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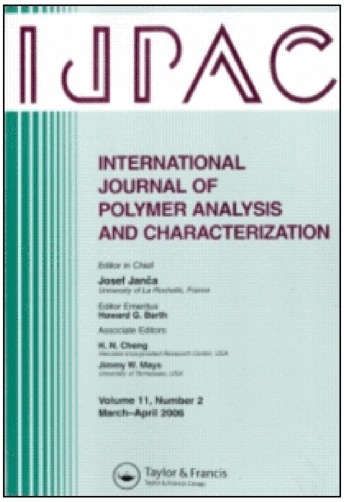

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Hydrodynamic Parameters of Linear Aromatic Polyester of 3-Phenylglutaric Acid and Bisphenol A

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Abstract: A series of samples of linear aromatic polyester of 3-phenylglutaric acid and bisphenol A was prepared with molecular weights ranging from 14 700 to 92 700. The polymers were characterized by size exclusion chromatography with triple light-scattering, viscosity, and concentration detection. Hydrodynamic parameters of the chain were determined using the theory of Yoshizaki, Yamakawa, and Nitta modified by Bohdanecký and Netopilík. The chain parameters are a useful reference in the study of aromatic hyperbranched polyesters.

Keywords: Chain parameters; Linear polyester; Size exclusion chromatography; Triple detection

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INTRODUCTION

Within the framework of the systematic study of the synthesis, structure, and properties of hyperbranched aromatic polyesters based on 4,4-bis-(4-hydroxyphenyl)pentanoic acid, we deemed it desirable to determine the hydrodynamic parameters of a linear polyester with a structure resembling that of the hyperbranched polymer. The linear polymer was obtained by polycondensation of 3-phenylglutaric acid (3-phenylpentanedioic acid) and bisphenol A (4,4(propane-2,2-diyl)diphenol). The systematic name of the product is poly[oxy(3-phenylpentanedioyl)oxy(1,4-phenylene)propane-2,2-diyl(1,4-phenylene)] (Figure 1). We have synthesized a series of the linear polymers with molecular weights ranging from 14 700 to 92 700 and characterized them by size exclusion chromatography with differential-refractometer, light-scattering, and viscosity detectors. The advantage of the triple detection is, among others, that no calibration is needed.

The molecular-weight dependence of intrinsic viscosity of the linear polymer, needed for characterization of branched polymers, has been expressed through the Mark-Houwink equation. Molecular weights of the polymers prepared were relatively low. This implies that the random-coil behavior may not have been reached yet. Therefore, experimental data were analyzed and parameters characterizing the chain structure calculated using the theory of Yamakawa and Fujii[1] as modified by Bohdanecký and Netopilík[2] The theory and its modification are appropriate for the evaluation of hydrodynamic data for dilute solutions of polymers that due to short chain length or chain stiffness, or both, cannot be treated as random coils.

CHAIN CONFORMATION PROPERTIES

In describing the solution behavior of short, stiff-chain, or flexible macromolecules, the concept of equivalent chain is useful. An equivalent chain

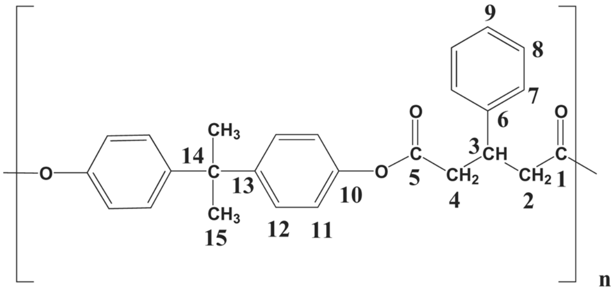

Figure 1. Formula of the aromatic polyester studied, poly[oxy(3-phenylpentanedioyl)oxy(1,4-phenylene)propane-2,2-diyl(1,4-phenylene)].

relates to a real polymer chain by the requirement that both chains must have the same end-to-end distance and the same contour length. The end-to-end distance is a quantity obtainable experimentally and the contour length can be calculated from the chemical structure of the chain and molecular weight of the polymer.

The Yamakawa theory, based on the wormlike touched bead model, describes the dependence of intrinsic viscosity, $[\eta]$, on molecular weight, M, by the equation.[1,3]

$$[\eta] = [\Phi_{0,\infty} \cdot (\langle R^2 \rangle_0 / M)_{\infty}^{3/2} \cdot M^{1/2}]\Gamma(L_{\mathrm{r}}; d_{\mathrm{b,r}}) \tag{1}$$

The right-hand side of the equation is a product of the classical Flory relation, valid for Gaussian coils under theta conditions, and the function $\Gamma(L_{\mathrm{r}}; d_{\mathrm{b,r}})$, which takes into account the non-Gaussian behavior of the chain. In Equation (1), $\Phi_{0,\infty}$ is the Flory viscosity function, $(\langle R^2 \rangle_0 / M)_{\infty}$ is the ratio of the mean-square end-to-end distance in the random-coil limit, $\langle R^2 \rangle_0$, and molecular weight, M. The function $\Gamma(L_{\mathrm{r}}; d_{\mathrm{b,r}})$ is given by Equations (25) and (26) in Yoshizaki et al.,[3] L_{r} is the number of segments of the equivalent chain (occasionally called also Kuhn statistical segments) defined as

$$L_{\mathrm{r}} \equiv L/\lambda^{-1} = M/(M_L \cdot \lambda^{-1}) \tag{2}$$

where L is the contour length of the chain, M_L is the molecular weight per unit contour length of the chain, λ^{-1} is the length of a segment of the equivalent chain

$$\lambda^{-1} = (\langle R^2 \rangle_0 / M)_{\infty} \cdot M_L \tag{3}$$

and $d_{\mathrm{b,r}}$ is the reduced bead diameter, i.e., the bead diameter, d_{b}, divided by the length of a segment of the equivalent chain:

$$d_{\mathrm{b,r}} = d_{\mathrm{b}}/\lambda^{-1} \tag{4}$$

The function in Equation (1) can be expressed by[2]

$$\Gamma(L_{\mathrm{r}}, d_{\mathrm{b,r}}) \cdot L_{\mathrm{r}} = A_0' + B_0' \cdot L_{\mathrm{r}}^{1/2} \tag{5}$$

where $B_0' \approx 1$ and the dependence of the parameter A_0' on the reduced bead diameter, $d_{\mathrm{b,r}}$, is given in Table 1 in Bohdanecký and Netopilík[2] The values of A_0' and B_0' can be determined from experimental data by plotting $[\eta]$ versus $M^{1/2}$ according to the equation

$$[\eta] = A_\eta' + K_0 \cdot M^{1/2} \tag{6}$$

where

$$A_\eta' = \Phi_{0,\infty}(\langle R^2 \rangle_0 / M)_{\infty}^{3/2} \cdot A_0' \cdot M_\lambda^{1/2} \tag{7}$$

In Equation (7), M_λ stands for the molecular weight per segment of the equivalent chain, i.e.,

$$M_\lambda = M_L \cdot \lambda^{-1} \tag{8}$$

and K_0 is

$$K_0 = \Phi_{0,\infty} \cdot (\langle R^2 \rangle_0 / M)_\infty^{3/2} \tag{9}$$

Having determined A'_0 from Equation (7), we find in Table 1 in Bohdanecký and Netopilík[2] the corresponding value of the reduced bead diameter, $d_{\mathrm{b,r}}$. Then, important chain-conformation parameters are easily calculated, such as the ratio $(\langle R^2 \rangle_0 / M)_\infty$ (Equation (9)), length of a segment of the equivalent chain, λ^{-1} (Equation (3)), molecular weight per segment of the equivalent chain, M_λ (Equation (8)), the bead diameter, d_b (Equation (4)), and the characteristic ratio C_∞.

DETERMINATION OF MOLECULAR WEIGHT AND RADIUS OF GYRATION

The dependence on the angle of observation of the intensity of light scattered from a dilute solution of a nonuniform polymer can be written in a form convenient for data evaluation as[4]

$$\frac{K(\mathrm{d}n/\mathrm{d}c)^2 c}{R(\theta)} = \frac{1}{M_\mathrm{w} P(\theta)} + 2A_2 c + \cdots \tag{10}$$

where $R(\theta)$ is the intensity of light scattered at an angle of observation θ, expressed in terms of the excess Rayleigh ratio, $\mathrm{d}n/\mathrm{d}c$ is the refractive index increment at the wavelength of the incident light in the medium, λ, K is an optical constant, c is the mass concentration of the polymer, M_w is the weight-average molecular weight, $P(\theta)$ is the average particle scattering function, and A_2 is the second virial coefficient. The initial slope of $1/P(\theta)$ as a function of $\sin^2(\theta/2)$ is proportional to the z-average radius of gyration

$$\overline{s_\mathrm{z}^2} = \frac{1}{M_\mathrm{w}} \sum_i w_i M_i s_i^2 \tag{11}$$

where w_i is the mass fraction of polymer molecules with radius of gyration s_i and molecular weight M_i.

The on-line light-scattering (LS) data in size-exclusion chromatography (SEC) are evaluated according to Equation (10) at a single concentration so low that the contribution of the second term on the right-hand side can be neglected. In the off-line mode, the LS measurements are taken at several concentrations and processed in the form of a Zimm plot.[4]

The molecules of most polymers characterized in the present study are so small that the angular dependence of the scattering intensity is hardly perceptible and the radius of gyration cannot be measured with adequate accuracy. Therefore, for those polymers, we have applied the iteration procedure suggested by the Viscoteck Corp[5]: the first approximation of the radius of gyration is obtained from the Flory-Fox equation

$$(s^2)^{3/2} = (1/6^{3/2})([\eta]M/\Phi_{0,\infty}) \tag{12}$$

where $\Phi_{0,\infty} = 2.5 \times 10^{23}\,\mathrm{mol}^{-1}$, $[\eta]$ is the intrinsic viscosity in $\mathrm{mL \cdot g^{-1}}$ and M is the molecular weight obtained from the scattering intensity at the angle of observation $\theta = 90^\circ$ using Equation (10) and assuming $P(90) = 1$. For that value of s^2, the value of $P(90)$ is calculated from the equation.[4,6]

$$P(\theta) = (2/x^2)[\mathrm{e}^{-x} - (1 - x)] \tag{13}$$

where $x = 16\pi^2(s^2/\lambda^2)\sin^2(\theta/2)$. This value of $P(90)$ substituted into Equation (10) yields the second approximation to M. The procedure is repeated until constant values of M, s^2, and $P(90)$ are obtained.

The particle scattering function expressed by Equation (13) is, strictly speaking, valid only for Gaussian coils, i.e., sufficiently long chains in a theta solvent. This requirement is not fulfilled for the present polymer. The error thus induced, however, is negligible because we operate in a range of small values of the variable x, where the value of $P(\theta)$ is only slightly affected by the particle shape.[6]

EXPERIMENTAL SECTION

Synthesis of the Polyester

The polymerization catalyst, 4-(dimethylamino)pyridinium tosylate (DPT), was synthesized and polymerization performed after Moore and Stupp.[7] The synthesis of the polyester was carried out as follows: bisphenol A (1.987 g, 8.7 mmol), 3-phenylglutaric acid (1.812 g, 8.3 mmol), and DPT (0.992 g, 3.37 mmol) were stirred in 40 mL methylene chloride under argon atmosphere. The reaction flask was flushed with argon, and dicyclohexylcarbodiimide (DCC) (4.635 g, 22.46 mmol) was added. The reaction mixture was stirred at room temperature for 96 h under argon atmosphere. After the reaction was complete the dicyclohexylurea was filtered off and washed with a small amount of methylene chloride. The resulting polymer was reprecipitated twice from methanol. The same reaction was carried out with 14.08 g (61.8 mmol) bisphenol A, 12.89 g (59.1 mmol) 3-phenylglutaric, 6.78 g (23.1 mmol) DPT, and 32.3 g (156.8 mmol) DCC in 220 mL methylene chloride. Samples of 30 mL were withdrawn after various time periods (4, 19, 25, 28, 42 h) from the reaction mixture and the polymer was precipitated as described above.

^{1}**H NMR** (DMSO-d$_6$): δ (ppm) 1.56 (s, 6H, $\mathbf{H}_{15}$); 2.91–3.12 (m, 4H, $\mathbf{H}_2$ $\mathbf{H}_4$); 3.64 (m, 1H, $\mathbf{H}_3$); 6.74–6.75 (d, 4H, $\mathbf{H}_{11}$); 7.12–7.14 (d, 4H, $\mathbf{H}_{12}$); 7.22–7.25 (t, 1H, $\mathbf{H}_9$); 7.31–7.34 (t, 2H, $\mathbf{H}_8$); 7.38–7.39 (d, 2H, $\mathbf{H}_7$); 9.14 (s, OH).

^{13}**C NMR** (DMSO-d$_6$): δ (ppm) 30.41 **C15**; 38.69 **C3**; 41.94 **C14**; 121.02 **C11**; 127.02 **C9**; 127.42 **C12**; 127.65 **C7**; 128.44 **C8**; 142.01 **C6**; 147.50 **C13**; 148.09 **C10**; 170.02 **C1 C5**.

Size Exclusion Chromatography Measurements

SEC measurements with the triple light-scattering, viscosity, and concentration detection were performed using a Pump Deltachrom (Watrex Co.), autosampler Midas, two columns with PL gel mixed, particle size 10 μm, separating according to the manufacturer in the range of molecular weights of approximately $400-1\times10^7$. The set was connected to a DAWN DSP-F light-scattering photometer (Wyatt Technology Corp.), measuring at 18 angles of observation, a Viscotek model TDA 301 modified differential viscometer (without internal light scattering and concentration detectors), and a Shodex differential refractometer. Mobile phase was tetrahydrofuran (THF) at ambient temperature (25°C). The flow rate was $0.5\,\mathrm{mL{\cdot}min^{-1}}$. The data were accumulated and processed using Trisec software[5] For sample 96 with distinct angular dependence of scattering intensity, Astra software[8] was employed. Some calculations were performed with laboratory-modified software.

The following parameters in the Trisec software were used (all in mL): variance of the band-broadening function, $\sigma = 0.239$ (standard deviation of the band-broadening function, all signals); the parameters of the exponentially modified function[9]: $\tau = 0.169$ (parameter of nonsymmetry, concentration elution curve) and $\tau = 0.123$ (viscometric and LS curves); offset (interdetector volume with respect to the concentration detector) $= 0.360$ (viscometric curve) and $= 0.630$ (LS curve). The parameters of the band-broadening function and interdetector volumes were determined using the Trisec software from the positions and shapes of light-scattering, viscometric, and concentration elution curves of a narrow molecular-weight-distribution polystyrene standard (30,000, Pressure Chemical).

In the off-line light-scattering measurements, the solutions were pumped at a rate of $0.5\,\mathrm{mL\cdot min^{-1}}$ by a Cole Parmer syringe pump through a Whatman filter of 0.1 nm pore size through the SEC measuring cell of the DAWN instrument.

RESULTS AND DISCUSSION

Table I summarizes the data found for the polyester samples by triple-detection SEC using the iteration procedure described above. The correction is the difference between the M_w values obtained by the iteration procedure or by assuming a constant value of $P(90) = 1$ as described by Equations (12) and (13) and the accompanying text. The correction for $P(90) < 1$ is below 1% except for the sample with the highest molecular weight, where it is 2.4%. The nonuniformity of all polymers, M_w/M_n, is about 1.5.

The molecular-weight dependence of the radius of gyration was obtained by the iteration procedure (Figure 2). The master curve for all samples can be described by the relation

$$s = 2.45 \times 10^{-2} M^{0.554} \tag{14}$$

For sample 96 with the highest molecular weight, we have compared the results obtained by on-line triple-detection SEC (Figure 3) and off-line measurement at four different concentrations. The on-line measurement offers two possibilities for determining the radius of gyration as a function of elution volume. The first one uses the multi-angle LS data for calculation of the radius of gyration according to Equations (10)

Table I. Weight-average molecular weights, M_w, of the polyester samples; per cent correction for M_w, induced by the iteration procedure; weight-to-number-average molecular weight ratios, M_w/M_n; intrinsic viscosities, $[\eta]$; and values of the MHKS exponent obtained in the on-line measurements, a, and calculated from Equations (17) and (19), a_{calc} and a_0, respectively

Sample[a]	$M_w \times 10^{-3}$	Correction %	M_w/M_n	$[\eta]$ mL/g	a	a_{calc}	a_0
4	14.7	0.33	1.42	23.1	0.680	0.671	0.764
19	15.2	0.33	1.54	23.4	0.695	0.670	0.757
25	24.6	0.33	1.66	32.4	0.654	0.663	0.682
28	26.3	0.56	1.50	34.7	0.661	0.662	0.674
42	35.5	0.71	1.58	40.7	0.672	0.658	0.643
96	92.7	2.40	1.68	76.8	0.641	0.644	0.580

[a] The codes of the samples express the time of polymerization in hours.

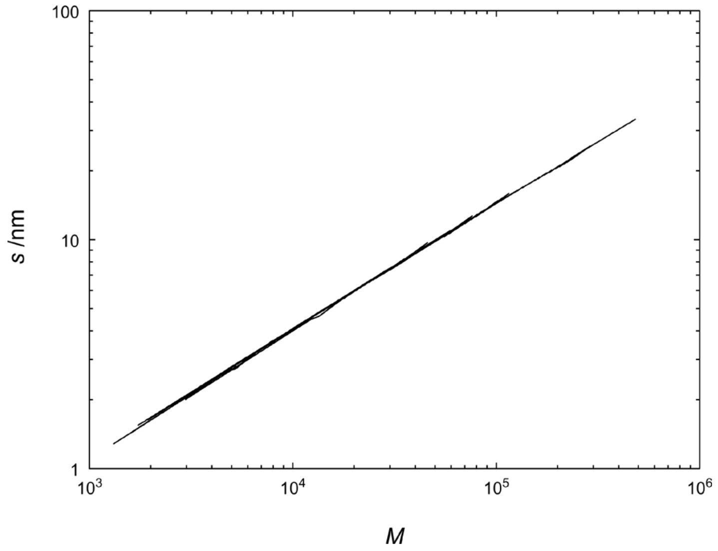

Figure 2. Dependence of radius of gyration, *s*, calculated from Equation (12) using the iteration procedure, on molecular weight, *M*.

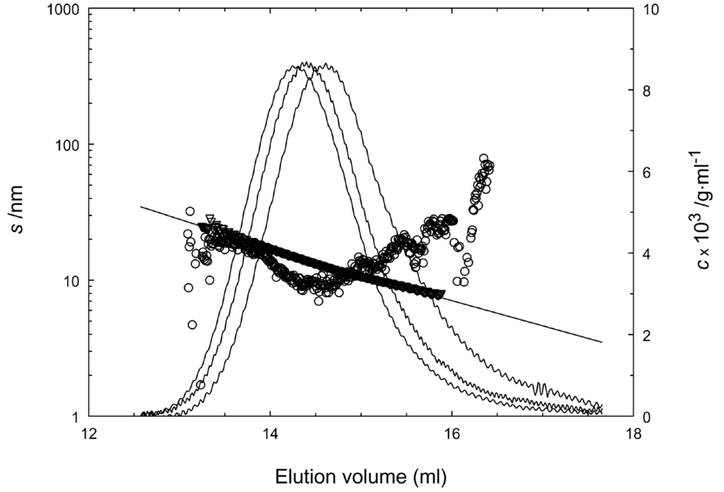

Figure 3. Comparison of the dependence of radius of gyration on elution volume for sample 96 from the angular extrapolation to zero angle according to Equation (10) (○) with values found from Equation (12) and using the iteration procedure (∇); the detection mode of the elution curves from left to right: light scattering, viscosity, concentration.

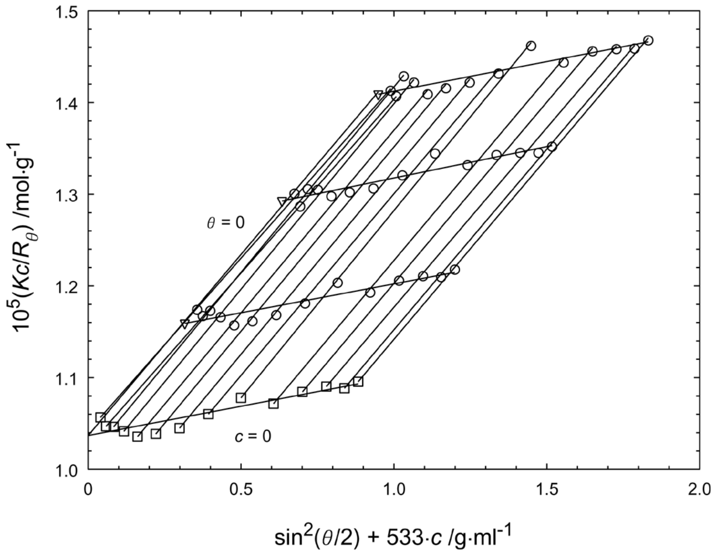

Figure 4. The Zimm plot for sample 96 in THF.

and (11), the other one employs the light-scattering intensity at 90° and the iteration procedure. Because of the small size of molecules measured, the s values for individual elution volumes from multi-angle data are highly scattered and do not enable us to plot a smooth dependence of the radius of gyration on elution volume. The iteration procedure, however, yields a tidy linear dependence of the radius of gyration on elution volume. From SEC data, the average values of molecular weight and radius of gyration for the whole polymer have been calculated. The off-line measurement at four concentrations was evaluated through a Zimm plot (Figure 4). In addition to molecular weight and radius of gyration, the Zimm plot yields the second virial coefficient, A_2. Its value, $A_2 = 9.9 \times 10^{-4}\,\mathrm{mol}^{-2}$, indicates that tetrahydrofuran is a thermodynamically good solvent for the linear polyester studied.

For sample 96, the average values of the radius of gyration obtained by the on-line multi-angle measurement, on-line iteration procedure, and from the Zimm plot were in fair agreement, 13.3, 14.9, and 13.4 nm, respectively.

The molecular-weight dependence of intrinsic viscosity (Figure 5) can be described by the common Mark-Houwink-Kuhn-Sakurada (MHKS) equation

$$[\eta] = 3.98 \times 10^{-2} \times M^{0.664} \tag{15}$$

with a variance of the double-logarithmic plot of 1.92×10^{-4}. The dependence, however, is somewhat curved and is more accurately expressed by

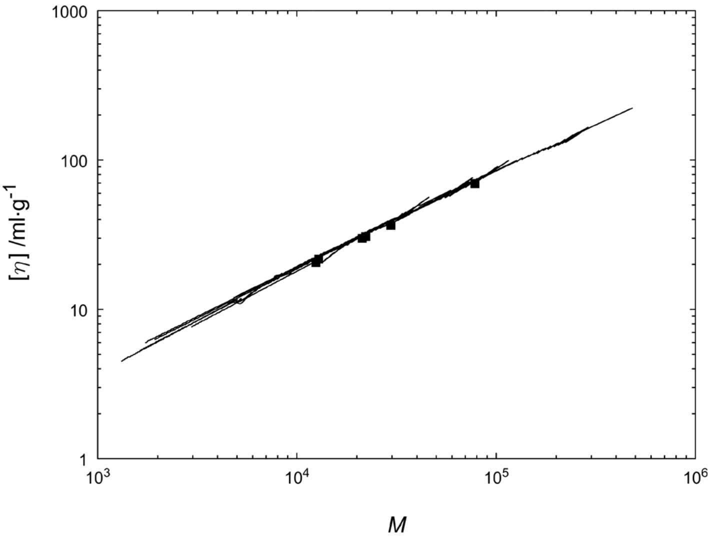

Figure 5. The Kuhn-Mark-Houwink-Sakurada plot for the polyester in THF.

a quadratic fit:

$$\mathbf{log}[\eta] = -1.71 + 0.82\,\mathbf{log}\,M - 0.0182\,\mathbf{log}^2 M \tag{16}$$

with a variance of 1.27×10^{-4}. The slope of that dependence

$$a_{\text{calc}} = 0.809 - 0.0332\,\mathbf{log}M \tag{17}$$

decreases with increasing molecular weight. The exponents calculated by means of Equation (17) for M_{w} values of the individual polymers measured (Table I) are close to the values of a obtained from on-line measurements. The decrease in the exponent with increasing molecular weight indicates a slow conversion of an extended semi-flexible chain towards a Gaussian coil at $M \to \infty$. The good accord of a and a_{calc} in Table I shows that, for moderately nonuniform polymers, the values of a obtained by on-line measurements are reliable.

The Stockmayer-Fixman plot of $[\eta]/M^{1/2}$ versus $M^{1/2}$ according to equation[10]

$$[\eta]/M^{1/2} = K_0 + C_\eta \cdot BM^{1/2} \tag{18}$$

where C_η is a numerical factor and B is a function of excluded volume, is not linear and curves strongly downwards for $M^{1/2} \to 0$ (Figure 6). This is a clear indication that the Gaussian-coil model does not describe the chain properties adequately.[11] (Note that the value of K_0 (Table II),

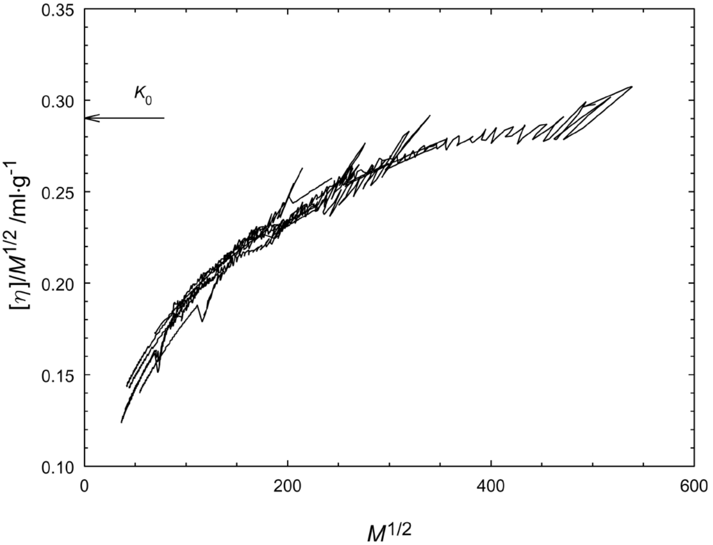

Figure 6. The Stockmayer-Fixman plot for the polyester in THF; the value of K_0 is denoted by an arrow.

denoted by an arrow in Figure 6, is not K_0 from Equation (18); this will be discussed below.)

In principle, the chain-conformation characteristics should be determined in theta solvents and in the limit of non-draining coil, i.e., for $M \to \infty$. As has been shown[2,12] for low-molecular-weight polymers, where the excluded-volume effect is weak, data for good solvents may be used as well. Discontinuous measurements of light scattering and viscosity of dilute solutions of low-molecular-weight narrow fractions are difficult to realize because of the large amounts of samples needed. An advantage of on-line triple detection is the possibility of performing such measurements with adequate accuracy using minute amounts of samples.

For the evaluation of experimental data, we need to know the average molecular weight per unit contour length, M_L. This quantity is calculated from the molecular weight of a monomer unit (Figure 1), $M_u = 400$, and the length of its projection on the chain axis in the all-trans conformation, l_u. The values of individual types of bond lengths (in Å) and valence angles were taken from Lide.[13]: C–O–C 1.42, 112°; aromatic ring 2.80; C–C–C 1.53, 112°; C–CO–C 1.52, 116°; thus, $l_u = 1.97 \times 10^{-7}$ cm.

The Bohdanecký plot for our polymers (Equation (6), Figure 7) is linear in a broad range of molecular weights. The curvature in the region

Table II. Chain-conformation parameters of the polyester

[a]A'_η mL/g	[a]K_0 mL/g	[b]$l_u \times 10^7$ cm	[c]$\left(\frac{\langle R^2 \rangle}{M}\right)_\infty \times 10^{16}$ cm^2	[d]$\lambda^{-1} \times 10^7$ cm	[e]M_λ	[f]$d_{b,r}$	[g]$d_b \times 10^8$ cm	[h]C_∞
−12.12	0.290	1.96	1.10	2.24	455	0.210	4.71	5.2

[a] Parameters of Equation (6).
[b] Projection of monomer repeating unit on the chain axis with all bonds in trans conformation.
[c] Ratio of the mean-square end-to-end distance in the random-coil limit and molecular weight.
[d] Length of a segment of the equivalent chain.
[e] Molecular weight per segment of the equivalent chain.
[f] Reduced bead diameter.
[g] Bead diameter.
[h] Characteristic ratio.

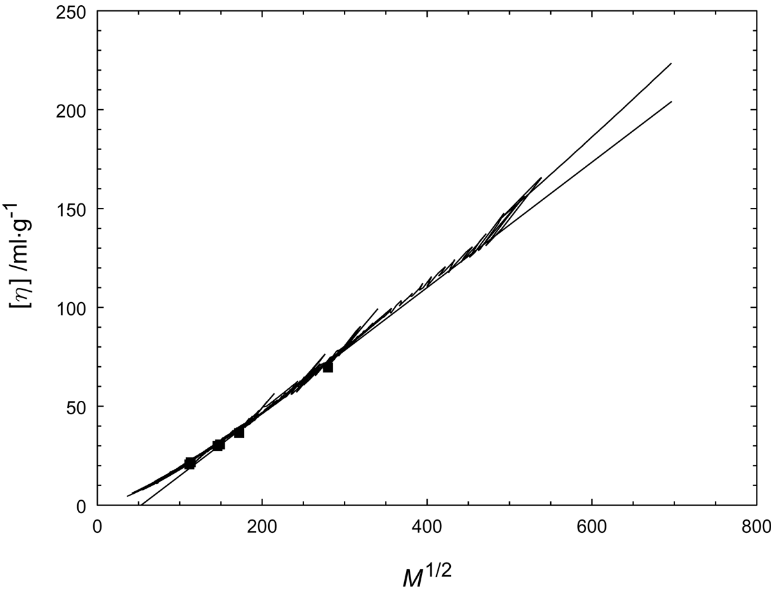

Figure 7. The Bohdanecký plot for the polyester in THF; for comparison, the points obtained for the whole polymer are denoted by (■).

of low molecular weights will be explained below. From the linear part of the dependence, we determine the parameters A'_η and K_0. From $K_0 = 0.29\,\mathrm{mL} \cdot g^{-1}$, a value of $(\langle R^2\rangle_0/M)_\infty^{3/2} = 1.16 \times 10^{-24}$ is calculated (Equation (9)). The product of the ratio $(\langle R^2\rangle_0/M)_\infty = 1.1 \times 10^{-16}\,\mathrm{cm}^2$ and $M_L = 2.41 \times 10^9\,\mathrm{cm}^{-1}$ yields the length of a segment of the equivalent chain, $\lambda^{-1} = 2.67 \times 10^{-7}\,\mathrm{cm}$ (Equation (3)). The product of λ^{-1} and M_L is the molecular weight per segment of the equivalent chain $M_\lambda = 640$ (Equation (8)). Having the values of $(\langle R^2\rangle_0/M)_\infty^{3/2}$ and M_λ, we obtain from Equation (7) $A'_0 = -1.96$ needed to find in Table 1 of Bohdanecký and Netopilík[2] the corresponding values of $d_{\mathrm{b,r}}$ and L_{r}^*. From the data tabulated for $0.2 < d_{\mathrm{b,r}} < 0.8$, we have plotted $d_{\mathrm{b,r}}$ as a function of A'_0 (Figure 8) and found $d_{\mathrm{b,r}} = 0.258$.

Now, we can come back to the curvature of the Bohdanecký plot (Equation (6), Figure 7) in the region of low molecular weights. The parameters of Equation (5) are valid for $L_{\mathrm{r}} > L_{\mathrm{r}}^*$, the values of L_{r}^* being given in Table 1 of Bohdanecký and Netopilík[2] as a function of $d_{\mathrm{b,r}}$.

For $A'_0 = -1.96$, L_{r}^* assumes a value between 16 and 25, the corresponding molecular weights (Equation (2)) being 9 000 and 14 000, respectively. The square roots of those values are around 100. And this is the low-molecular-weight region where the Bohdanecký plot (Figure 7)

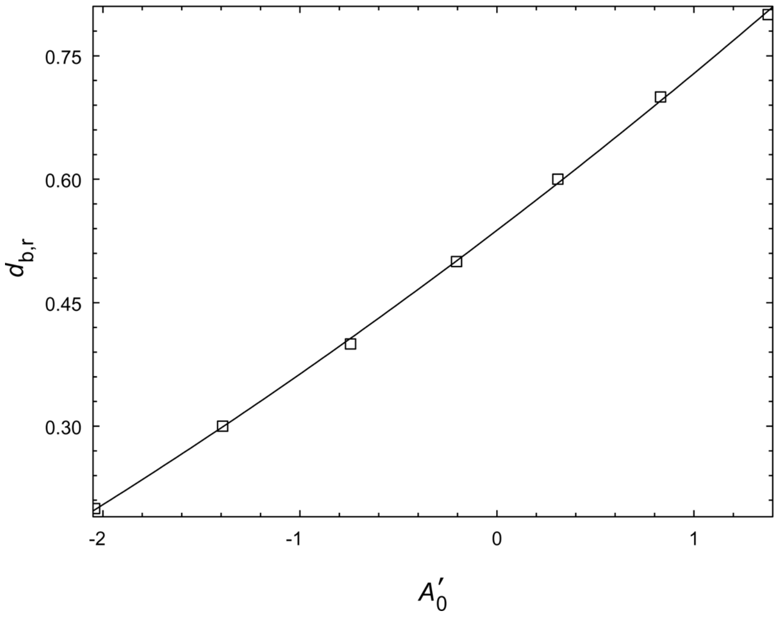

Figure 8. Dependence of the reduced chain diameter, $d_{b,r}$, on the parameter A'_0 in Equation (5).

curves upwards with decreasing molecular weight, as predicted by theory (see Bohdanecký and Netopilík[2] Figure 1, curve 1).

According to Bohdanecký, the MHKS exponent for the short or stiff chains not behaving as random coils varies in theta solvents with molecular weight. The dependence is described by the equation (Bohdanecký and Netopilík[2] Equation (10))

$$a_0 = (1/2)/[1 + A'_0 \cdot (M_\lambda/M^{1/2}] \tag{19}$$

For $A'_0 < 0$, it predicts a decrease in a_0 with increasing molecular weight, as has been observed experimentally (Table I). Figure 6 indicates that the excluded-volume effect may already operate for polymers with the highest molecular weights.

To calculate the characteristic ratio in the random coil limit, C_∞, we employ its definition[14]

$$C_\infty = \left[\langle R^2\rangle_0 \Big/ \left(\sum_i N_i l_i^2\right)\right]_\infty = \left(M_0 \Big/ \sum_i N_i l_i^2\right)(\langle R^2\rangle_0/M)_\infty \tag{20}$$

where N_i is the number of bonds of type i in a polymer molecule of a degree of polymerization $N = M/M_0$ and l_i is the length of a main-chain bond of type *i*

$$N_i = n_i N \tag{21}$$

where n_i is the number of main-chain bonds of type *i* in a constitutional repeating unit. Using the above values of bond lengths, we arrive at a value of $C_\infty = 5.2$, which is between the values found in the literature[14] for polyethylene (6.4–7.1) and poly(oxyethylene) (4.8). Originally, we speculated that aromatic rings in the backbone might increase the chain stiffness. Comparison with tabulated data (e.g., $C_\infty = 3.1 - 4.3$ for poly(ethylene terephthalate)), however, shows that oxygen atoms in the backbone substantially increase the flexibility of the chain, and this effect outweighs the potential chain stiffening due to the presence of aromatic rings in the backbone. The value of the bead diameter, $d_b = 4.71 \times 10^{-8}$ cm, appears to be reasonable with respect to the constitution of the chain.

CONCLUSIONS

1. Size exclusion chromatography with concentration, light-scattering, and viscosity detection is a powerful tool for study of polymer-chain conformation, even in the low-molecular-weight region.
2. Radii of gyration for linear polymers with low molecular weights can be obtained from light-scattering and viscosity data using the Flory-Fox theory.
3. Conformation characteristics of linear aromatic polyester of 3-phenylglutaric acid and bisphenol A, such as the parameters of the Mark-Houwink-Kuhn-Sakurada equation, chain-segment length, chain diameter, and characteristic ratio have been determined using the theory of Yamakawa et al. in the modification by Bohdanecký and Netopilík.

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