++	++	-	-
9a	++	++	+	++
9b	++	++	+	++
9c	++	++	+	++
9d	++	++	+	++
9e	++	++	+	+

++ = soluble, + = partially soluble - = insoluble

The molecular weight of the samples were measured by vapor osmometry and GPC (see Tab.2). Concerning the GPC measurements, the reference substance was the flexible polymer polystyrene whereas the investigated polymers have ridgid rods.

More detailed investigations of other disturbances of the polymer chain as well as a study of different polycondenzation methods to get higher molecular weights will be published soon.

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Received: 13 July 1994/Accepted: 2 August 1994