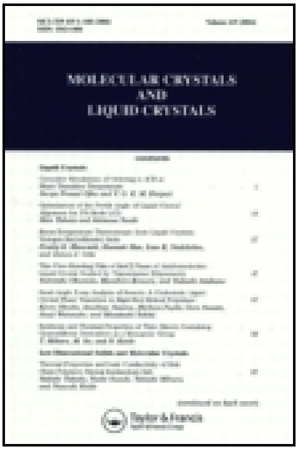

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Synthesis and Properties of Stiff-Chain Polyesters Based on the Terphenyl Moiety

U. Tiesler [a] , T. Pulina [a] , M. Rehahn [a] & M. Ballauff [a]

[a] Polymer-Institut, Universität (TH) Karlsruhe, Kaiserstraße 12, 76128, Karlsruhe, Germany

Version of record first published: 24 Sep 2006.

To cite this article: U. Tiesler , T. Pulina , M. Rehahn & M. Ballauff (1994): Synthesis and Properties of Stiff-Chain Polyesters Based on the Terphenyl Moiety, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 243:1, 299-311

To link to this article: http://dx.doi.org/10.1080/10587259408037772

Mol. Cryst. Liq. Cryst., 1994, Vol. 243, pp. 299–311
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Printed in the United States of America

Synthesis and Properties of Stiff-Chain Polyesters Based on the Terphenyl Moiety

U. TIESLER, T. PULINA, M. REHAHN and M. BALLAUFF

Polymer-Institut, Universität (TH) Karlsruhe, Kaiserstraße 12, 76128 Karlsruhe, Germany

(Received June 2, 1992; in final form June 28, 1993)

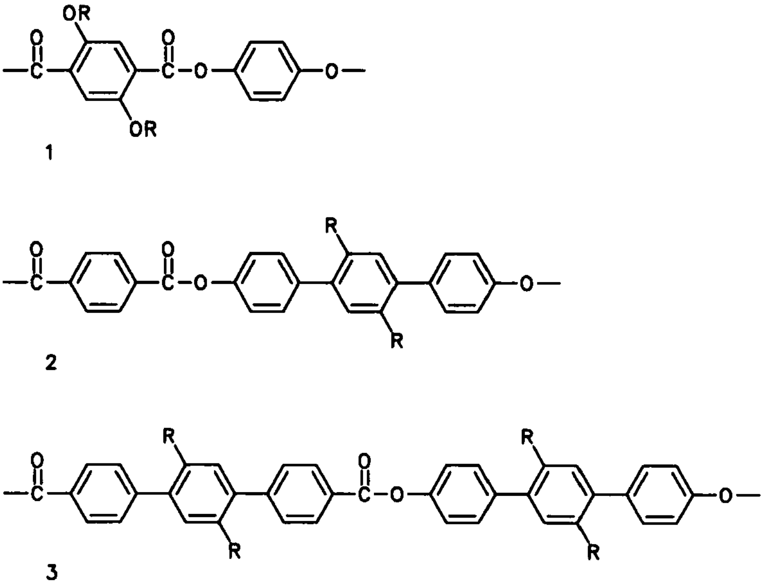
The synthesis and the characterization of rigid-rod polyesters **2** and **3** deriving from 2′,5′-dihexyl-*p*-terphenyl-4,4″-diol **7** and from 2′,5′-dihexyl-*p*-terphenyl-4,4″-dicarboxylic dichloride **8** together with a facile synthesis of monomers **7** and **8** is described. It is shown that these polyesters exhibit a very good solubility in common organic solvents. Therefore these materials present interesting model compounds for comprehensive studies of rigid-rod polymers in solution.

Keywords: stiff-chain polyesters, terphenyl, rigid-rod polymers

INTRODUCTION

Stiff-chain polymers with flexible side chains[1,2] present a very interesting class of macromolecular materials since the rod-like shape of the main chains leads to the formation of liquid crystalline phases. The side chains increase the solubility and lower the melting point in a well-controlled fashion. As a consequence, by varying the number and the length of the side chains the various transitions can be shifted to a range of temperature where thermal decomposition does not play any role. This is of particular interest for studies at high temperatures in the vicinity of the isotropic state. In addition to this, most of the materials investigated up to now exhibit a sufficient solubility in common organic solvents which allows studies in dilute solution. Thus the notion[3] of the side chains as a "bound solvent" is fully corroborated by the experimental findings obtained from these systems.

In many cases *n*-alkyl or *n*-alkoxy side chains were employed, in some cases oligoethyleneoxy chains.[1] For typical aromatic main chain polyesters as e.g. polyester **1** and in particular for stiff-chain polyamides the number of alkyl side chains and/or their length necessary to ensure good solubility and a melting point low enough to study liquid crystalline phases is quite high.[1,4] On the other hand, the marked difference of the polarity of main and side chains leads to strong segregation in the solid state as well as in the liquid crystalline phases.[1,5] The resulting phases exhibit therefore a layered structure which clearly is a consequence of the microphase separation of main and side chains. Concomitantly,



SCHEME 1

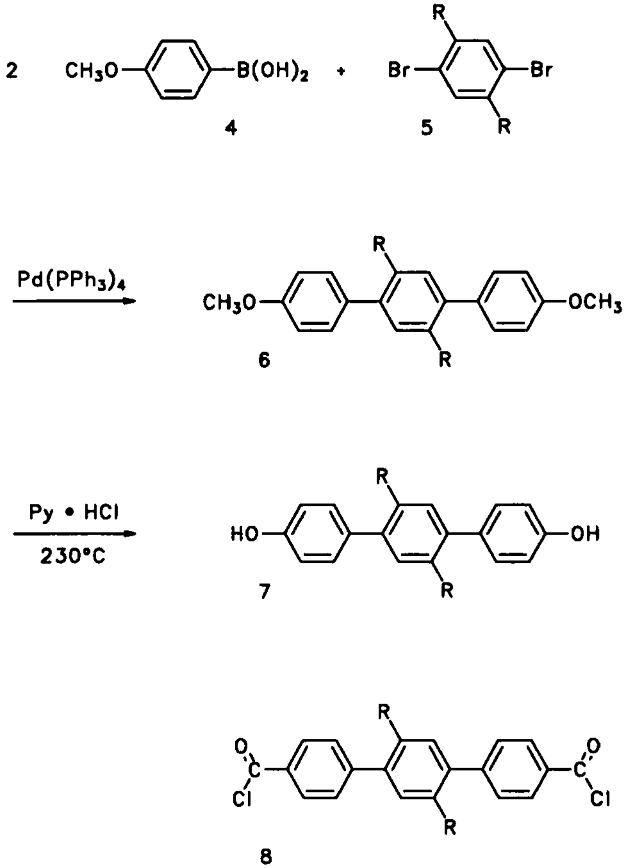
there is a tendency for association in solution which renders investigations in solution by e.g. light scattering a difficult or in many cases an impossible task.[5] This is due to the fact that very often a given organic solvent is only suited to solubilize either the main or the side chains. Replacement of the *n*-alkyl groups by oligoethylene oxide moieties[6] partly remedies this problem but is followed by a decrease in thermal stability.

In a number of recent publications[7,8] it has been shown that the Pd-catalyzed coupling of benzeneboronic acids with aromatic bromides is an excellent method for synthesizing substituted poly(*p*-phenylene)s and their respective oligomers.[9] Thus, synthetic routes to derivatives of terphenyl or higher oligomers are now available. In this publication we present the synthesis and a first survey of the properties of polyesters **2** and **3** obtained from the terphenyl monomers **7** and **8**. A facile route to monomer **7** will be given also. Polyesters **2** and **3** which have been studied recently by Kallitsis *et al.*[10] present highly interesting materials since twisted biphenyl and terphenyl moieties are known to prevent crystallization and to increase solubility.[11] Therefore polyesters **2** and **3** certainly will exhibit an improved solubility despite the fact that the number of side chains per repeating unit is less than in polymer **1**. In addition to this, the extended aromatic part of these materials certainly will be followed by a higher persistence length of the main chains as compared to polyester **1**. On the other hand, the decreased number of side chains per repeating unit will largely suppress side chain crystallization which also will lead to an improved solubility. It will be shown that for these reasons polyesters **2** and **3** present good model systems for investigations of stiff chains polymers in solution.

SYNTHETIC ROUTES

For the synthesis of monomer **7** the following route turned out to be most suitable: 4-Methoxybenzeneboronic acid[16] and 2,5-di-*n*-hexyl-1,4-dibromobenzene are coupled to yield compound **6**. Cleavage of the ether groups is achieved easily by heating of **6** with pyridinium hydrochloride to elevated temperatures. Monomer **8** was synthesized along the lines given previously by Kallitsis *et al.*[9]

For polycondensation a precalculated excess of the phenolic compound **7** was reacted with terephthaloyl dichloride **9** (polyester **2**) or the acid dichloride **8** (polyester **3**) in presence of triethyl amine. After completion of the polycondensation the OH endgroups were closed by treating the reaction mixture with *p*-anisoyl chloride. By this method free endgroups can be largely suppressed. A previous investigation[5] had shown that carboxyl or hydroxy endgroups may be responsible for a part of the association phenomena hampering investigations in solution.



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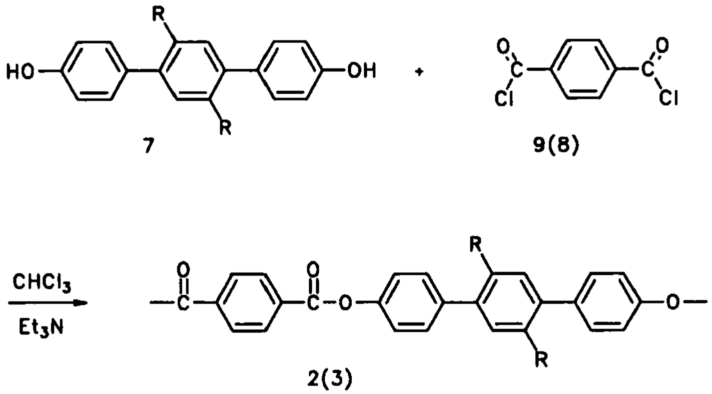

SCHEME 3

EXPERIMENTAL

Materials

p-Methoxybromobenzene, *p*-anisoyl chloride, pyridinium hydrochloride and trimethylborate were purchased from Fluka and used as received. The catalyst $Pd(PPh_3)_4$ (Aldrich) was also used without further purification. Triethyl amine, chloroform and toluene used in the course of polycondensations were analytical grade and carefully dried prior to use. *o*-Dichlorobenzene (Fluka p.a.) and cyclohexene (Fluka p.a.) were used as received. All reactions were carried out under atmosphere of dry nitrogen.

Methods

^{1}H- and ^{13}C-NMR-spectra were recorded at room temperature (**2** at 353 K) in deuterated chloroform, tetrachloroethane, or dimethylsulfoxide using a Bruker AM 400 spectrometer. Tetramethylsilane served as an internal standard. Osmometric measurements were performed using a Knauer membrane osmometer 01.00 at 60°C in *o*-dichlorobenzene. A membrane made from regenerated cellulose (Knauer Y1245 organ. feinst) proved to be suitable under these conditions. Light scattering experiments were done using a Sofica light scattering apparatus equipped with a laser operating at 632.8 nm. The refractive increment was determined using a Brice-Phoenix differential refractometer. Thermal analysis was performed using a Mettler DSC 30 at heating rates of 20 K/min. For polarizing microscopy a Mettler FP 82 hotstage was mounted on a Zeiss Universalmikroskop. Gel permeation chromatography (GPC) was run using two columns (PSS gel SVD 10^3 Å, 5 μm, and SVD 10^5 Å, 5 μm) with chloroform (stabilized with 60 ppm amylene) as eluent. Viscosity measurements were performed in chloroform at 25°C using an Ubbelohde viscosimeter. Wide-angle x-ray diffractograms (WAXS) were monitored with a Siemens D5000 goniometer equipped with a hotstage and a monochromator using Cu-K_α radiation.

2′,5′-Di-n-hexyl-4,4″-dimethoxy-p-terphenyl **6**. 33.4 g (0.22 mol) **4** and 40.4 g (0.10

mol) of **5** are suspended in a mixture of 200 ml aqueous 2N-Na_2CO_3 solution and 200 ml toluene together with 600 mg $Pd(PPh_3)_4$ and refluxed with good stirring. After 10 hours the organic phase is separated, dried over $MgSO_4$ and filtered through silica gel to remove the catalyst. The crude product **6** which resulted after removal of the solvent in very good yield (95%) could be directly used for the next step. Recrystallization from ethanol/water lead to crystals with a melting point of 26–28°C.

^1H-NMR ($CDCl_3$): $\delta = 0.81$ (t; 6H, CH_3), 1.22 (m; 12H, CH_2), 1.45 (m; 4H, β-CH_2), 2.57 (t; 4H, α-CH_2), 3.78 (s; 6H, O—CH_3), 6.92, 7.27 (2d; 8H, aromatic-$H^{2,2'',3,3''}$), 7.11 (s; 2H, aromatic-$H^{3'6'}$)

^{13}C-NMR ($CDCl_3$): $\delta = 13.97$ (q; CH_3), 22.46, 29.18, 31.33, 31.49, 32.64 (5t; CH_2), 55.21 (q; O—CH_3), 113.37 (d; aromatic-$C^{3,3''}$), 130.27 (d; aromatic-$C^{2,2''}$), 130.96 (d; aromatic-$C^{3',6'}$), 134.40 (s; aromatic-$C^{1,1''}$), 137.49 (s; aromatic-$C^{2',5'}$), 140.14 (s; aromatic-$C^{1',4'}$), 158.46 (s; aromatic-$C^{4,4''}$)

2′,5′-Di-n-hexyl-p-terphenyl-4,4″-diol **7**. 46 g (0.10 mol) of **6** was heated with 116 g pyridinium hydrochloride to 230°C with good stirring for 10 hours. After cooling down the melt was crushed into small pieces. 300 ml acidified water and 300 ml tert.-butylmethyl ether were added and the whole mixture was stirred for 20 minutes. The aqueous phase was extracted three times with 200 ml tert.-butylmethyl ether. The combined organic phases were dried with $MgSO_4$ and the ether removed in vacuo. Recrystallization from *n*-hexane/toluene (3/1) yielded 33 g **7** (77%). m.p.: 139–140°C.

^1H-NMR ($CDCl_3$/DMSO-d_6): $\delta = 0.82$ (t; 6H, CH_3), 1.18 (m; 12H, CH_2), 1.45 (m; 4H, β-CH_2), 2.54 (m; 4H, α-CH_2), 6.85, 7.13 (2d; 8H, aromatic-$H^{2,3,2'',3''}$), 7.03 (s; 2H, aromatic-$H^{3',6'}$), 9.04 (s; 2H, 2OH)

^{13}C-NMR ($CDCl_3$/DMSO-d_6): 13.29 (q; CH_3), 21.63, 28.36, 30.56, 30.63, 31.78 (5t; CH_2), 114.19 (d; aromatic-$C^{3,3''}$), 129.38 (d; aromatic-$C^{2,2''}$), 130.11 (d; aromatic-$C^{3',6''}$), 131.99 (s; aromatic-$C^{1,1''}$), 136.54 (s; aromatic-$C^{2',5'}$), 139.34 (s; aromatic-$C^{1',4'}$), 155.35 (s; aromatic-$C^{4,4''}$)

2′,5′-Di-n-hexyl-p-terphenyl-4,4″-dicarboxylic acid diethylester. 10.0 g (0.03 mol) 2,5-di-*n*-hexyl-1,4-benzenediboronic acid and 15.1 g (0.066 mol) ethyl *p*-bromobenzoate together with 350 mg $Pd(PPh_3)_4$ were suspended in a mixture of 100 ml aqueous 1 N Na_2CO_3 solution and 100 ml toluene under an atmosphere of nitrogen and refluxed for 48 hours. The organic phase was dried with $MgSO_4$ and the catalyst removed by filtration over silica gel. The crude product was sufficiently pure for the next step. Recrystallization from ethanol yielded white crystals with a melting point of 73–74°C.

^1H-NMR ($CDCl_3$): $\delta = 0.80$ (t; 6H, CH_3), 1.18 (m; 12H, CH_2), 1.46 (m; 10H, β-CH_2,—O—CH_2—$C\underline{H}_3$), 2.58 (t; 4H, α-CH_2), 4.45 (q; 4H, —O—CH_2), 7.14 (s; 2H, aromatic-$H^{3',6'}$), 7.45, 8.13 (2d; 8H, aromatic-$H^{2,3,2'',3''}$)

^{13}C-NMR ($CDCl_3$): $\delta = 14.10$, 14.58 (2q; CH_3, —O—CH_2—$C\underline{H}_3$), 22.80, 29.34, 31.71, 31.84, 32.93 (5t, CH_2), 61.11 (t; —O—CH_2), 128.97 (s; aromatic-$C^{4,4''}$), 129.13, 129.56 (2d; aromatic-$C^{2,3,2'',3''}$), 131.16 (d; aromatic-$C^{3',6'}$), 137.90 (s; aromatic-$C^{2',5'}$), 140.62 (s; aromatic-C1′,4′), 146.79 (s; aromatic-$C^{1,1''}$), 166.98 (s; $\underline{C}$OOEt)

2′,5′-Di-n-hexyl-p-terphenyl-4,4″-dicarboxylic dichloride **8**. 13 g of the diethyl ester was dissolved in 150 ml ethanol with slight warming and 50 ml of aqueous 20% KOH were added. The mixture was kept at 50°C for 24 hours. After adding 50 ml of dilute HCl and cooling to room temperature the free acid was filtered off, washed carefully with water and dried in vacuo. Recrystallization from 700 ml ethanol yielded white needles (yield: ca. 90%) which melt around 290°C with decomposition.

^{1}H-NMR (DMSO-d_6/acetone-d_6): δ = 0.80 (t; 6H, CH_3), 1.17 (m; 12H, CH_2), 1.50 (m; 4H, β-CH_2), 2.60 (t; 4H, α-CH_2), 7.15 (s; 2H, aromatic-$H^{3',6'}$), 7.50, 8.10 (2d; 8H, aromatic-$H^{2,3,2'',3''}$), 12.90 (broad s; 2H, COOH)

^{13}C-NMR (DMSO-d_6/acetone-d_6): δ = 13.61 (q; CH_3), 22.32, 28.86, 31.13, 31.23, 32.44 (5t; CH_2), 129.48, 129.56 (2d; aromatic-$C^{2,3,2'',3''}$), 130.09 (s; aromatic-$C^{4,4''}$), 130.98 (d; aromatic-$C^{3',6'}$), 137.60 (s; aromatic-$C^{2',5'}$), 140.55 (s; aromatic-$C^{1',4'}$), 146.20 (s; aromatic-$C^{1,1''}$), 167.83 (s; $\underline{C}$OOH)

The free acid could be converted into the acid chloride **8** by suspending it in 40 ml toluene and refluxing with an excess of thionyl chloride for 24 hours in practically quantitative yield. Recrystallization was done using hexane. m.p.: 124–125°C.

^{1}H-NMR ($CDCl_3$): δ = 0.80 (t; 6H, CH_3), 1.21 (m; 12H, CH_2), 1.48 (m; 4H, β-CH_2), 2.57 (t; 4H, α-CH_2), 7.16 (s; 2H, aromatic-$H^{3',6'}$) 7.53, 8.20 (2d; 8H, aromatic-$H^{2,3,2'',3''}$) ^{13}C-NMR ($CDCl_3$): δ = 14.23 (q; CH_3), 22.78, 29.10, 31.58, 31.72, 32.86 (5t; CH_2), 130.10, 131.62 (2d; aromatic-$C^{2,3,2'',3''}$), 131.04 (d; aromatic-$C^{3',6''}$), 132.28 (s; aromatic-$C^{4,4''}$), 138.08 (s; aromatic-$C^{2',5'}$), 140.00 (s; aromatic-$C^{1',4'}$), 149.56 (s; aromatic-$C^{1,1''}$), 167.95 (s; COCl)

Polycondensation. For a given degree of polymerization precalculated amounts of the phenolic component **7** were dissolved with 10 mmol of the respective acid chloride in 50 ml of dry mixture of $CHCl_3$/toluene (10/1) with slight warming. After dissolution of all educts 4 ml triethyl amine in 6 ml chloroform were added dropwise. The extent of reaction could be followed by a strong rise of the solution viscosity. After stirring for 4 hours at 60°C a fourfold excess of anisoyl chloride dissolved in 5 ml chloroform was added and the mixture stirred for an additional hour. The polyester was precipitated into methanol and purified by dissolution in chloroform and reprecipitation into methanol. Polymer **2**: ^{1}H-NMR ($C_2D_2Cl_4$): δ = 0.86 (6H, CH_3), 1.25 (12 H, CH_2), 1.53 (4H, β-CH_2), 2.61 (4H, α-CH_2), 7.33 (2H, aromatic-$H^{3',6'}$), 7.44, 7.61 (8H, aromatic-$H^{2,3,2'',3''}$), 8.37 (4H, terephthalic-H)

^{13}C-NMR ($C_2D_2Cl_4$): δ = 13.67 (q; CH_3), 22.67, 28.83, 30.91, 31.28, 32.41 (5t; CH_2), 120.75 (d; aromatic-$C^{3,3''}$), 130.04, 130.20 (2d; aromatic-$C^{2,2''}$, terephthalic-$C^{2,3,5,6}$), 130.68 (d; aromatic-$C^{3',6'}$), 133.99 (s; terephthalic-$C^{1,4}$), 137.26 (s; aromatic-$C^{2',5'}$), 139.73, 139.89 (2s; aromatic-$C^{1,4',1',1''}$), 149.54 (s; aromatic-$C^{4,4''}$), 164.02 (s; -COOR)

Polymer **3**: ^{1}H-NMR ($CDCl_3$): δ = 0.85 (6H, CH_3), 1.22 (12H, CH_2), 1.50 (4H, β-CH_2), 2.62 (4H, α-CH_2), 7.19 (2H, aromatic-$H^{3',6'}$), 7.35 (O-aromatic-$H^{2,2''}$), 7.45 (O-aromatic-$H^{3,3''}$), 7.54 (CO-aromatic-$H^{2,2''}$), 8.31 (CO-aromatic-$H^{3,3''}$)

^{13}C-NMR ($CDCl_3$): 13.97 (q; CH_3), 22.46, 29.12, 31.46, 32.60 (5t; CH_2), 115.0 (q; Ar—O—CH_3), 121.20 (d; O—Ar—$C^{3,3''}$), 129.5–132.0 (all other Ar—C), 137.56 (s; Ar—$C^{2',5'}$), 140.50 (s; Ar—$C^{3,3''}$), 147.40 (s; CO—Ar—$C^{1,1''}$), 150.83 (s; O—Ar—$C^{4,4''}$), 165.12 (COOR)

RESULTS AND DISCUSSION

As expected from the considerations given in the introduction polyesters **2** and **3** exhibit a good solubility in common organic solvents as e.g. chloroform. Also, the tendency of gelation at elevated concentration seems to be less pronounced than in other systems studied so far.[1,5] Thus the number average molecular weight M_n of all materials could be determined by osmometry in *o*-DCB at 60°C. Figure 1 shows the reduced osmotic pressure as function of concentration. With exception of the smallest molecular weight the osmotic virial coefficient A_2 is constant within the limits of error as expected for stiff-chain polymers.[12] The extrapolation to vanishing concentration can be done with good accuracy. There is no indication

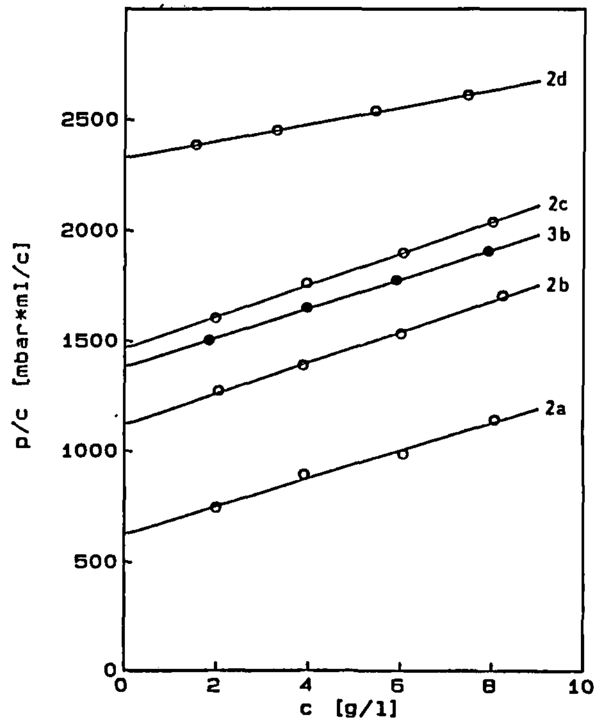

FIGURE 1 Reduced osmotic pressure of solutions of **2** and **3** in *o*-dichlorobenzene as function of concentration.

TABLE I

Characterization of Polyesters **2** and **3**

$P_{theor.}$	M_n(osmom.)	$P_{n,osm.}$	$[\eta]/cm^3\ g^{-1}$	$M_{w,LS}$	P_w/P_n	$\langle s^2\rangle^{1/2}/nm$	$A_{2,osm}\ 10^3$	$A_{2,LS}\ 10^3$
∞	42.500	76	867	130.000	3.0	64	2.3	1.7
60	24.800	44	463	47.200	1.9	32	2.5	2.6
40	19.000	34	395	31.100	1.6	31	2.6	2.4
20	11.700	21	236	20.400	1.7	25	1.4	2.5
∞	42.700	48	868	-	-	-	3.6	-
40	23.800	26	413	-	-	-	2.2	-
20	17.700	19	374	-	-	-	1.8	-

nol·cm^{3}g^{-2}.

of strong association which would show up in a downward curvature of the plots in Figure 1. The values of M_n therefore can be obtained with good accuracy. Table I gathers the respective data together with the resulting virial coefficients.

The reduced viscosities and the intrinsic viscosities (cf. Figure 2 and Table I) are considerably higher than the respective data obtained from polyesters **1** for comparable molecular weights.[5] This directly points to a much higher persistence length of materials **2** and **3**. The high stiffness also leads to deviations from linearity in the plots (Figures 2a and 2b) even at small concentrations. Therefore only data obtained in the dilute regime ($[\eta] \cdot c < 1$) were used for the extrapolation of the intrinsic viscosities. On the other hand, these deviations give clear indication of the onset of hydrodynamic interaction between the rod-like macromolecules which will be analyzed in a forthcoming publication.

The solubility of polyesters **2** is high enough to allow light scattering studies in solution. Previous investigations of polyester **1** had shown that the mixture of the isorefractive solvents chloroform and cylcohexene is most suitable for this purpose since it minimizes association. Also, the refractive index increment found for solutions of **2** in this mixture is quite high (0.161 cm³/g). A typical Zimm-plot is displayed in Figure 3 showing that both extrapolations can be done with sufficient accuracy. Also, the data of the second virial coefficient A_2 compare favourably with the respective values obtained from osmometry (see Table I). Values at smaller

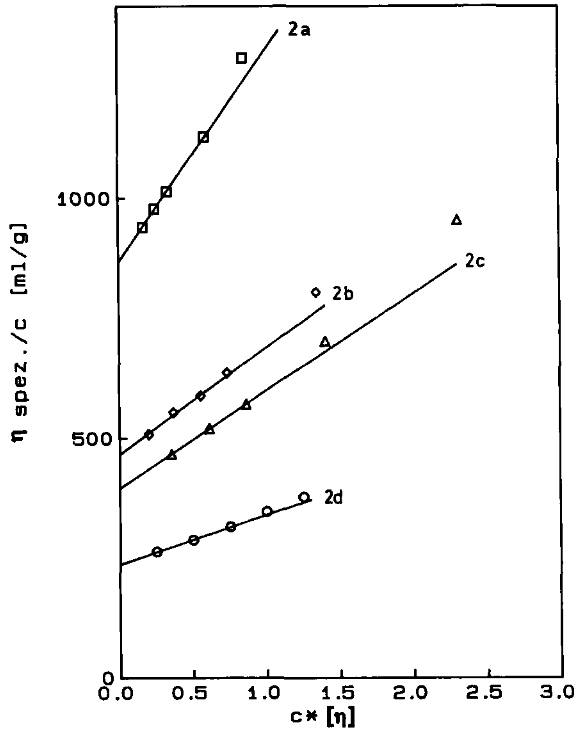

FIGURE 2a Specific viscosity of polyesters **2** as function of the overlap parameter $[\eta] \cdot c$ for different molecular weights.

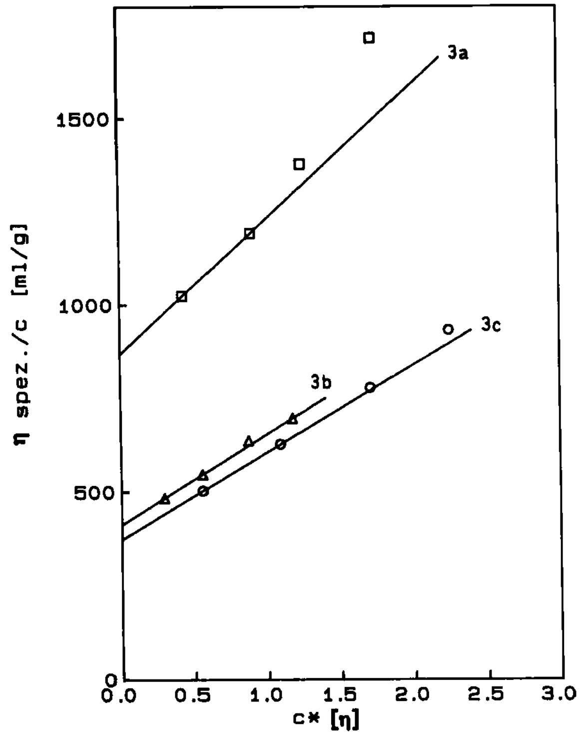

FIGURE 2b Specific viscosity of polyesters **3** as function of the overlap parameter [η] · *c* for different molecular weights.

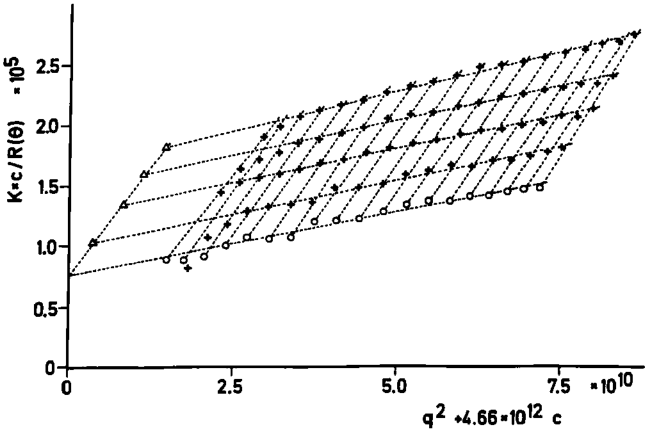

FIGURE 3 Zimm-plot of light scattering measurements of polyester **2b** monitored at 25°C in a mixture of chloroform/cyclohexene (3/1).

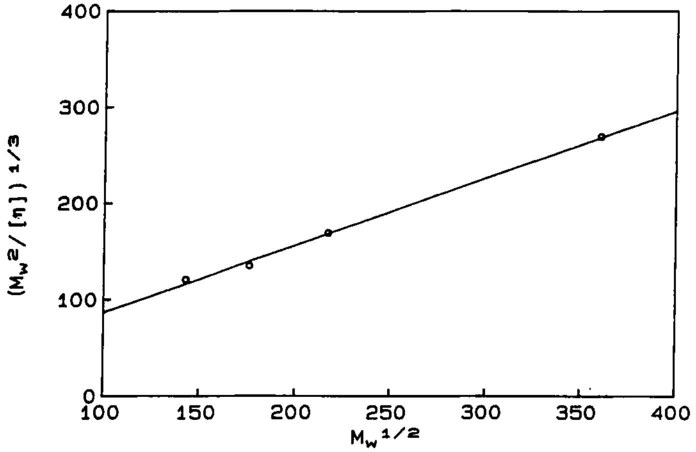

FIGURE 4 Bohdanecky plot of the intrinsic viscosities of polyesters **2**.

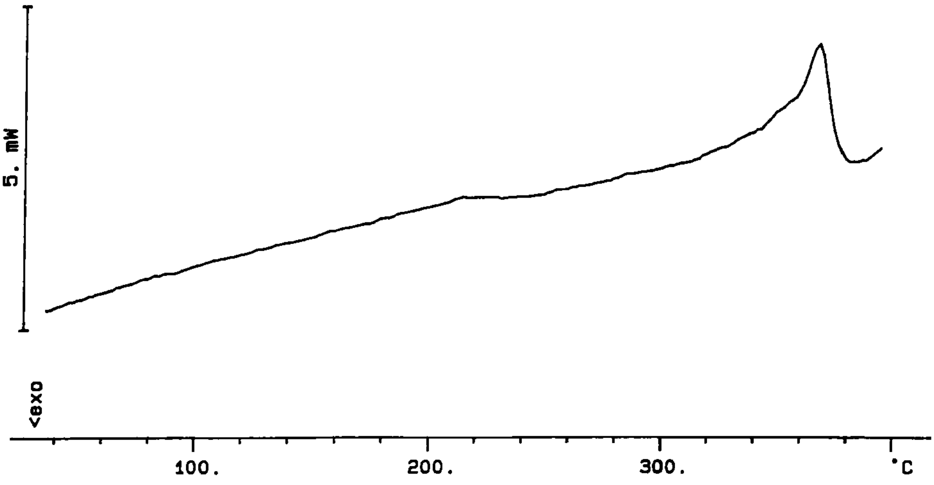

FIGURE 5 Thermal analysis of polyester **2b** monitored with 20 K/min.

angles, however, reveal a residual tendency for association in this regime of concentration. Therefore the present data of the radius of gyration given in Table I must be still regarded as approximative. Smaller concentrations could not be employed because of the deterioration of the signal-to-noise ratio. Attempts to measure the scattering intensities for solutions of polyester **3** in the same regime of concentration failed so far since the resulting angular dependence pointed to non-negligible association under these conditions.

The present data obtained from osmometry and light scattering give also indication about the breadth of the molecular weight distribution. The polydispersity as expressed by M_w/M_n seems to increase with molecular weight but more data are needed for an extended discussion of this point. The GPC analysis furthermore showed that all materials investigated here exhibit an unimodal distribution.

Although the present light scattering experiments suggest that the concentrations employed should be lowered further, the weight average molecular weights of **2** can be obtained in sufficient accuracy. These data gathered in Table I together with the respective intrinsic viscosities may serve for an estimate of the persistence length of polyesters **2** using Bohdanecky's method.[13] The application of this procedure to data of the intrinsic viscosity has been discussed at length recently[5,14] and for details of the method the reader is referred to References 5, 13 and 14. Figure 4 displays the Bohdanecky plot of the intrinsic viscosities of polyesters **2**. The evaluation along the lines given in Reference 13 leads to a persistence length of 7.2 nm. As expected from the general considerations given above the persistence length resulting from this procedure is higher than the one found for polyesters **1**. The stiffness of the latter material is mainly determined by the out-of-plane fluctuations of the ester bond[15] which may be enhanced by the substitution in ortho position. For polyesters **2** and **3** this effect certainly will be present too but much less pronounced since the ratio of the phenyl groups to the ester bonds is more favourable here. Also, there is no substituent in *o*-position to the ester group.

The enhanced stiffness of the main chains together with the reduced number of side chains per repeating unit is followed by a different phase behaviour when compared to polyesters **1** (cf. Reference 5 for a discussion of the phase behaviour of **1**). In agreement with the findings of Kallitsis *et al.*[10] the WAXS diffractograms exhibit only a broad peak in the region of low angles and a broad halo in the wide angle region. Thus there is no pronounced long range organization of the molecules as found in systems with more side chains per repeating unit.[1,2] Obviously the distance between the side chains is too great to allow a regular packing as found[1,5] for polyesters **1**.

Since there is no indication of crystallization or regular packing in polyesters **2** and **3** the thermal analysis only exhibits a single signal at elevated temperatures. Figure 5 displays a typical result of a DSC run of polyester **2b** (cf. Table I) monitored at 20 K/min. It has to be noted that the pristine materials exhibited small signals throughout the whole range of temperatures of thermal analysis. The respective WAXS analysis, however, did not reveal any significant change in this range of temperatures. Therefore the polyesters were first heated to 200°C with 20 K/min and then cooled down with the same rate. Subsequent runs (see Figure 5) then only revealed a single high temperature transition. As could be shown by polarizing microscopy this temperature (cf. Table I) is the transition to the isotropic state. The fine Schlieren texture seen by polarizing microscopy below this point indicates the occurrence of a nematic phase but this conclusion is tentative in absence of further information.

Acknowledgment

Financial support by the EC (BRITE/EURAM project BE 4490-90), by the AIF (grant 8528), and by the Bundesministerium für Forschung und Technologie is gratefully acknowledged.

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