*Macromolecules* **1993,** *26,* 5457–5460

# Viscosimetric Study of Poly(2′,5′-dialkyl-*p*-terphenylene terephthalate): Statistical Segment Length and Conformational Transition

**J. K. Kallitsis,**[*,†] **K. Gravalos, and A. Dondos**[‡]

*Departments of Chemistry and Chemical Engineering, University of Patras, 26110 Patras, Greece, and the Institute of Electronic Structure and Laser Research, Iraklion, Krete, Greece*

*Received January 29, 1993; Revised Manuscript Received June 2, 1993*[●]

ABSTRACT: The conformational behavior in solution and in the temperature range 30–85 °C for the title polyester was investigated using simple viscosimetric methods. The obtained unperturbed dimensions parameter and the statistical segment length have shown that this polyester behaves in solution as a rigid polymer. Comparison with the persistence length values obtained for related polymers indicates a significant increase in rigidity, caused by the introduction of the terphenyl unit. The temperature dependence of both the unperturbed dimensions and the persistence length indicates the existence of a conformational transition at 60 °C. These results are in good agreement with those obtained in the solid state, showing the existence for this polymer of a memory effect.

## Introduction

Rigid polymers with flexible side chains have attracted much attention in recent years. The increased solubility caused by the introduction of the side chains enables improved processability of various types of rigid polymers: aromatic polyesters,[1–4] polyamides,[5,6] polyimides,[5,7] and poly(phenylene sulfides).[8] On the other hand, the introduction of side chains leads to a variety of supermolecular structures which have been extensively studied using various methods such as X-ray analysis[9] and solid-state NMR spectroscopy.[10,11] An interesting study of aromatic polyesters having aliphatic side chains has appeared recently. The various phases formed from these liquid crystalline materials were studied using different techniques.[12]

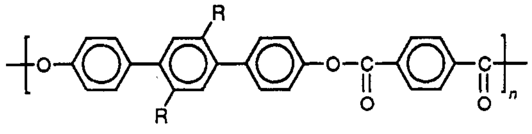
The rigidity increase caused by the introduction of the terphenyl moiety into the polymer backbone has attracted attention.[8,13,14] The observed insolubility of the unsubstituted polymers makes their systematic study, e.g., as a function of the terphenyl units in the main chain, impossible.

On the contrary, the facile synthesis of *p*-terphenylene monomers carrying flexible side chains permits us to synthesize polyesters containing the terphenyl unit in the main chain that are still soluble in common solvents. The interesting behavior of these materials in the solid state was reported recently.[2] The solubility of the studied polymers permits us in this article to perform a conformational study using viscosimetric measurements. The methods based on this technique are described in the literature[15–17] and have already been used to determine the unperturbed dimensions or the persistence length of wormlike or rigid polymers.[18–20]

The principal aim of this work is the conformational study of polyester I in dilute solutions. More precisely, the rigidity of polyester I is tested by the estimation of either the unperturbed dimensions parameter or the statistical segment length using the above-cited methods based on the relation between viscosity and molecular weight. By using the viscosity values obtained at different temperatures, a new interesting feature is obtained for this rigid polymer; the unperturbed dimensions parameter and the persistence length change very sharply at 60 °C, in very good agreement with the observed transition in the solid state.[2]

**Table I. Intrinsic Viscosities of the Synthesized Polymers**

| | [η] (mL/g) | | |
|---|---|---|---|
| sample | 30 °C | 60 °C | 85 °C |
| R1 | 15 | 15 | |
| R2 | 90 | 89 | 71 |
| R3 | 134 | 130 | 98 |
| R4 | 150 | 148 | 117 |
| R5 | 190 | 190 | 152 |
| F1 | 80 | 80 | 65 |
| F2 | 109 | 109 | 83 |
| F3 | 236 | 235 | 196 |
| F4 | 250 | 250 | 200 |
| F5 | 350 | 345 | 280 |



I, R = $C_6H_{13}$

## Experimental Section

Polymer I was synthesized according to the previously reported method.[2] Molecular weight determination ($\bar{M}_n$) was conducted in a Hewlett-Packard vapor pressure osmometer (VPO) Model 302B at 50 °C, using *o*-dichlorobenzene as solvent. Viscosity measurements at various temperatures were performed in an Ubbelohde viscometer using as solvents chloroform or *o*-dichlorobenzene. The intrinsic viscosity index [η] is given in mL/g.

## Results

**1. Intrinsic Viscosity.** The [η] values of our polymer samples are shown in Table I. Some samples were studied as received (R), and others were obtained after fractionation (F). Linear plots of $\eta_{inh}$ versus concentration were obtained in all examined cases (see, for example, Figure 1). The concentrations were below 0.5 g/dL because gelation was observed at higher concentrations at room temperature. For all samples intrinsic viscosities were obtained at 30, 60, and 85 °C using *o*-dichlorobenzene as solvent. For some samples the temperature dependence

---

[†] Department of Chemistry and the Institute of Electronic Structure and Laser Research.

[‡] Department of Chemical Engineering.

[●] Abstract published in *Advance ACS Abstracts,* September 1, 1993.

0024-9297/93/2226-5457$04.00/0

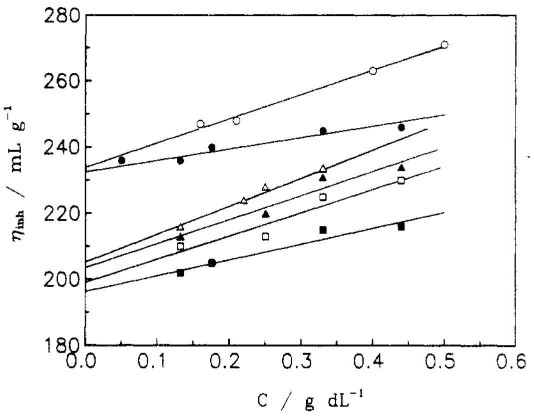


**Figure 1.** Plot of $\eta_{inh}$ versus concentration of fraction F3 at various temperatures: 30 (○), 60 (●), 65 (△), 70 (▲), 80 (□), and 85 °C (■).

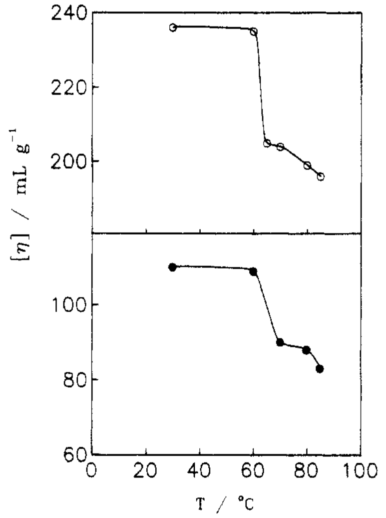


**Figure 2.** Intrinsic viscosity variation with the temperature of samples F2 (●) and F3 (○).

**Table II. Molecular Weight Determination by VPO**

| sample | [η] (mL/g) | $\bar{M}_n$ |
|---|---|---|
| R1 | 15 | 900 |
| R2 | 90 | 4000 |
| R3 | 134 | 7000 |
| R4 | 150 | 8000 |
| R5 | 190 | 9600 |
| F2 | 109 | 5500 |
| F3 | 236 | 11000 |
| F4 | 250 | 12500 |
| F5 | 350 | 18000 |

of [η] was also investigated. A representative example is shown in Figure 1. A sharp discontinuity at ca. 60 °C is observed as shown in Figure 2. The sharp viscosity change shows that a transition occurs at that temperature. The nature of this transition will be discussed later in relation with the solid-state properties of this material.

**2. Molecular Weights.** The number-average molecular weights $\bar{M}_n$ of the different samples were determined using vapor pressure osmometry (VPO) at 50 °C with o-dichlorobenzene as solvent. The results are shown in Table II. The log–log plot of intrinsic viscosity versus number-average molecular weight is shown in Figure 3, and the obtained Mark–Houwink–Sakurada (MHS) equation is

$$[\eta] = 1.29 \times 10^{-2} \bar{M}_n^{\ 1.05} \qquad (1)$$

**3. Unperturbed Dimensions and Persistence Length.** There are several methods using the relation

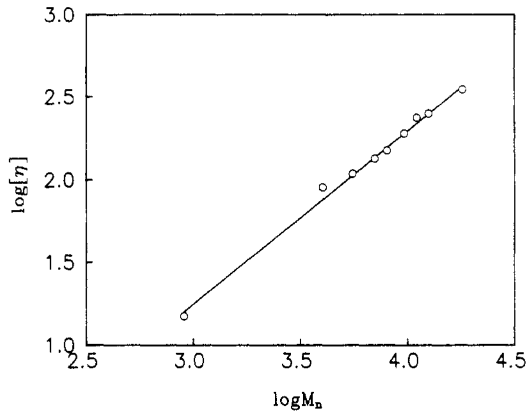


**Figure 3.** Plot of log[η] versus log $\bar{M}_n$ in o-dichlorobenzene at 30 °C.

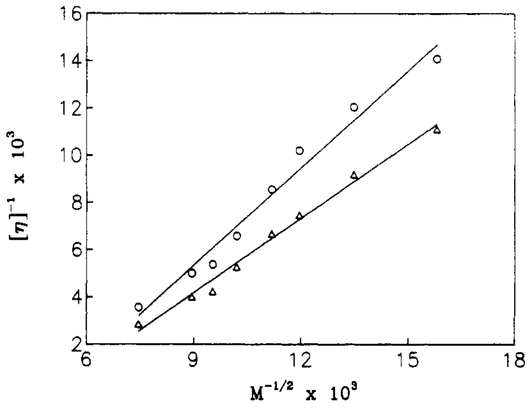


**Figure 4.** Intrinsic viscosity data plotted according to the D–B treatment: (△) at 30 °C; (○) at 85 °C.

between intrinsic viscosity and molecular weight to obtain the unperturbed dimensions and the persistence length of rigid polymers.[15,16,18–21]

According to the Dondos–Benoit (**D–B**) relation, the unperturbed dimensions parameter $K_\Theta$ is obtained as follows:

$$[\eta]^{-1} = -A_2 + A_1 M^{-1/2} \qquad (2)$$

where $K_\Theta$ is equal to $A_1^{-1}$. This method is applicable in the case of wormlike polymers even when fractions with a low number of statistical segments are studied,[19,20] which is the case in our system. Plotting $[\eta]^{-1}$ versus $\bar{M}_n^{-1/2}$ with the results of intrinsic viscosity obtained at 30 °C, we obtain the straight line shown in Figure 4, and from its slope we calculate $K_\Theta = 95 \times 10^{-2}$ mL g$^{-3/2}$ mol$^{1/2}$. This value is high enough to consider that our polymer is a rigid polymer. Let us mention that for polystyrene the value of $K_\Theta$ is equal to $8 \times 10^{-2}$.

According to the Bohdanecky (B) method, the persistence length, $q$, is obtained using the following equation:[16]

$$(\langle M\rangle^2/[\eta])^{1/3} = A + B\langle M\rangle^{1/2} \qquad (3)$$

where $A = A_0 M_L \phi_0^{-1/3}$ and $B = 1.05\phi_0^{-1/3}(2q/M_L)^{-1/2}$. $\phi_0$ is the limiting value of $\phi$ ($\phi_0 = 2.86 \times 10^{23}$) for nondraining coils in the limit of infinite molecular weight. A plot of $(M^2/[\eta])^{1/3}$ versus $M^{1/2}$ with [η] values at 30 °C was made according to eq 3 (Figure 5). The slope was found equal to 0.556. To obtain the $q$ value, we also need the value of $M_L$, which is defined as the ratio of the molecular weight $M$ to the contour length $L$ of the polymer (the molecular weight per unit length). Taking the bond length values from related polymers,[22,23] we found the projection length $l$ = 20.61 Å. The weight of the repeat unit is 560 Da, and the molecular weight per unit chain length is $M_L$ = 27.18

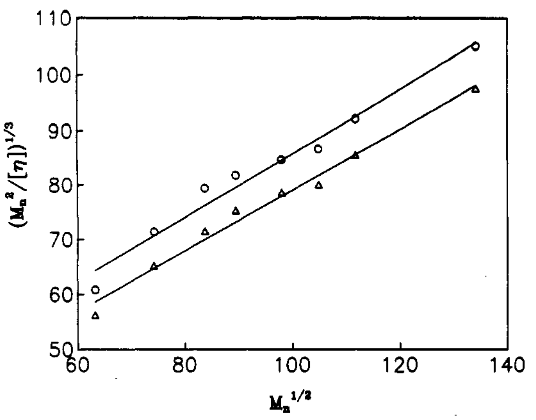


**Figure 5.** Intrinsic viscosity data plotted according to the B treatment: (△) at 30 °C; (○) at 85 °C.

**Table III. Unperturbed Dimensions Parameter and Persistence Length Values Derived from Different Methods**

| temp (°C) | $q$ (Å) | $K_\Theta$ (mL g$^{-2/3}$ mol$^{1/2}$) |
|---|---|---|
| 30 | 112 | $95 \times 10^{-2}$ |
| 60 | 112 | $95 \times 10^{-2}$ |
| 70 | 105 | $78 \times 10^{-2}$ |
| 85 | 103 | $73 \times 10^{-2}$ |

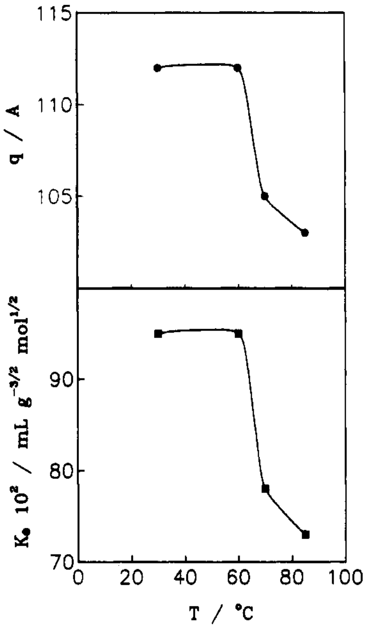


**Figure 6.** Temperature dependence of the unperturbed dimensions parameter $K_\Theta$ and the persistence length $q$.

Da/Å. Finally, the obtained value of $q$ was equal to 112 Å. Because of the dependence of the calculated $q$ value on polydispersity,[24] the same calculation was made using only samples with low polydispersity indices ($I < 1.6$). The derived value of $q$ was 124 Å.

The same calculations were performed with the viscosimetric results obtained with fractions of the same polymer at 85 °C. Using the D–B method (Figure 4), we obtain $K_\Theta = 73 \times 10^{-2}$. Finally applying the **B** method (Figure 5) at the same conditions, we obtain $q = 103$ Å. We also performed viscosimetric measurements at 60 and 70 °C, and the obtained results are presented in Table III. The variations of $K_\Theta$ and $q$ as a function of temperature obtained by the above two methods are presented in Figure 6. As we can see in this figure, a transition is observed above 60 °C which predicts an important decrease of the chain rigidity.

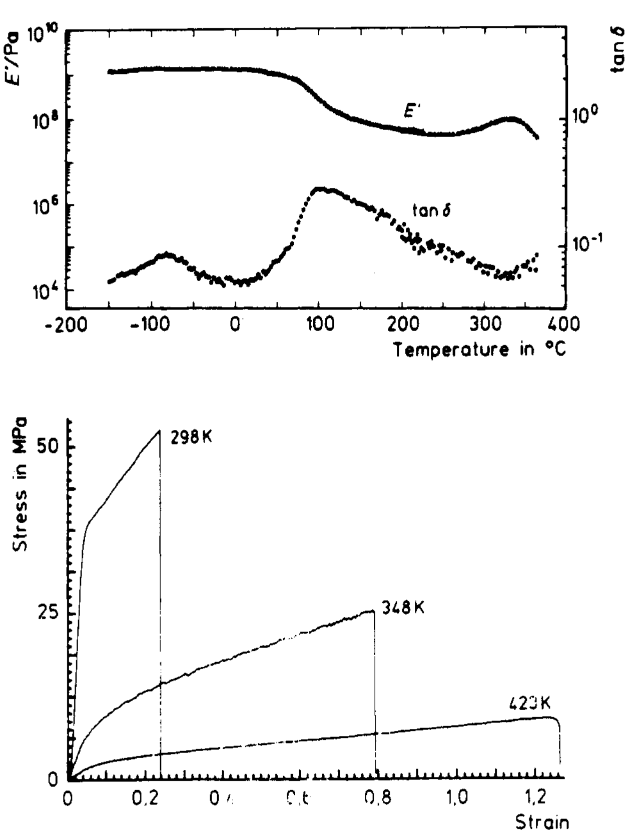


**Figure 7.** DMA and stress–strain curves of polymer I (from ref 2).

## Discussion and Conclusions

The above-obtained viscosimetric results convince us that the effect of the introduction of both the aliphatic side chains and the terphenyl unit in the main chain of the studied polyester can be revealed. Using simple viscosimetric methods, we obtain to some extent the conformational behavior of our polymer in dilute solutions by the determination of the statistical segment or the chain rigidity in a temperature range from 30 to 85 °C. Moreover, this study has shown that polyester I exhibits a transition at 60 °C, and this transition was related with the dynamic mechanical spectrum of the polyester (Figure 7).

We assume that our polymer is rigid because, despite the well-known semirigidity of aromatic polyesters, we have introduced the rigid terphenyl moiety in the main chain. In fact, the influence of the introduction of the terphenyl group can be examined by comparing the persistence length obtained by the Bohdanecky approach with those obtained for other polyesters which are available in the literature. The substituted poly(phenylhydroquinone-*co*-terephthalic acid) has a persistence length of 61 Å using the above method.[21] It should be noted that in the above treatment the $\bar{M}_w$ values have been used instead of our $\bar{M}_n$ values. In our case, the persistence length was found to be at least 112 Å, which reveals the significant rigidity increase caused by the introduction of the terphenyl unit. The relatively low value of the persistence length obtained for that polymer compared to the very high value calculated by Erman, Flory, and Hummel[25] for poly(hydroquinone-*co*-terephthalic acid), $q = 785$ Å, or even the reduced value of 470 Å as reported by Krigbaum et al.[21] shows that a reduction of the $q$ is observed in our case. This reduction could in principle be attributed to the changes of the conformation of the terphenyl moiety as was found by crystal structure analysis of some disubstituted terphenyl models.[26]

The nature of the secondary transition appearing in the DMA spectrum from our previous work[2] (Figure 7) at ca. 60 °C is not well defined. We have proposed that an order–disorder transition occurs at this temperature region which primarily involves all segments of the side chains and leads to some small rearrangements of the main chain. With the results obtained in this work in dilute solutions, we can show that both the persistence length and the unperturbed dimensions of the polymer below and above that transition present a significant variation. These results are in favor of a rearrangement of the main chain taking place and suggest that this phenomenon is the same in the solid state as in solution. The decrease of the persistence length reported in this work is in agreement with the previous findings,[2] because the stress–strain properties of the polymer as a function of temperature (Figure 7) show that the elongation at break at 75 °C changes significantly compared with that at 25 °C. The observed similarity in the behavior of polyester I in solution and in the solid state could be attributed to the fact that even in the solid state the main chain is immersed in a continuous phase formed from the mobile side chains; the addition of the solvent simply dilutes the continuous phase. In the present work we do not have a transition from a wormlike to a flexible polymer because even above 60 °C the polymer maintains its characteristics as a rigid polymer (high values of $q$ and $K_\Theta$ and a value of the exponent $a$ in the MHS equation equal to 1.0).

In conclusion, we can say that simple viscometric methods have successfully been applied for the determination of the conformational characteristics of polyester I. By determining the $q$ and $K_\Theta$ values, we have shown that this polymer is rigid and that the introduction of the terphenyl unit results in a significant increase of its rigidity compared to other polyesters. Finally, the observed conformational transition of 60 °C, which leads to a decrease of its rigidity, seems to concern both the main chain and the aliphatic side chains.[12]

## References and Notes

(1) Ballauff, M. *Makromol. Chem., Rapid Commun.* **1986**, *7*, 407.
(2) Kallitsis, J.; Wegner, G.; Pakula, T. *Macromol. Chem.* **1992**, *193*, 1031.
(3) Hatke, W.; Schmidt, H. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32* (1), 214.
(4) Krigbaum, W. R.; Hakemi, H.; Kotek, R. *Macromolecules* **1985**, *18*, 965.
(5) Duran, R.; Ballauff, M.; Wenzel, M.; Wegner, G. *Macromolecules* **1988**, *21*, 2897.
(6) Helmer-Metzmann, F.; Ballauff, M.; Schults, R. C.; Wegner, G. *Makromol. Chem.* **1989**, *190*, 985.
(7) Giesa, R.; Keller, U.; Schmidt, H. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 396.
(8) Kallitsis, J.; Naarmann, H. *Makromol. Chem.* **1992**, *193*, 2345.
(9) Biswas, A.; Deutscher, K.; Blackwell, J.; Wegner, G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33* (1), 286.
(10) Claus, J.; Schmidt-Rohr, K.; Adam, A.; Boeffel, C.; Spiess, H. W. *Macromolecules* **1992**, *25*, 5208.
(11) Baldwin-French, C.; Adam, A.; Falk, U.; Boeffel, C.; Spiess, H. W. *New Polym. Mater.* **1990**, *2*, 267.
(12) Schrauwen, C.; Pakula, T.; Wegner, G. *Makromol. Chem.* **1992**, *193*, 11.
(13) Meurise, P.; Noel, C.; Monnerie, L.; Fayolle, B. *Br. Polym. J.* **1981**, *13*, 55.
(14) Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909.
(15) Yamakawa, H.; Fujii, M. *Macromolecules* **1974**, *7*, 128.
(16) Bohdanecky, M. *Macromolecules* **1983**, *16*, 1483.
(17) Dondos, A.; Benoit, H. *Polymer* **1977**, *18*, 1161.
(18) Krigbaum, W.; Tanaka, T.; Brelsford, G.; Ciferri, A. *Macromolecules* **1991**, *24*, 4142.
(19) Staikos, G.; Dondos, A. *Eur. Polym. J.* **1983**, *19*, 555.
(20) Dondos, A. *Makromol. Chem., Macromol. Symp.* **1992**, *62*, 129.
(21) Krigbaum, W.; Tanaka, T. *Macromolecules* **1988**, *21*, 743.
(22) Jung, B.; Schurmann, B. *Macromolecules* **1989**, *22*, 477.
(23) Hummel, J. P.; Flory, P. J. *Macromolecules* **1980**, *13*, 479.
(24) Fortelny, I.; Kovar, J.; Zivny, A.; Bohdanecky, M. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 181.
(25) Erman, B.; Flory, P. J.; Hummel, J. P. *Macromolecules* **1980**, *13*, 484.
(26) Nastopoulos, V.; Kallitsis, J.; Naarmann, H., unpublished results.