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Correlation between Intrinsic Viscosity and Flow Birefringence for the Rigid Chains of an Aromatic Polyamide in Solution*

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Theories of flow birefringence and intrinsic viscosity, as developed for wormlike chains in the non-Gaussian range of the molecule length, have been analyzed. As a result, a new presentation is suggested for dynamo-optical data in a form, suitable for the determination of the conformational and optical parameters of the macromolecules: Kuhn's random link A , segment diameter d , and optical anisotropy β per unit length of the chain. A model developed for wormlike cylinders with rounded caps was applied to the data obtained for the rigid-chain polybenzimidazolterephthalamide.

Keywords: Wormlike cylinders; Persistence length; Random link; Contour length; Optical anisotropy; Flory's viscosity coefficient

INTRODUCTION

The investigation of the Maxwell effect (flow birefringence) in polymer solutions is a well-known method for the determination of conformational and optical parameters of the macromolecule.^[1,2] Each macromolecule can be characterized by a contour length $L(=M/M_L$, where M is molar mass and M_L is the molar mass per unit contour length of the molecule), by a number N of random links (with $N=L/A=L/2q$,

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where q is the persistence length and A is the length of the random link), and by a hard-core diameter d . The dynamo-optical constant $[n]$ is defined by $[n] = \lim(\Delta n/gc\eta_0)_{g \rightarrow 0, c \rightarrow 0}$ where Δn is the birefringence induced in the polymer solution by shear flow, g is the shear rate, c is the solute concentration and η_0 is the solvent viscosity.

A number of authors, including Tsvetkov,^[3,4] Gotlib and Svetlov^[5,6] and Shimada and Yamakawa,^[7] related birefringence Δn to the optical anisotropy and the degree of coiling of the macromolecule L/A . Intramolecular hydrodynamic interaction and thermodynamic quality of the solvent (excluded volume) both affect the value of $[n]$, whereas the ratio of $[n]$ to the intrinsic viscosity $[\eta]$ (known as the stress optical coefficient) is insensitive to the excluded volume effects. Therefore, this ratio $[n]/[\eta]$ is more often used for a theoretical interpretation of the experimental flow birefringence (FB) data than $[n]$ itself.^[8] Within the low molar mass range, where $L/A \rightarrow 0$ (rodlike chain approximation), the dependence of $[n]/[\eta]$ on L/A is determined by the optical anisotropy β of the unit length of the chain, whereas in the high molar mass range, with $L/A \rightarrow \infty$ (Gaussian coil approximation) this dependence is determined by the optical anisotropy of the random link βA . Hence, if the experimental FB data are available over a sufficiently wide range of molar masses, one can evaluate both, the value of β (from the initial slope of $[n]/[\eta]$, as plotted against L/A) and the length A of the random link (from the ratio of the limiting value of $([n]/[\eta])_\infty$, and the said initial slope).

This evaluation becomes more critical, if the FB data are available only in a narrow range of L/A values in the middle between the mentioned two limits of L/A , in the range of non-Gaussian chains.^[3,4] In this range the treatment must be based on a direct comparison of the experimental data points with the theoretically predicted dependence of $[n]/[\eta]$ on M . The reliability of the conclusions depends here on the adequacy of the chosen model as well as on the width of the range of molecular masses available and, also, on the accuracy of the determination of the molar masses. The situation is particularly intricate, if a reliable molar mass determination is difficult.

Recently Garmonova^[9] compared experimental dynamo-optical and viscometric data with the predictions of the wormlike chain model. In the present study this method is replaced by a more accurate one. According to this latter method, the conformational and the

optical parameters are obtained from the coordinates of the maximum of a spline approximation curve, which is drawn through the points representing the combination of experimental data $([n]/[\eta])/[\eta]^{1/2}$ as plotted against $\log [\eta]$. This spline approximation curve is compared with tabulated theoretical values of FB and intrinsic viscosity, as obtained for the model of a wormlike cylinder with rounded caps. This method is applicable only to a polymer-solvent system, in which form-effects^[3,4] are absent. It goes without saying that it is also assumed that the applied theories have to fit the FB and intrinsic viscosity data with the same values of the conformational parameters.

METHOD

The polymer molecule is characterized by the same values of A , d , and M_L for the description of the FB and viscosity phenomena. An explicit use of contour length L can be avoided by linking $[n]/[\eta]$ to $[\eta]$ through the parameters d , A , β and M_L . This can be accomplished by assuming that the dependence of the dynamo-optical properties on M can well be approximated for the kinetically rigid wormlike chains by Equation (1) over the whole range of changing conformational properties (from the straight rod to the Gaussian coil):^[3,4]

$$([n]/[\eta])^{-1} = ([n]/[\eta])_{\infty}^{-1} [1 + (A/L)], \quad (1)$$

where $([n]/[\eta])_{\infty}$ is the value of $([n]/[\eta])$ in the Gaussian coil limit, $L/A \rightarrow \infty$. This value is determined by the optical anisotropy of the random link βA .^[10]

$$([n]/[\eta])_{\infty} = B\beta A. \quad (2)$$

Here B is an optical coefficient, $B \equiv (4\pi/45kT)(n_0^2 + 2)^2/n_0$, with n_0 being the refractive index of the solvent, k the Boltzmann constant and T the absolute temperature.

We now use Flory's well-known equation for the intrinsic viscosity which is valid for molecules in unperturbed state:

$$[\eta] = \Phi(LA)^{3/2}/M, \quad (3)$$

where Φ is Flory's coefficient. For practical reasons this equation is rearranged as follows:

$$[\eta]/A^2 = \Phi(L/M)(L/A)^{1/2}. \quad (3a)$$

In combining Equations (1), (2) and (3a), one arrives at

$$\frac{[n]/[\eta]}{[\eta]^{1/2}} \times \text{Const}_1^* = P_T^*, \quad (4)$$

where M/L is replaced by M_L and the following notations are accepted:

$$\text{Const}_1^* \equiv 1/B\beta M_L^{1/2} \quad (5)$$

and

$$P_T^* \equiv [\Phi(L/A)^{1/2}]^{-1/2}/(1 + A/L). \quad (6)$$

Taking the logarithm of Equation (3a) one obtains:

$$\log[\eta] + \text{Const}_2^* = Q^*, \quad (7)$$

with the following notation:

$$\text{Const}_2^* \equiv -\log(A^2/M_L), \quad (8)$$

$$Q^* \equiv \log[\Phi(L/A)^{1/2}]. \quad (9)$$

Parameters P_T^* and Q^* are connected with L/A and Φ by Equations (6) and (9). In the general case of non-Gaussian chain molecules the value of Flory's coefficient Φ depends on the contour length and the diameter of the polymer chain, which are of influence on the draining effect. Therefore the parameters P_T^* and Q^* also depend on L/A and d/A and can be tabulated, if Flory's function $\Phi(L/A, d/A)$ is known.

Parameter P_T^* , however, is related by a constant multiplier to the experimental value of the stress optical coefficient $[n]/[\eta]$ through Equation (4). In turn, parameter Q^* is related to $\log[\eta]$ by Equation (7). This fact enables us to perform a joint treatment of the dynamo-optical and the viscometric data and compare them with the theoretical results. The experimental dependence of $([n]/[\eta])/[\eta]^{1/2}$ on $\log[\eta]$

can be brought into coincidence with the model function $P_7^*(Q^*)$ by the choice of suitable values of Const_1^* and Const_2^* . In the next step, the values of β and A can be obtained from Const_1^* and Const_2^* with the aid of Equations (5) and (8).

RESULTS AND DISCUSSION

As a model developed by Yamakawa and Yoshizaki,^[11] a wormlike cylinder was used with its ends being covered by hemispheres. The axis of this flexible cylinder coincides with a thread characterized by a certain persistence length q . The values of Flory's function Φ were evaluated using Equations (25)–(33) given in the cited work. They are presented in Figure 1 for different reduced lengths and diameters (L/A and d/A) of our special wormlike cylinders. They differ from those calculated by Yamakawa and Fujii^[12] for ordinary wormlike cylinders (without caps) only in the range of low values of L/A .

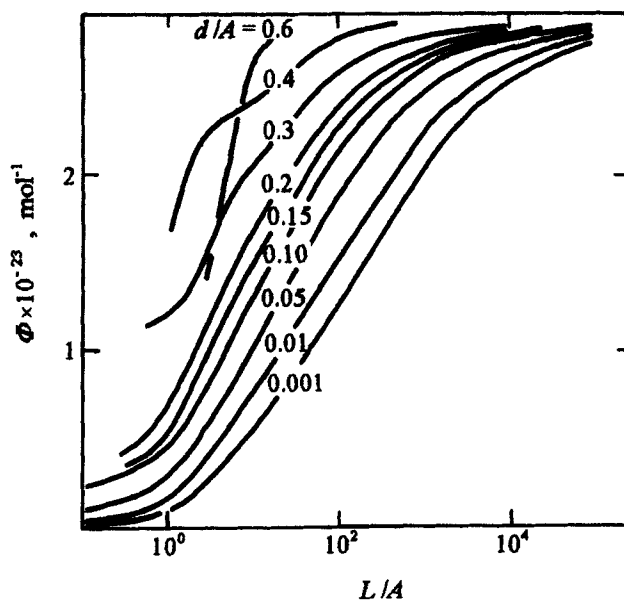


FIGURE 1 Semilogarithmic plot of Flory's coefficient Φ versus reduced chain length as predicted by the theories for the wormlike cylinder model with rounded caps.^[11] Numbers at the curves indicate the d/A values.

TABLE I Abscissa Q_{\max} and ordinate $P_{T,\max}$ of the maximum of P_T as a function of Q and the corresponding $(L/A)_{\max}$ values, as calculated for wormlike model chains with different d/A values by Equations (6), (9) and (10) according to the theory given by Yamakawa and Yoshizaki^[11] and Tsvetkov^[3,4]

d/A	$P_{T,\max}$	Q_{\max}	$(L/A)_{\max}$
0.001	64.31	0.780	0.187
0.002	58.60	0.994	0.226
0.005	49.03	1.340	0.297
0.010	42.98	1.609	0.378
0.015	39.39	1.778	0.439
0.020	36.84	1.904	0.492
0.025	34.87	2.005	0.540
0.030	33.27	2.088	0.583
0.035	31.93	2.161	0.625
0.040	30.78	2.225	0.663
0.045	29.77	2.282	0.700
0.050	28.87	2.333	0.734
0.060	27.33	2.421	0.798
0.070	26.06	2.497	0.858
0.080	24.97	2.564	0.915
0.090	24.02	2.622	0.966
0.100	23.18	2.675	1.017
0.110	22.43	2.723	1.064
0.120	21.75	2.766	1.107
0.130	21.14	2.806	1.149
0.140	20.57	2.844	1.191
0.150	20.05	2.878	1.227
0.160	19.57	2.911	1.264
0.170	19.12	2.942	1.301
0.180	18.71	2.970	1.335
0.200	17.95	3.025	1.404
0.300	15.16	3.241	1.722

Insertion of our values of Φ into Equations (6) and (9) furnishes the model parameters P_T^* and Q^* for different values of L/A and d/A (Table I). From the experimental units usually used, these calculations were made in terms of

$$\begin{aligned} P_T &= 10^{13} P_T^*, \\ Q &= Q^* - 20. \end{aligned} \quad (10)$$

Accordingly,

$$\begin{aligned} \text{Const}_1 &= 10^{13} \text{Const}_1^*, \\ \text{Const}_2 &= \text{Const}_2^* - 20. \end{aligned} \quad (11)$$

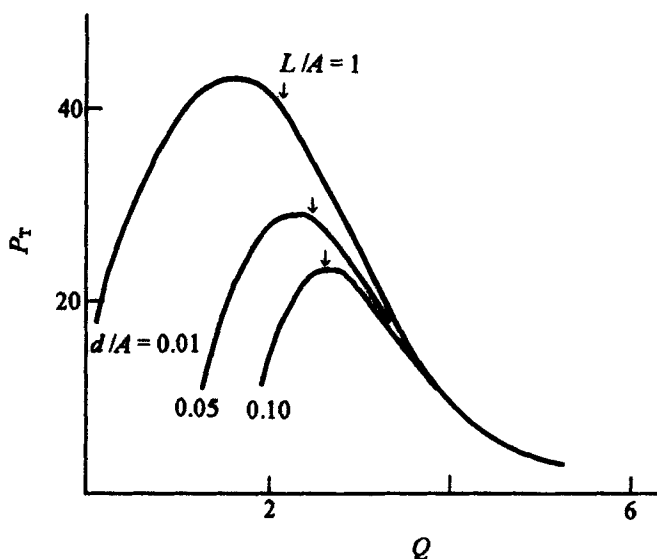


FIGURE 2 Model function P_T plotted against Q according to Equations (6), (9), and (10) for the worlike cylinder model with rounded caps for different reduced chain diameters d/A .

Figure 2 illustrates some principal results. One learns that P_T is a unimodal function of Q with a maximum predicted to occur in the range of reduced lengths of $0.3 < L/A < 1.4$ for chains possessing equal diameters in the range $0.005 < d/A < 0.2$.

Figure 2 also shows that, with decreasing d/A , the maximum of $P_T(Q)$ function increases in height and shifts to lower values of Q (lower L/A), this shift becomes more pronounced with further decreasing d/A (Figure 3). Hence, lower values of d/A can be determined with higher accuracy. The coordinates of the maximum, Q_{\max} and P_{\max} , as calculated for chains of different lengths and diameters, are collected in Table I.

From Figure 2 we also learn that, with decreasing d/A the curve $P_T(Q)$ becomes wider. This results in a reduction of the accuracy in the determination of the location Q_{\max} of the maximum. For practical purposes, the location of the maximum of the wider experimental curve might be more reliably presented by the abscissa Q_{av} of the "median" point located at equal distances from the left and right

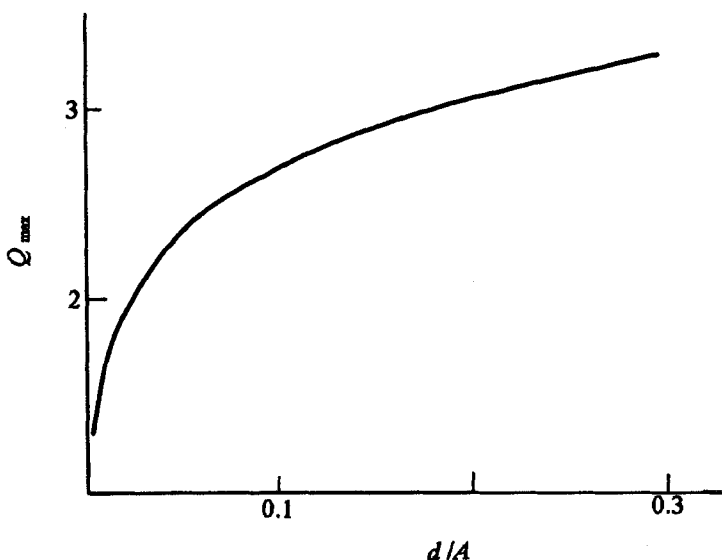


FIGURE 3 Change in the abscissa of the maximum of the $P_T(Q)$ function with increasing d/A .

branches of the $P_T(Q)$ at a chosen level of P_T . Clearly, the abscissa of this median point approaches Q_{\max} with $P_T \rightarrow P_{T,\max}$. For this reason Q_{av} is used below instead of Q_{\max} . The relative width $\Delta Q/Q_{\text{av}}$ of the $P_T(Q)$ curve, as obtained at different levels of P_T (5, 10, 20 and 30% of $P_{T,\max}$), was calculated analytically. These values of $\Delta Q/Q_{\text{av}}$ are collected in Table II. The pertinent values of Q_{av}^2 are given in Table III.

The data of these tables clearly show that the width of the $P_T(Q)$ curve, as found close to the position of the maximum, is sensitive to a reduced diameter of the chain d/A . As a consequence, the relative width of the experimental dependence of $([\eta]/[\eta])/[\eta]^{1/2}$ on $\log[\eta]$, as measured close to the maximum, might be used for an estimate of d/A . In turn, the value of Q_{\max} depends on A^2/M_L (by Equation (8)), whereas $P_{T,\max}$ is related to $\beta M_L^{1/2}$ (by Equation (5)). Therefore, Q_{\max} and $P_{T,\max}$ might be used for the determination of A and β .

The question may arise how the results obtained in this way depend on the approximation used in Equation (1). To answer this question, the function $P(Q)$ was calculated for a wormlike chain with a reduced

TABLE II Relative width $\Delta Q/Q_{av}$ of the $P_T(Q)$ curve at the level $P_T/P_{T,max}$, as calculated for wormlike model chains with different d/A values by Equations (6), (9) and (10) according to results of Yamakawa and Yoshizaki^[11] and Tsvetkov^[3,4]

d/A	$P_T/P_{T,max}$			
	0.95	0.90	0.80	0.70
0.005	1.6573	1.7176	1.8387	1.9598
0.006	1.6137	1.6695	1.7810	1.8919
0.007	1.5756	1.6276	1.7314	1.8344
0.008	0.6126	0.8686	1.2326	1.5146
0.009	0.5813	0.8237	1.1674	1.4340
0.010	0.5549	0.7858	1.1123	1.3660
0.012	0.5121	0.7241	1.0235	1.2569
0.015	0.4641	0.6553	0.9249	1.1365
0.020	0.4084	0.5758	0.8125	0.9993
0.030	0.3399	0.4786	0.6799	0.8349
0.040	0.2971	0.4186	0.5974	0.7353
0.050	0.2667	0.3766	0.5397	0.6664
0.060	0.2437	0.3452	0.4965	0.6151
0.070	0.2254	0.3207	0.4627	0.5750
0.080	0.2105	0.3013	0.4353	0.5424
0.090	0.1980	0.2838	0.4125	0.5152
0.100	0.1874	0.2696	0.3932	0.4918
0.120	0.1709	0.2474	0.3606	0.4538
0.150	0.1544	0.2230	0.3260	0.4123
0.200	0.1317	0.1931	0.2857	0.3644

TABLE III Average abscissa Q_{av} of the $P_T(Q)$ curve at the level of $P_T/P_{T,max}$, as calculated for wormlike model chains with different d/A values by Equations (3), (6) and (9) according to results of Yamakawa and Yoshizaki^[11] and Tsvetkov^[3,4]

d/A	$P_T/P_{T,max}$			
	0.95	0.90	0.80	0.70
0.008	1.5216	1.5232	1.5270	1.5446
0.009	1.5692	1.5718	1.5773	1.5972
0.010	1.6125	1.6159	1.6228	1.6445
0.012	1.6889	1.6930	1.7024	1.7272
0.015	1.7844	1.7896	1.8016	1.8300
0.020	1.9110	1.9170	1.9330	1.9650
0.030	2.0959	2.1026	2.1286	2.1598
0.040	2.2312	2.2386	2.2682	2.3014
0.050	2.3382	2.3464	2.3784	2.4135
0.060	2.4272	2.4363	2.4698	2.5065
0.070	2.5032	2.5139	2.5484	2.5862
0.080	2.5696	2.5826	2.6174	2.6558
0.090	2.6288	2.6418	2.6790	2.7174
0.100	2.6822	2.6963	2.7345	2.7726
0.120	2.7760	2.7928	2.8292	2.8684
0.150	2.8949	2.9124	2.9496	2.9884
0.200	3.0427	3.0644	3.1047	3.1439

diameter $d/A = 0.05$ in two ways: the function $P_T(Q)$ was calculated using the approximation of Equation (1) and the function $P_S(Q)$ was calculated according to the FB theory, as developed by Gotlib and Svetlov^[5,6] for the dependence of the stress optical coefficient on the molar mass M . As is well-known, this coefficient is often used in the treatment of FB data.^[7,8] The mentioned functions are compared in Figure 4. It can easily be seen that for a chain with a reduced length in the range $1 < L/A \leq 100$, $P_S(Q)$ and $P_T(Q)$ differ by no more than 5%. This difference is close to the experimental error. We may conclude, therefore, that the application of the two different FB theories to the experimental FB data leads to variations in the conformational and optical parameters, which do not exceed the uncertainties of the experimental determination.

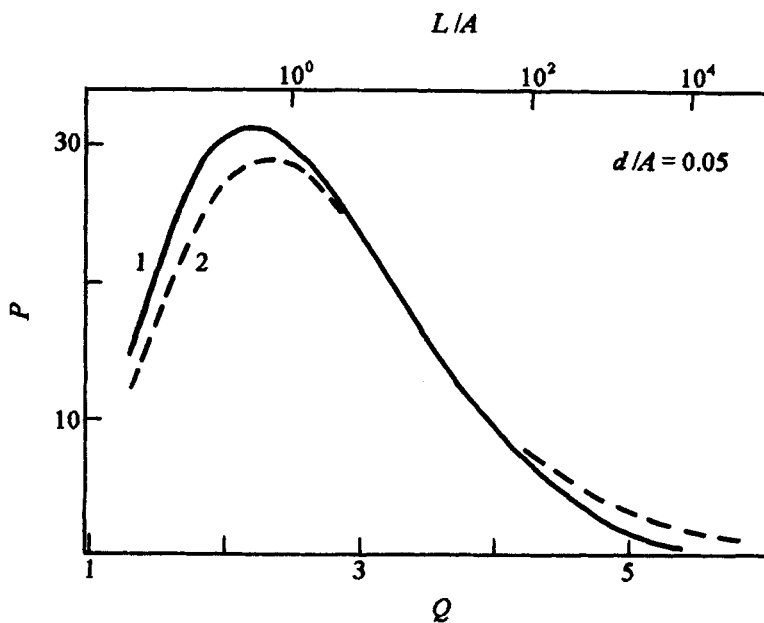


FIGURE 4 P_S and P_T plotted against Q (curves 1 and 2, respectively) for the worm-like cylinder model with rounded caps for $d/A = 0.05$, and calculated with the assumption of different molar mass dependences of $[\eta]/[\eta]$ by (1) Gotlib-Svetlov^[6] and (2) Tsvetkov.^[3,4]

RESULTS AND DISCUSSION

Experimental FB data, as obtained by Lavrenko *et al.*^[13] for solutions of polybenzimidazolterephthalamide in sulfuric acid are presented in Figure 5 as data points for $[n]/[\eta]$ (points 1) and for $([n]/[\eta])/[\eta]^{1/2}$ (points 2) in a plot against $\log[\eta]$. Solid curve 2 is the spline-approximation of the points 2. One can see that $[n]/[\eta]$ increases monotonically with $[\eta]$ (points 1) without reaching the expected saturation. Such behavior is typical for rigid chain polymers.^[14] In contrast, curve 2 has a well-defined maximum. Let us compare the experimental curve 2 with the one given by the model function $P_T(Q)$.

The relative values of the width of curve 2 on the levels $P_T = 0.9P_{T,\max}$ and $0.8P_{T,\max}$ are equal to $\Delta Q/Q_{\text{av}} = 0.55$ and 0.83 , respectively. According to Table II, these values are predicted for a chain with $d/A = 0.020 \pm 0.002$.

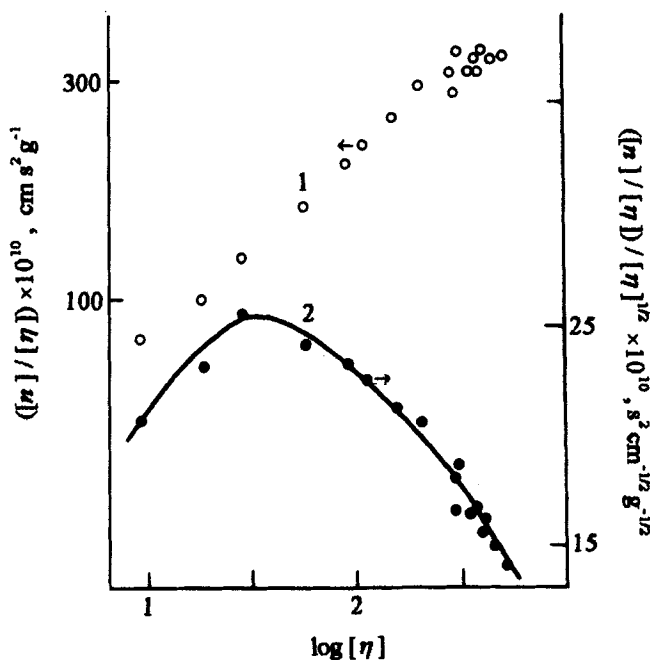


FIGURE 5 Experimental values of $[n]/[\eta]$ and $([n]/[\eta])/[\eta]^{1/2}$ (points 1 and 2, respectively) versus $\log[\eta]$ as obtained by Lavvenko *et al.*^[13] for rigid chain polybenzimidazolterephthalamide in 96% H_2SO_4 . Solid curve 2 represents the spline-approximation.

The abscissae of the median points of curve 2 at the levels 0.9 and 0.8 are 1.58 and 1.61, respectively. The average value, viz $(\log [\eta])_{av} = 1.595$, might be compared with $Q_{av} = 1.925$, as given Table III for the chains with the values of $d/A = 0.02$ determined above. Using Equations (7) and (11) we obtain $\text{Const}_2 = 0.330 \pm 0.007$. Inserting this value and $M_L = 19.56 \times 10^{10} \text{ g mol}^{-1} \text{ m}^{-1}$ into Equations (11) and (8), one obtains for the length of the random link $A = 30 \pm 2 \text{ nm}$ and for the chain diameter $d = 0.6 \pm 0.1 \text{ nm}$.

The height of the maximum of the experimental curve 2 of Figure 5 is equal to 25.2×10^{10} . With this value and with $d/A = 0.02$ for the model chain value of $P_{T,max} = 36.84$ can be read from Table I. Insertion of these values into Equations (4) and (11) yield $\text{Const}_1 = 1.46$. Using in Equations (5) and (11), this value of Const_1 together with the above quoted value of M_L and value^[13] of $B = 7.9 \times 10^{20} \text{ J}^{-1}$ for the stress optical coefficient of Equation (2), one obtains $\beta = 19.6 \times 10^{13} \text{ m}^2$. The latter value is in good agreement with an optical anisotropy per unit length of the chain, as found previously by Tsvetkov^[14] for aromatic polyamidobenzimidazoles of similar structure.

CONCLUSIONS

In the past, several authors (e.g., Doudos and Benoit;^[15] Dondos and Staikos;^[16] Lavrenko^[17,18]) have tried to replace nonlinear experimental interdependences by linear relations between properly chosen new (composite) parameters. For example, Tsvetkov^[14] has shown that – for a certain family of polymers and in a restricted range of molar masses – a linear relation exists between the reciprocal values of the stress optical coefficient and the molar mass. However, because of the mentioned restrictions no physical law can be deduced from those linear relations. As a consequence, a direct comparison between the unchanged results and their theoretical predictions should be favored^[3–7] in the general case. In the present paper, however, a compromise was made. A nonlinear presentation was admitted for the interdependence of properly chosen parameters for a comparison between experimental and theoretical relations. The higher power of $[\eta]$ used herein puts obviously higher standards on the adequacy of the theories of intrinsic viscosity and FB.

Excluded volume effects (which may hardly be noticeable in the specific low L/A range discussed above) and polydispersity of the polymer sample may be the reasons of underestimated A -values and overestimated d -values. The β -values are affected in different directions: excluded volume effects lead to lower values, whereas higher values are expected when polydispersity is taken into account.

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