

Analysis of the Conformation of a Stiff-Chain Polyester by Measurements of the Magnetic Birefringence in Solution

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ABSTRACT: The analysis of the conformation of a stiff-chain polyester by magnetic birefringence is presented. The specific Cotton–Mouton constant, C_2^b , has been measured for five different molecular weights of the polyester. A general analysis of the data is presented, including the effect of polydispersity. A weak dependence of C_2^b on molecular weight is found, which shows that the persistence length of the polyester is approximately 11 nm. Estimates of the specific Cotton–Mouton constant per unit length by using group increments compare favorably with the measured value.

Introduction

The birefringence induced by electrical (Kerr effect) or magnetic fields (Cotton–Mouton effect) in polymer solutions has long been studied to obtain information on the conformation of dissolved macromolecules.^{1,2} The magnetic birefringence is of particular interest, since there is no correction for the local magnetic field or disturbances due to electric currents. The Cotton–Mouton (CM) constant is directly proportional to the product of the optical and magnetic anisotropy of the chains, which can be analyzed quantitatively to yield the persistence length of the dissolved chains. Thus, measurements of the CM constant have been applied to the study of the conformation of macromolecules^{3,4} and, in particular, to the analysis of polyelectrolytes.^{5,6}

All experimental studies conducted so far^{3–6} indicate that measurements of the magnetic birefringence are, indeed, highly useful for characterizing macromolecular compounds in solution and may, therefore, supplement studies by scattering methods. As shown by Maret and Weill,⁵ the CM constant is less sensitive toward excluded volume interactions than quantities such as, e.g., the radius of gyration. This is due to the fact that the CM constant probes the quantity

$$\sum_i \sum_j \left\langle \frac{3 \cos^2 \theta_{ij} - 1}{2} \right\rangle$$

for all elements i and j along the chain, whereas the end-to-end distance of the chain is related to the double sum over $\cos \theta_{ij}$. This argument shows, as well, that the CM constant is more sensitive to small deviations from a linear chain conformation than the radius of gyration. Measurements of the magnetic birefringence should,

therefore, allow the persistence length to be determined for rather stiff and/or short chains.

An important prerequisite of the analysis⁵ of the CM constant is the additivity of the respective group contributions to the optical and magnetic anisotropy. A discussion of such group additivity schemes in terms of the rotational isomeric state (RIS) model can be found in Flory's monograph.² The treatment based on the wormlike chain is also based on the additivity of the contributions to the respective anisotropies along the chain (cf. ref 5).

A critical test of the group additivity scheme with regard to the calculation of the CM constant has been performed recently⁷ using a set of defined oligomers. The optical anisotropies of these compounds have been determined by depolarized Rayleigh scattering^{2,8,9} (DRS), whereas the diamagnetic anisotropies are available from Flygare's scheme,¹⁰ the validity of which has been shown repeatedly (see, e.g., ref 11). The comparison of the measured and calculated CM constants showed that application of group contribution schemes gives good agreement for these compounds with experimental data. Together with earlier results⁹ pertaining to the analysis of the tensor of optical polarizability, this demonstrates the general applicability of the group additivity scheme if suitably chosen increments are used therein.

Here we present an extension of the previous work^{7,9} to the analysis of the poly(*p*-terphenylene terephthalate)s, termed TPPEs, synthesized and characterized recently (Chart 1).¹² The choice of this material derives from the fact that this polyester exhibits a rather high stiffness, with a persistence length of 9 nm, as determined by viscosimetric means. The structure of the repeating unit is akin to the low-molecular-weight systems studied previously.^{7–9} The CM data obtained herein may, therefore, be analyzed by using the increment obtained in the course of this work. To supplement these data, a trimeric model compound akin to the repeating unit of the TPPE has been synthesized

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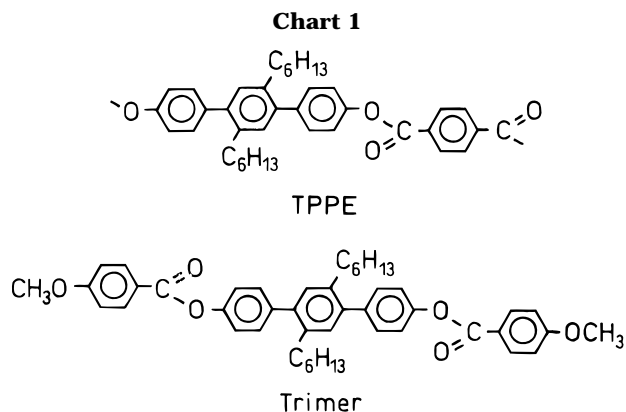


Table 1. Specific Cotton–Mouton Constants C_2^b and Characterization of the Polyesters TPPE

sample	M_w	L_w/nm^c	$C_2^b \times 10^{16}/\text{mA}^{-2}$
trimer	699	3.0	531
TPPE-1	11 300 ^a	44.4	1580
TPPE-2	20 400 ^b	80.2	1750
TPPE-3	31 100 ^b	122	1770
TPPE-4	47 200 ^b	185	1730
TPPE-5	130 000 ^b	511	1750

^a Calculated from viscosimetry and gel permeation chromatography.²¹ ^b Taken from ref 12. ^c Weight-average contour length.

as well (Chart 1). Its CM constant is evaluated to yield the additional increments necessary to estimate the respective data of the TPPE polyesters. In addition to this, the optical anisotropy is deduced from DRS data of this oligomer. The details of the DRS measurements will be given elsewhere.¹³

Experimental Section

Materials. All chemicals were purchased from Fluka or Merck-Schuchardt unless stated otherwise. 1,4-Dioxane (Merck-Schuchardt, zur Synthese) was purified by distillation; chloroform (p.a.) was used without further purification.

The trimer was synthesized from 2',5'-di-*n*-hexyl-*p*-terphenyl-4,4''-diol (cf. ref 12 for the details of the synthesis of this compound) by reaction with *p*-anisoyl chloride (Aldrich). Thus, 4.3 g of the diol were dissolved in 100 mL of a mixture of chloroform and toluene (9:1 by volume). Next, 3.5 g of anisoyl chloride and subsequently 2.5 mL of triethylamine were added with stirring. After 10 min, the solution was washed with water and dried with MgSO₄. The product that resulted after evaporation was recrystallized from a 2:1 mixture of ethanol/toluene (yield, 90%). It melts at 151 °C to an isotropic liquid. The structure of the trimer was confirmed by ¹H- and ¹³C-NMR spectroscopy.

The TPPE polyesters were synthesized as described previously.¹² Table 1 gathers the molecular weights of the samples used herein.

Measurements and Evaluation of Data. The magnetic birefringence has been determined using the experimental setup described previously.⁵ As a light source, an argon ion laser operating at 488 nm was used. The magnetic field was generated by a Bitter magnet operating up to higher fields ($B_{\text{max}} = 17.5$ T) than in previous work.⁷ All measurements were done at 25 °C in chloroform. Dilute solutions of the polyesters have been placed in cells of 3 cm path length, and the birefringence, Δn , was measured during a sweep of the magnetic field. A full sweep cycle of the magnetic field was performed within 90 s.

As demonstrated in Figure 1, the birefringence, Δn , is found to be strictly proportional to the square of the strength of the magnetic field, B^2 . Therefore, the Δn data obtained during a

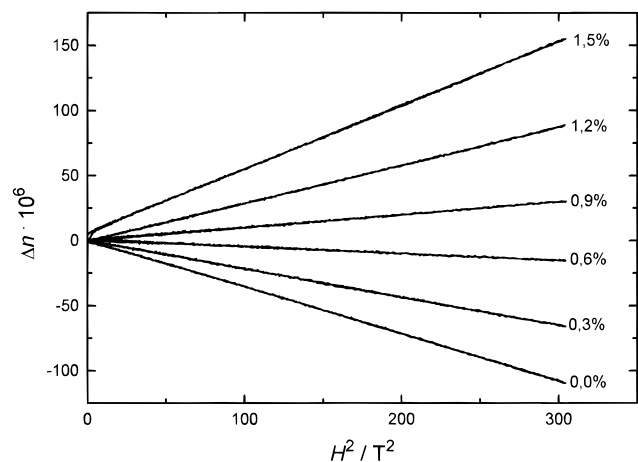


Figure 1. Birefringence of solutions of polyester TPPE-4 versus the square of the magnetic field (cf. eq 1) for different polymer concentrations.

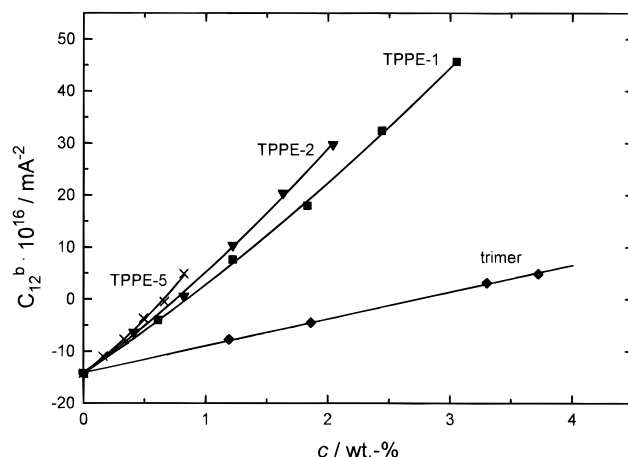


Figure 2. Plot of the bulk CM constants (cf. eq 1) versus weight concentration for polyesters TPPE-1, -2, and -5 and for the trimer.

sweep of the magnetic field could be well described by the bulk CM constant, C^b , of the sample, defined as

$$C^b = \Delta n \mu_0^2 / \lambda B^2 \quad (1)$$

with λ being the wavelength of the laser and μ_0 the permittivity of the vacuum.

The specific bulk CM constants, i.e., the bulk CM constants normalized to the weight concentration of the solute, w_2 , were determined by plotting the bulk CM constants of the solution versus the weight concentration of the solute. Figure 2 displays several examples of such a plot. Even at the low polymer concentrations employed for the measurements, a small deviation from linearity was observed. Therefore, a nonlinear fit procedure has been used to extract the slope at vanishing concentration.

The margin of error of the C_2^b is difficult to determine but can be estimated to be of the order of 10% at most. Table 1 contains the specific Cotton–Mouton constants, $C_2^b = (dC^b/dw_2)_0$, at infinite dilution of all compounds thus obtained. The slight nonlinearity points to the onset of binary interaction between the polymer molecules.^{14,15} The accuracy of the present data does not suffice, however, to discuss this point in more detail.

The DRS measurements on the trimer and the data evaluation are published elsewhere.¹³ For the trimer, the optical anisotropy, $\langle \gamma^2 \rangle$, is 1601 Å.⁶

Results and Discussion

Theory and Evaluation of Data. (i) Monodisperse Systems. Given the validity of the group addi-

tivity scheme, the analysis of the magnetic birefringence of the polyesters can be done along the lines given by Benoit et al.¹⁶ and by Maret and Weill.⁵ We first consider the tensors $\hat{\alpha}_0$ and $\hat{\kappa}_0$ of the optical polarizability α_0 and the magnetic susceptibility κ_0 of the repeating unit. By definition,

$$\hat{\alpha}_0 = \alpha_0 - \frac{1}{3}\text{tr}(\alpha_0)E \quad (2)$$

and

$$\hat{\kappa}_0 = \kappa_0 - \frac{1}{3}\text{tr}(\kappa_0)E \quad (3)$$

with $E = \text{diag}(1,1,1)$. The tensor $\hat{\alpha}_0$ is decomposed into a cylindrical part and an acylindrical part by

$$\hat{\alpha}_0 = \Delta\alpha_0 J + \Delta\alpha_0^+ J^+ \quad (4)$$

where $J = \text{diag}(2/3, -1/3, -1/3)$ and $J^+ = \text{diag}(0, 1/2, -1/2)$. The respective anisotropies are defined by

$$\Delta\alpha_0 = \alpha_{xx} - \frac{1}{2}(\alpha_{yy} + \alpha_{zz}) \quad (5)$$

and

$$\Delta\alpha_0^+ = \alpha_{yy} - \alpha_{zz} \quad (6)$$

An analogous definition can be used for the respective tensor $\hat{\kappa}_0$ of the magnetic susceptibility of the chains to describe its cylindrical and acylindrical contributions.

An analysis of the tensors $\hat{\alpha}_0$ and $\hat{\kappa}_0$ of the repeating unit along the lines given recently⁷⁻⁹ shows that the cylindrical terms dominate for the trimeric model compound. This is due to the fact that the subsequent phenyl rings adopt finite torsional angles, which leads to the cancellation of the acylindrical terms of the respective compounds. The same holds true in good approximation for the repeating unit of the polyesters under consideration here, which consist of four phenyl groups.

The contributions of the side chains are difficult to assess since their average conformation is not known. It is evident from the above discussion, however, that their acylindrical contributions to the above traceless tensors is rather small, since uncorrelated rotations of subsequent repeating units will lead to cancellation of these terms and to an approximately cylindrical symmetry of the chains.

Given these assumptions, the TPPE polyesters can be treated within the frame of the wormlike chain model. According to Maret and Weill,⁵ the specific CM constant of a monodisperse wormlike chain is given by

$$C_2^b = KqF(x) \quad (7)$$

where $x = 3L/q$ denotes the reduced contour length, L is the contour length of the chain, and q is the persistence length.

The function $F(x)$ describes^{5,16} the dependence of C_2^b on the contour length L :

$$F(x) = 1 - \frac{1}{x} [1 - \exp(-x)] \quad (8)$$

For the limit of short chains, $F(L) \rightarrow (3/2)L/q$, whereas for the limit of very long chains, $F(L) \rightarrow 1$. In the latter limit, the specific CM constant will become independent of molecular weight, as expected.

The constant K is given by

$$K = \frac{\mu_0}{405\epsilon_0} \frac{(n_1^2 + 2)^2}{n_1} \frac{N_A \rho_1}{\lambda k T} \frac{\Delta\alpha_0 \Delta\kappa_0}{l_0 M_0} \quad (9)$$

where N_A is Avogadro's number, k is the Boltzmann constant, T is the absolute temperature, l_0 (2.2 nm for the TPPE; estimated from the data in refs 17 and 18) is the length of the repeating unit, and M_0 (560 g/mol) the mass of the repeating unit, n_1 and ρ_1 are the refractive index and the density of the solvent, respectively, and ϵ_0 is the dielectric constant of the vacuum. It must be understood that the above analysis requires K to be independent of molecular weight, i.e., the validity of the group additivity scheme must be assumed (cf. Introduction).

In this context, the definition of the specific CM constant refers to infinite dilution; hence, the local field correction and the density of the medium is defined by the pure solvent. This is different from the definition of the molar quantities employed previously.⁷

(ii) Polydisperse Samples. For polydisperse samples, we obtain for the C_2^b

$$C_2^b = Kq \sum_i w_i F(x_i) \quad (10)$$

where w_i and x_i are the weight fraction and the reduced contour length ($x_i = 3L_i/q$), respectively, of species i . Thus, the magnetic birefringence measures the weight-average Cotton–Mouton constant. To assess the effect of nonuniformity in detail, it is expedient to render the weight fractions by a Schulz–Zimm distribution,

$$w(L) = \frac{L^m}{\Gamma(m+1)} y^{m+1} \exp(-yL) \quad (11)$$

where $y = (m+1)/L_w$, $m = (L_w/L_n - 1)^{-1}$, and L_w and L_n are the weight-average and the number-average contour lengths, respectively. Introduction into eq 10 leads to

$$C_b^2 = Kq \left[1 - \frac{m+1}{mx_w} \left(1 - \left(1 + \frac{x_w}{m+1} \right)^{-m} \right) \right] \quad (12)$$

with the reduced contour length, x_w , being defined by $x_w = 3L_w/q$. A comparison with the CM constant resulting from eq 7 immediately shows that the effect of polydispersity needs to be taken into account; neglecting this effect would lead to values of the persistence length being much too high to be reconciled with other experimental data.

For a most probable distribution, a particularly simple relation is obtained:

$$\frac{Kq}{C_2^b} = 1 + \frac{2}{x_w} \quad (13)$$

Again, for small x_w , the specific CM constant $C_2^b \rightarrow K(3/2)L_w$; for large x_w , the specific CM constant becomes independent of molecular weight.

Trial calculations using eq 12 with different nonuniformities, as expressed by m , show that the width of the distribution has a minor influence, in particular at high x_w . For the present set of data, a plot of the reciprocal specific CM constant versus L_w^{-1} should, therefore, lead to straight lines with intercept $(Kq)^{-1}$. Figure 3 shows such a plot, which leads to a value of $Kq = 1850 \times 10^{-16} \text{ mA}^{-2}$. This limit corresponds to the CM constant C_2^b at infinite chain length. The constant

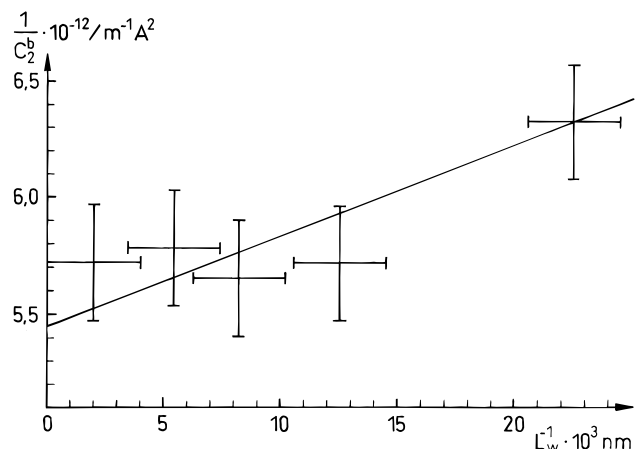


Figure 3. Plot of the reciprocal specific CM constants according to eq 13 versus the reciprocal contour length, L_w . See text for further explanation.

K can be estimated from the slope to be $173 \times 10^{-7} \text{ A}^{-2}$, which would give a persistence length of approximately 11 nm. This is in good agreement with the figure deduced previously (9 nm, ref 12). It must be stated clearly, however, that the dependence of C_2^b on molecular weight observed herein is too small for the persistence length to be determined accurately; the persistence length deduced herein is afflicted by an error of the order or 20% at least. But the present data show unambiguously that the TPPE polyester must be regarded as a semiflexible chain; the above data are not compatible with much higher values of q .

Estimate of K . The above data (see Table 1) lead to a value of $Kq = 1850 \times 10^{-16} \text{ mA}^{-2}$. It remains to compare this value with an estimation from incremental schemes. As already remarked above, the repeating unit is treated as a cylindrical entity by disregarding the acylindrical terms of the tensors $\hat{\alpha}_0$ and $\hat{\kappa}_0$.

At first, $\Delta\alpha_0$ is deduced from the optical anisotropy, γ^2 , of the trimer measured by DRS. In general, the optical anisotropy $\langle\gamma^2\rangle$ follows as^{2,8}

$$\langle\gamma^2\rangle = \text{tr}(\hat{\alpha}\hat{\alpha}) = (\Delta\alpha)^2 + \frac{3}{4}(\Delta\alpha^+)^2 \quad (14)$$

By virtue of the above approximation, i.e., neglecting the acylindrical contributions, $\langle\gamma^2\rangle$ of the trimer may be approximated by $(\Delta\alpha_{\text{trimer}})^2$. Thus, the measured value of $\langle\gamma^2\rangle = 1601 \text{ \AA}^6$ leads to $\Delta\alpha_{\text{trimer}} = 44.53 \times 10^{-40} \text{ Asm}^2 \text{ V}^{-1}$. This anisotropy includes the cylindrical contribution of the side chains as well as the contributions of one *p*-methoxyphenyl group and of the other methoxy group. To obtain the respective anisotropies of the repeating unit of TPPE polyesters, one has to subtract, therefore, the respective contribution Γ of the anisoyl endgroup of the trimer. From the previous analysis, we obtain for $\Delta\alpha(\text{anisoyl group}) = 7.97 \text{ \AA}^3 (= \Delta\alpha''\text{-substituted of ref 7}) + 2(0.072 \text{ \AA}^3) (= \Gamma \text{ of ref 7})$. Within these approximations, we obtain $\Delta\alpha_0 = 35.50 \times 10^{-40} \text{ Asm}^2 \text{ V}^{-1}$ for the repeating unit of the polyester.

The specific CM constant of the trimer (cf. Table 1) may be used to estimate $\Delta\kappa_0$ of the repeating unit. Here, the same approximation applies, and the acylindrical contribution of $\hat{\kappa}$ is dismissed. Using $\Delta\alpha_{\text{trimer}} = 44.53 \times 10^{-40} \text{ Asm}^2 \text{ V}^{-1}$ as derived above, the diamagnetic anisotropy, $\Delta\kappa_{\text{trimer}}$, of the trimer follows as $30.2 \times 10^{-34} \text{ m}^3$. The latter value is higher than the one calculated

Table 2. Eigenvalues of the Local Group of Bond Susceptibilities⁵ ($10^{-12} \text{ m}^3/\text{mol}$)

	k_{xx}	k_{yy}	k_{zz}
C-C ^a	-99.3	-2.5	-2.5
C-H ^a	-70.4	-39.0	-39.0
C-O ^b	-90.5	-84.2	-47.8
C=O ^c	-16.3	+27.6	-163
-CH ₃	-119	-84.2	-84.2
benzene ^d	-439	-439	-1189
phenyl ^e	-298	-361	-1111

^a Axis 1 along the bond. ^b Axis 1 along the bond and axis 2 in the plane of the pendant oxygen bond. ^c Axis 1 along the bond and axis 2 in the plane of the pendant carbon bond. ^d Axes 1 and 2 in the plane of the benzene ring. ^e Axis 1 along the bond to the pendant group and axis 3 perpendicular to the ring.

from Flygare's increments by disregarding the contribution of the side chains. Using the increments tabulated in Table 2, the diamagnetic anisotropy of the trimer without side chains would be approximately $28 \times 10^{-34} \text{ m}^3$. From this result, it is obvious that the side chains contribute to the anisotropy. The present method of deriving the anisotropies directly from substituted model compounds, however, will minimize the error thus inferred.

To calculate the magnetic anisotropy $\Delta\kappa_0$ of the repeating unit from this result, the same calculation as already done for $\Delta\alpha_0$ (see above) needs to be done. Thus, the contribution of the methoxy groups and the phenyl group of the trimer must be subtracted from $\Delta\kappa_{\text{trimer}}$. Both contributions together amount to $5.30 \times 10^{-34} \text{ m}^3$, as calculated from the increments gathered in Table 2. By inserting the respective anisotropies thus obtained ($\Delta\alpha_0 = 35.5 \times 10^{-40} \text{ Asm}^2 \text{ V}^{-1}$; $\Delta\kappa_0 = 24.9 \times 10^{-34} \text{ m}^3$), we arrive at $K = 132 \times 10^{-7} \text{ A}^{-2}$. In view of the approximate character of the calculation, this result may be considered as satisfactory agreement of theory and experiment. Taking this value of K together with Kq from the experiment, a persistence length of 13.9 nm would result, which still is in the range expected for these systems.^{19,20}

Conclusion

The magnetic birefringence of a semiflexible polyester in solution has been measured and analyzed, taking into account the polydispersity of the polymers. The analysis of the CM data has unambiguously shown that the TPPE polyesters represent semiflexible chains with a persistence length of approximately 11 nm. It is important to include the effect of polydispersity; otherwise, much higher values of q would result, in clear contradiction to previous findings.^{12,19,20} The theoretically estimated value of the constant K , which is the specific CM constant per unit length, was $K = 132 \times 10^{-7} \text{ A}^{-2}$. This figure is smaller than the experimental value ($173 \times 10^{-7} \text{ A}^{-2}$, cf. above). Given the various assumptions and approximations necessary for such a calculation, this result may still be considered satisfactory. It shows that measurements of the CM constant as function of molecular weight are suitable to deduce the persistence length. The present set of molecular weights is too small, however, and does not extend to values low enough to determine the persistence length with greater precision.

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