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Chain Rigidity of Substituted Aromatic Polyesters Containing Oligophenyl Units in the Main Chain

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ABSTRACT: Asymmetrically phenyl substituted polyesters are soluble even when terphenyl (**1**) or quinquephenyl (**2**) moieties are introduced in the main chain. The polymers were fractionated from 1,1,2,2-tetrachloroethane solutions with methanol. The fractions obtained were studied in detail by viscosimetry, light scattering, and size-exclusion chromatography (SEC). A conformational analysis in solution was performed by treating the intrinsic viscosities as a function of molecular weight. The results obtained gave a Kuhn length of 224 Å for polyester **1** and 340 Å for polyester **2**. These results show that in dilute solutions the polyesters studied do not behave as perfect rigid rods. However, the persistence length values obtained here are considerably higher than those derived for substituted aromatic polyesters.

Introduction

Rigid-rod macromolecules containing aliphatic or aromatic substituents have attracted considerable attention because of their improved processability compared to their unsubstituted analogues. Aromatic polyesters bearing lateral alkyl[1−3] or alkoxy[4,5] substituents have been studied thoroughly in regard to their improved solubility and mesomorphic properties. However, alkyl or alkoxy side groups lower thermal stability; therefore, substituents of increased thermal stability recently have received increased attention.[6−13]

The possibility of extending the aromatic part in aromatic polyesters has been studied.[9−14] Introduction of substituted *p*-terphenyl moieties into the main chain led to polymers with considerably increased rigidity, which were also soluble in common solvents.[15,16] A further increase in the aromatic part to the quinquephenyl moiety[9,17] led to soluble polymers when either aliphatic[9] or asymmetrically phenyl substituted diols or diacids were used.[17]

Because of the increased solubility of the substituted aromatic polyesters, their main chain stiffness could be tested by estimation of the persistence length.[3,5,8,15,16,18] The unsubstituted polyesters are not soluble; therefore, there are no experimental results on their persistence length. Experimental values for the substituted aromatic polyesters were significantly lower than the theoretical predictions,[19] and the observed differences were attributed to the torsional fluctuation about the ester bond.[3,20]

In the present work, we report on the characterization of phenyl-substituted polyesters containng the terphenyl (**1**) and quinquephenyl (**2**) units (Scheme 1) in the main chain. Molecular weights ($\overline{M}_w$) were determined by using static light scattering. The rigidity of the polymers synthesized was tested by estimation of the statistical segment length using the relationship between viscosity and molecular weight.

Scheme 1

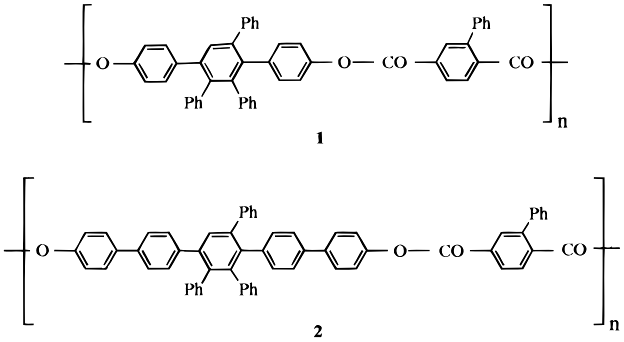

Table 1. Viscosity Data for Polyesters 1 and 2

Polyester **1**			Polyester **2**		
fraction	$[\eta]_{30°C}$ (mL/g)	$[\eta]_{60°C}$ (mL/g)	fraction	$[\eta]_{30°C}$ (mL/g)	$[\eta]_{60°C}$ (mL/g)
1a	483	400	**2a**	328	280
1b	180	152	**2b**	280	235
1c	148	115	**2c**	111	94
1d	72	62	**2d**	49	40
1e	41	28			

Experimental Section

The synthesis of the polyesters was carried out as in the case of the 2,5-diphenylterephthalic acid analogue,[9] as was published previously.[17] Fractionation of polyester **1** was performed by dissolving 3 g of polymer in 300 mL of 1,1,2,2-tetrachloroethane. Five fractions were obtained by successive precipitation with methanol added gradually at 22 °C. Each gel phase was precipitated by pouring in an excess of methanol. All fractions were dried at 80 °C in a vacuum oven for 48 h. Fractionation of polymer **2** was performed similarly in 1,1,2,2-tetrachloroethane with methanol. The results of the various fractions are shown in Table 1.

Intrinsic viscosity measurements were performed in 1,1,2,2-tetrachloroethane at 30 and 60 °C using an Ubbelohde-type viscometer in a Schott Gerate AVS 310.

Light scattering experiments were performed by using a Sematech (France) Model SEM RD computer spectrogoniometer equipped with a laser operating at 632.8 nm. The Zimm plots are given directly from the software controlling the apparatus. The refractive index increment (d*n*/d*c*) was determined by using a Chromatix KMX-16 laser differential refractometer at the same wavelength but different concentration and extrapolated to the vanishing concentration. The values obtained were 0.204 and 0.198 for polyesters **1** and **2**, respectively. All measurements were made using 1,1,2,2-tetrachloroethane at 45 °C. The solutions were first heated at 60 °C for 2 days and then sonicated in a Soniprep 150 apparatus. To remove dust particles, the solvent and all solutions were filtered through 0.2 μm pore size filters (Millipore Waters).

Size-exclusion chromatography was performed using a Waters 600E chromatograph coupled with a 901 photodiode array detector at 254 nm through Ultrastyragel columns with 500, 10^4, and 10^5 Å at 25 °C, with chloroform as solvent.

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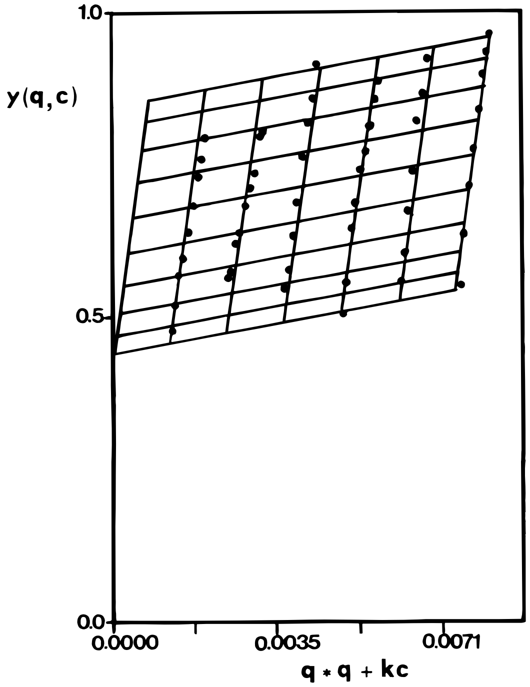

Figure 1. Zimm plot of light scattering measurements for fraction **1a** at 45 °C in 1,1,2,2-tetrachloroethane, at concentrations $c = 0.25, 0.49, 0.74, 0.99, 1.23$, and 1.48 g/L. The axes are normalized.

Samples of 1 mg were first dissolved in a few drops of 1,1,2,2-tetrachloroethane, and then 1 mL of chloroform was added. The same system was used for calibration with polystyrene standards.

Results

Intrinsic Viscosities. Intrinsic viscosity values $[\eta]$, at 30 and 60 °C for fractions of polyesters **1** and **2** are collected in Table 1. Linear plots of η_{sp}/c versus c were obtained in the regime of concentrations used in this study ($c < 0.4$ g/dL) and allowed reliable extrapolation to vanishing concentration with good accuracy. In both cases, viscosity was significantly decreased with temperature. Usually, $[\eta]$ decreases with temperature for extended chain polymers.[21] The present results show a stronger decrease, which at the moment cannot be explained.

Static Light Scattering. The solutions of the different fractions of the polymers studied were first sonicated and then used for the light scattering experiments. Sonication facilitates the dissolution of the polymers. Intrinsic viscosity was determined before and after sonication and in all cases was similar within experimental accuracy. Concentrations used were below 0.2 g/dL, and because of the high value of the refractive index increment, measurements at very low concentrations (0.02 g/dL) could be performed without problems. Figures 1 and 2 display the light scattering intensities for the higher molecular weight fractions for both structures in Zimm plots. Data analysis was performed to obtain the weight-average molecular weight, $\bar{M}_w$, the radius of gyration, R_g, and the second virial coefficient, A_2. The calculated results are shown in Table 2.

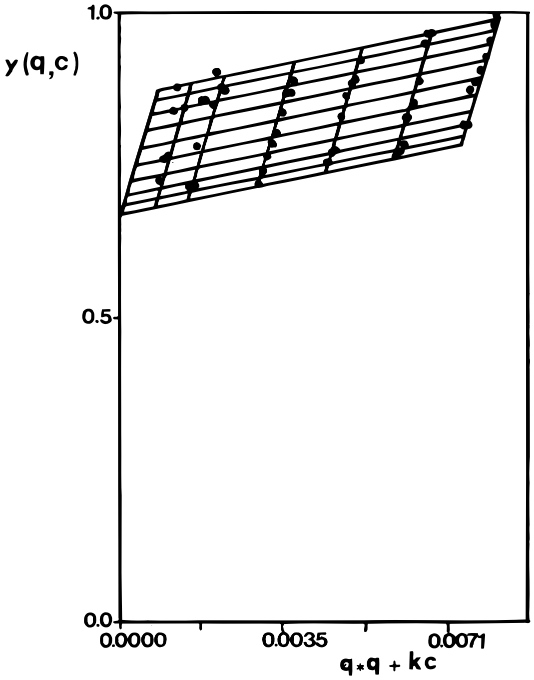

Figure 2. Zimm plot of light scattering measurements for fraction **2a** at 45 °C in 1,1,2,2-tetrachloroethane, at concentrations $c = 0.20, 0.40, 0.80, 1.20, 1.60$, and 2.00 g/L. The axes are normalized.

Table 2. Light Scattering Results

fraction	$\bar{M}_w$	R_g (nm)	10^3A_2 (cm^3 g mol^{-1})	$(\bar{M}_w/\bar{M}_n)^a$
		Polyester **1**		
1a	85 800	55.4	0.8	1.74
1b	30 700	35.5	2.5	1.28
1c	26 100	31.5	2.8	1.27
1d	15 200	42.0	3.5	1.40
1e	8 500	31.7	2.6	
		Polyester **2**		
2a	30 000	33.2	1.5	1.58
2b	26 100	40.9	1.2	1.82
2c	13 400	26.9	3.5	1.51
2d	6 500	30.6	3.3	1.43

[a] From GPC in chloroform.

Molecular Weight Dependencies and Persistence Length. Figure 3 illustrates the log–log plot of intrinsic viscosity versus the weight-average molecular weight for both structures. At 30 °C, the Mark–Houwink equations are as follows ($[\eta]$ in mL/g):

$$\text{polyester 1, } [\eta] = (2.19 \times 10^{-3})\bar{M}_w^{\;1.09}$$

$$\text{polyester 2, } [\eta] = (7.78 \times 10^{-4})\bar{M}_w^{\;1.26}$$

and at 60 °C the equations are

$$\text{polyester 1, } [\eta] = (9.45 \times 10^{-4})\bar{M}_w^{\;1.15}$$

$$\text{polyester 2, } [\eta] = (5.32 \times 10^{-4})\bar{M}_w^{\;1.28}$$

These relations represent only approximations because of the rather narrow molecular weight range investigated and the limited accuracy of the experimental data. In any case, the high values of the exponent α support a higher rigidity of the polymers studied compared to the poly(3-alkyl-4-hydroxybenzoate)s,[3] poly(1,4-phenylene-2,5-dialkoxyterephthalate)s,[5] and poly(phenylhydroquinoneterephthalate),[18] where comprehensive studies in solution have been published.

A more quantitative discussion on the hydrodynamic data may be based on the wormlike chain model developed by Yamakawa and Fujii.[22] On the basis of this theory, Bohdanecky[23] has given a simple procedure

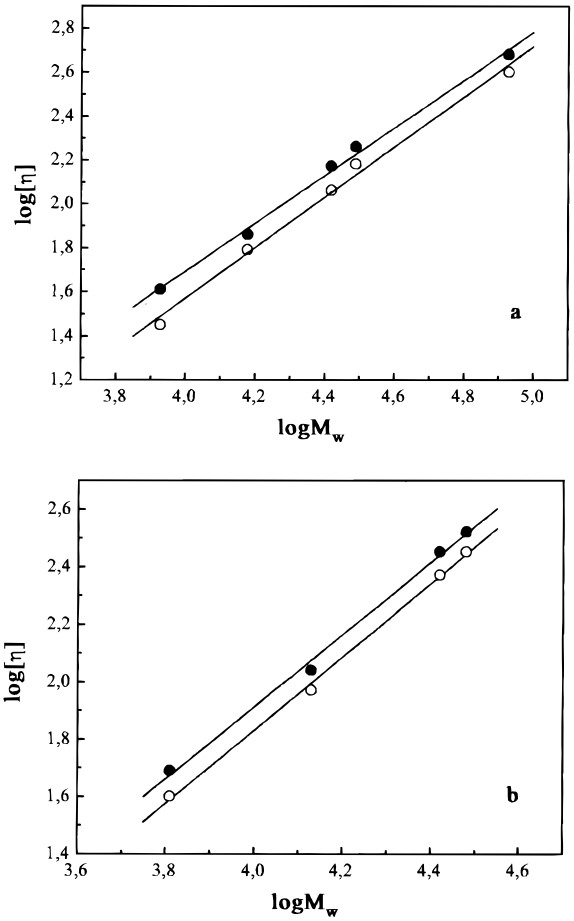

Figure 3. Mark–Houwink plots of the intrinsic viscosities of polyesters **1** (a) and **2** (b) measured in 1,1,2,2-tetrachloroethane at 30 (●) and 60 °C (○).

for the determination of the persistence length, using the following plot:

$$(M^2/[\eta])^{1/3} = A_n + B_n M^{1/2}$$

where the intercept A_n depends on the reduced hydrodynamic diameter d_r,

$$B_n = B_0 \Phi_{0,\infty}^{-1/3} (\langle R_0^2\rangle/M)_\infty^{-1/2}$$

and

$$(\langle R_0^2\rangle/M)_\infty = 2q/M_L$$

Here $\langle R_0^2\rangle$ is the mean square end-to-end distance of the chain, and $\Phi_{0,\infty}$ is the limiting value of Φ (2.86×10^{23} mol^{-1}) for nondraining coils in the limit of infinite molecular weight. B_0 is a slowly decreasing function of d_r, and to a first approximation it may be replaced by the mean value $B_0 = 1.05$. $2q$ is the length of a Kuhn segment, and M_L is the molecular weight per unit length. Figure 4a shows the Bohdanecky plots at 30 and 60 °C for polyester **1**, and Figure 4b shows the plots for polyester **2**.

At 30 °C the slope was found to equal 0.619 and 0.469 for polymers **1** and **2**, respectively. Taking into account the bond length values from related polymers,[20,24] the projection lengths 20.61 Å for **1** and 28.75 Å for polymer **2** were found. By using $M_L = 33.77$ Å^{-1} for polymer **1** and $M_L = 29.50$ Å^{-1} for polymer **2**, q was calculated to equal 112 and 170 Å for polymers **1** and **2**, respectively.

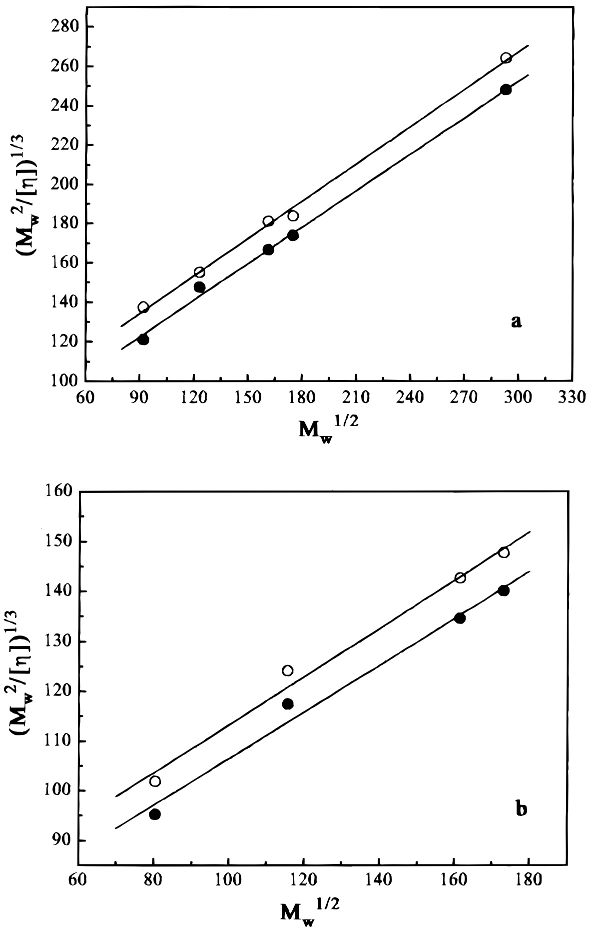

Figure 4. Bohdanecky plots for polyesters **1** (a) and **2** (b) in 1,1,2,2-tetrachloroethane at 30 (●) and 60 °C (○).

The same calculations were performed with the viscosimetric results obtained at 60 °C. By using the Bohdanecky plot, slopes of 0.634 and 0.483 were obtained, which led to a persistence length value of 107 Å for polymer **1** and 161 Å for polymer **2**.

The effective hydrodynamic diameter d of the chains was evaluated from the intercept A_n. According to Bohdanecky,

$$d_r^2/A_0 = (4\Phi_{0,\infty}/1.215\pi N_A)(\bar{u}/A_n)B_n^4$$

with $d_r = d/2q$ being the reduced hydrodynamic diameter of the chain, and $\bar{u}$ is the partial specific volume of the polymer solution. The quantity A_0 is related to d_r by the following equation:[23]

$$\log(d_r^2/A_0) = 0.173 + 2.158 \log(d_r) \quad (d_r < 0.1)$$

The partial specific volume $\bar{u}$ was approximated by 1 cm^3/g. From these data, the hydrodynamic diameter could be estimated to be on the order of 8 Å (7.9 Å for polymer **1** and 7.6 Å for polymer **2**). Values of a similar magnitude have been obtained previously.[3,5,21]

Discussion

Fractionation of the polymers was efficient since fractions with low polydispersity (up to 1.8) were obtained. These fractions were used for the present study to reduce the influence of polydispersity on the calculated persistence length values.[25] Attempts were made to calibrate the SEC measurements. As expected, calibration based on polystyrene standards gave over-

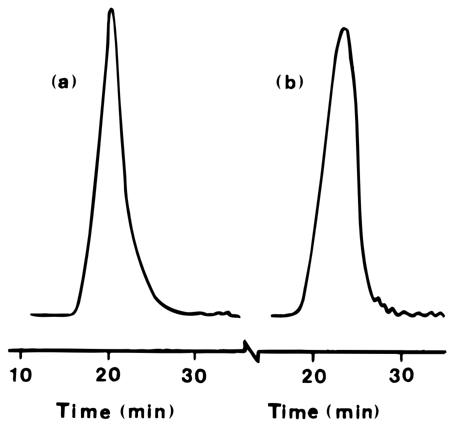

Figure 5. Size-exclusion chromatograms of fractions **1a** (a) and **2b** (b) in chloroform at 25 °C.

estimated results (in some cases 1 order of magnitude). By using universal calibration, the values obtained show serious discrepancies with the absolute molar masses determined by light scattering. In all cases unimodal distributions were obtained, as shown in Figure 5 for the fractions **1a** and **2b**.

The solubility of our systems in solvents like 1,1,2,2-tetrachloroethane enables us to determine the molecular weight and the radius of gyration by light scattering. The high refractive index increment also permits the use of diluted solutions (0.2−0.02 g/dL) without the problems caused by possible association. The problems initially encountered with the light scattering experiments were overcome by sonication of the solutions before the measurements. The second virial coefficient A_2 for the fractions of both polymers was between 0.8×10^{-3} and 3.5×10^{-3}, showing that 1,1,2,2-tetrachloroethane is a rather good solvent. The A_2 values of the fractions are slightly different, but do not vary systematically with molecular weight.

By using the $\bar{M}_w$ values determined by light scattering, the persistence length values were calculated. The stiffness of the aromatic polyesters is a point of great interest. Since the unsubstituted polyesters are not soluble, there are no experimental results on their persistence length. Calculations by Erman et al.[19] using the rotational isomeric state model led to persistence lengths of 785 Å for poly(hydroquinone-*co*-terephthalic acid) and 700 Å for poly(4-hydroxybenzoate). Molecular dynamics calculations performed by Jung and Schurmann[20] led to a much smaller value for the persistence length [$q = 60$ Å for poly(4-hydroxybenzoate)], taking into account the torsional fluctuation about the ester bonds.

Several substituted aromatic polyesters have been tested for their rigidity. Alkyl-substituted poly(4-hydroxy benzoate)s[3] gave persistence length values of 45 Å for the propyl-substituted and 95 Å for the hexadecyl-substituted polymers. Substituted polymers having a poly(hydroquinone-*co*-terephthalic acid) backbone were also studied.[5,18] The phenyl-substituted analogue gave a value of 61 Å by using the Bohdanecky method and values of 60−150 Å by using different techniques for the estimation of the persistence length.[18] Poly(1,4-phenylene-2,5-dialkoxyterephthalate)s with hexyloxy and (hexadecyl)oxy side groups have also been analyzed by a similar way. Values of 50 Å for the hexyloxy-substituted and 65 Å for the (hexadecyl)oxy-substituted polyesters were calculated.[5] As shown, the structure of the side chain affects the persistence length value due to steric hindrance.

Increases in the rigidity of the polymer backbone by introduction of the terphenyl unit into the main chain led to an increase in the persistence length. Thus, poly(2′,5′-dihexyl-*p*-terphenyl terephthalate) gave a q value of 72 Å when $\bar{M}_w$ values were used[16] for the Bohdanecky approach. If the $\bar{M}_n$ values reported in the same publication are used, a q value of as high as 166 Å will be obtained. Previous work on the same polymer led to a q value of 112 Å using $\bar{M}_n$ values. As shown earlier, comparisons are valid when the same method and same expression for the molecular weights are used. From the present results, a clear increase in rigidity is obtained when phenyl substituents were used to increase solubility. The value of 112 Å for our polymer **1** is significantly higher than that of 72 Å obtained for the same polymer backbone bearing hexyl side groups.

Further increase in the oligophenyl part, as in polymer **2**, is accompanied by an increase in the persistence length to 170 Å. Since the values of the persistence length obtained from the Bohdanecky procedure must be regarded as a lower bound,[26] and since the differences in the q values estimated by using different methods vary by up to a factor of 2.5,[18] polymer **2** could be regarded as rigid. The persistence length value of 170 Å, using the Bohdanecky treatment with $\bar{M}_w$ values, is one of the higher q values reported so far for synthetic polymers.

The effect of temperature on the chain rigidity was also examined. In both cases, a small decrease in the persistence length was obtained between 30 and 60 °C. In previous work,[15] q remained unaltered over this temperature range, followed by a decrease above 60 °C. Given the limits of error, it is difficult to rationalize the small decrease obtained here. It should also be noted that in this case the $[\eta]$ values decreased significantly (about 20%) from 30 to 60 °C, while the decrease in q was lower than 5%.

Conclusions

Asymmetric phenyl substitution was proven efficient for the increase in the solubility of the aromatic polyesters containing terphenyl or quinquephenyl units in the main chain. The improved solubility enables the systematic characterization of these polymers by means of static light scattering, viscosimetry, and size-exclusion chromatography. The Mark−Houwink equations were calculated, and the resulting values for the exponent α were on the order of 1.1−1.3. Estimation of the persistence length was based on viscosimetric data. The resulting q values are 112 Å for the polymer with the terphenyl unit and 170 Å for the quinquephenyl unit-containing polymer. The rigidity increase caused by the introduction of the quinquephenyl moiety was mainly due to the increased stiffness of the monomer unit since the same number of monomers (about 11) was contained in a Kuhn statistic length, in both cases. Further increase in the oligophenyl unit in the main chain is questionable and will probably lead to insoluble polymers if only aromatic substituents are be used.

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