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Synthesis and Characterization of Rigid Rod Poly(*p*-phenylenes)

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ABSTRACT: The polymer PP, which consists of a poly(*p*-phenylene) backbone with sulfonate ester and dodecyl side groups, is synthesized by a Pd-catalyzed coupling of the 1,3-propanediol diester of 2-dodecyl-5-methyl-1,4-benzenediboronic acid with 2,2′-bis(3,5-di-*tert*-butylbenzenesulfonato)-4,4′-dibromobiphenyl. Polymers with various molar masses are obtained, which are soluble without aggregation in conventional organic solvents. The good solubility of this rodlike polymer allows the accurate determination of the molar mass by light scattering, osmometry, and SEC with universal calibration. The dependence of the intrinsic viscosity [η] on the molar mass is determined from both the Mark−Houwink−Sakurada equation and the wormlike chain model. The low value of the persistence length (13 nm) indicates that these polymers are relatively flexible. It is shown that an approximate value of the persistence length, together with the parameters of the Mark−Houwink−Sakurada equation and the wormlike chain model, can be determined using only a single polydisperse sample.

Introduction

Recently, rigid rod polymers have received much attention because of their unique behavior as compared to flexible random coil polymers. The material properties of rigid rod polymers arise from their highly anisotropic shape, which explains, e.g., the high degrees of molecular orientation that can be obtained in fibers spun from lyotropic solutions.

Polymers with a poly(*p*-phenylene) backbone are considered as typical rigid rod polymers due to the linear configuration of the phenylene repeat units, suggesting a high stiffness for these molecules. Flexible side chains attached to the rigid backbone are necessary to improve solubility and avoid aggregation. The synthesis of poly(*p*-phenylenes) with a large variety of side groups has been pioneered by Rehan, Schlüter, and Wegner.[1,2]

In this work we use a polymer henceforth called PP, composed of a poly(*p*-phenylene) backbone with sulfonate ester and dodecyl side groups shown in Figure 1.

Poly(*p*-phenylenes) which have regularly attached dodecyl side chains only, still show aggregation phenomena, which hamper their characterization in solution.[3] Because of the head−tail isomerism of the dodecyl-carrying phenyl moiety, two isomeric structures of the repeat unit are present in the polymer PP. In addition, the dodecyl chains alternate as side groups with the voluminous sulfonate ester groups, which explains the good solubility of this polymer in conventional solvents like THF and toluene. This good solubility allows the accurate determination of the molar mass by light scattering, osmometry, and SEC.

Polymer PP has been designed as a precursor polymer for a rigid rod polyelectrolyte, synthesized from PP by saponification of the sulfonate residues.[4]

Experimental Section

Synthesis. Polymer PP was synthesized by a Pd-catalyzed coupling of the 1,3-propanediol diester of 2-dodecyl-5-methyl-1,4-benzenediboronic acid (monomer 1) with 2,2′-bis(3,5-di-*tert*-butylbenzenesulfonato)-4,4′-dibromobiphenyl (monomer 2) shown in Figure 2.

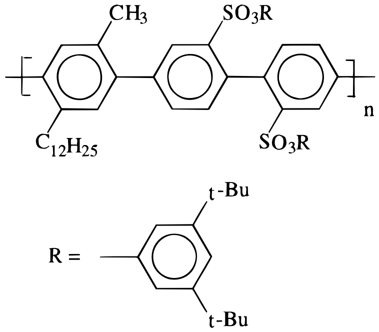

Figure 1. Polymer PP, consisting of a poly(*p*-phenylene) backbone with sulfonate ester and dodecyl side chains.

The synthesis of the monomers has been published elsewhere.[4] Pd(PPh$_3$)$_4$ was synthesized according to the literature procedure.[5] THF was freed of peroxides by refluxing over sodium and was distilled prior to use. Water was decontaminated of oxygen by a stream of nitrogen. All other chemicals were purchased from Aldrich and used as received.

The polymerizations were carried out under a nitrogen atmosphere. Monomers 1 and 2 were dissolved in a mixture of 28.7 g of NaHCO$_3$, 285 mL of THF and 170 mL of water. The amount of the monomers was calculated to give a theoretical yield of 27 g. Pd(PPh$_3$)$_4$ was added (5×10^{-3} molar equivalent compared to monomer 1). The resulting suspension was stirred between 18 and 94 h (Table 1). Bromobenzene (0.44 g, 3 mmol) was then added to end cap the polymer. After an additional 2 h the polymer was precipitated by pouring it into 1.5 L of ethanol. The product was washed with water, dried, and redissolved in toluene. The filtered solution was concentrated and the polymer precipitated in a 5-fold excess of ethanol and dried, giving a yield of 80−95% (Table 1). ^{1}H- and ^{13}C-NMR spectra were obtained with a Varian XL-200, 200 MHz, or a Bruker 300 MHz NMR spectrometer. For, e.g., polymer P5 the following results were obtained.

^{1}H-NMR (CDCl$_3$): $\delta = 0.86$ (t, 6.6 Hz, 3 H), 1.20 (m, 36 H), 1.50 (b, 2 H), 2.30 (b, 2 H), 6.90 (s, 4 H), 7.06 (s, 1 H), 7.2 (b, 1 H), 7.3 (b, 2 H), 7.31 (s, 2 H), 7.6 (b, 2 H), 8.00 (s, 2 H).

^{13}C-NMR (CDCl$_3$): $\delta = 14.53$, 20.19, 23.53, 29.64, 29.80, 29.97, 31.33, 32.01, 32.19, 33.06, 31.59, 35.182, 117.21, 121.36, 130.86, 131.95, 132.92, 133.59, 133.58, 134.58, 136.20, 137.17, 138.47, 139.02, 142.26, 149.27, 153.04.

C$_{59}$H$_{78}$S$_2$O$_6$ (946.39) Calcd: C, 74.80; H, 8.30; S, 6.77. Found: C, 74.45; H, 8.03; S, 6.76.

Polymers with various molar masses were obtained by changing the ratio of the two monomers. The used ratios together with the reaction times are given in Table 1. At a

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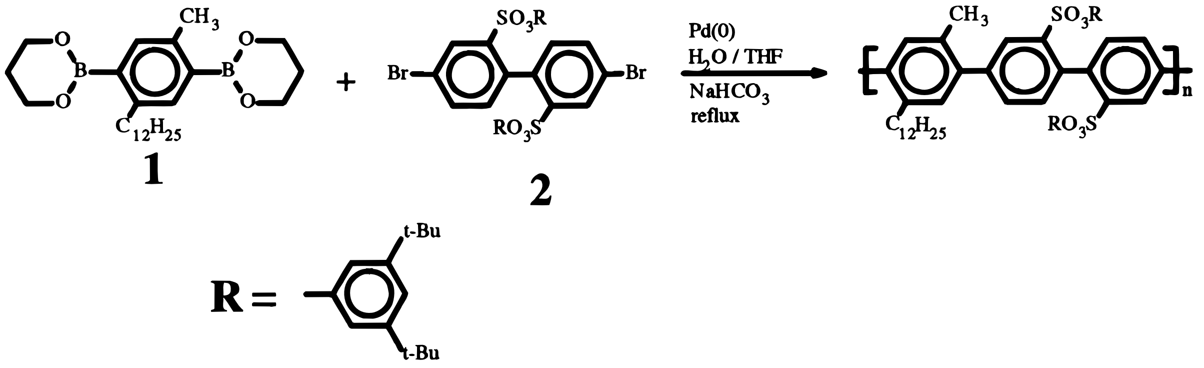

Figure 2. Synthesis of the polymer PP by a Pd-catalyzed coupling of the monomers 1 and 2.

ratio of 1:1, reproducibility of the molar mass is difficult, but a reaction time of 18 h is sufficient to produce high molar masses.

Methods

Static Light Scattering. The refractive index increment d*n*/d*c* was measured at $\lambda = 633$ nm using a scanning Michelson interferometer.[6] For the static light scattering experiments a commercial instrument (ALV) with a krypton ion laser (Spectra Physics, $\lambda = 647.1$ nm) was used. Scattering intensities were measured in both toluene and trichloroethylene with a photomultiplier over an angular range between 30 and 150°.

Membrane Osmometry. The number average molar mass M_n was determined in toluene, using a recently developed osmometer with a hollow fiber membrane.[7,8]

Size Exclusion Chromatography. The SEC diagrams were measured in THF (flow rate 1 mL min^{-1}) at room temperature, using a combination of three Styragel columns (porosity 10^3, 10^5, and 10^6) and an UV detector operating at $\lambda = 254$ nm.

Viscometry. The intrinsic viscosity in THF at room temperature was determined with an Ubbelohde capillary viscometer.

Results and Discussion

Light Scattering. Static light scattering was used to determine the weight average molar mass. Zimm diagrams were constructed, making use of the following equations:

$$\frac{K_c}{R(\theta)} = \frac{1}{M_w}\left(1 + \frac{q^2\langle R_g^{\ 2}\rangle_z}{3}\right) + 2A_2c \qquad (1)$$

with

$$K = \frac{4\pi^2 n^2}{N_A \lambda_0^{\ 4}}\left(\frac{dn}{dc}\right)^2 \qquad (2)$$

$$q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2} \qquad (3)$$

Here, the Rayleigh ratio $R(\theta)$ depends on the intensity of the scattered light at different scattering angles θ, M_w is the weight average molar mass, c is the concentration, $\langle R_g^{\ 2}\rangle_z$ is the z-average mean square radius of gyration, A_2 is the second virial coefficient, λ_0 is the wavelength in vacuum, and n is the refractive index of the solvent.

Table 1. Ratio of the Two Monomers, the Reaction Time, and the Yield for the Different Samples[a]

no.	ratio 2/1	reacn time/h	yield/%
P1[b]			40
P2	0.975	18	89
P3	1	94	87
P4	1	18	89
P5	1	48	95
P6	1.0125	18	80
P7	1.025	18	86
P8	1.035	18	85
P9	1.06	18	85

[a] The molar mass decreases from P1 to P9. [b] High molar mass fraction of P2 made by dissolving 2 g of P2 in 200 mL of toluene and precipitation by addition of 100 mL of ethanol.

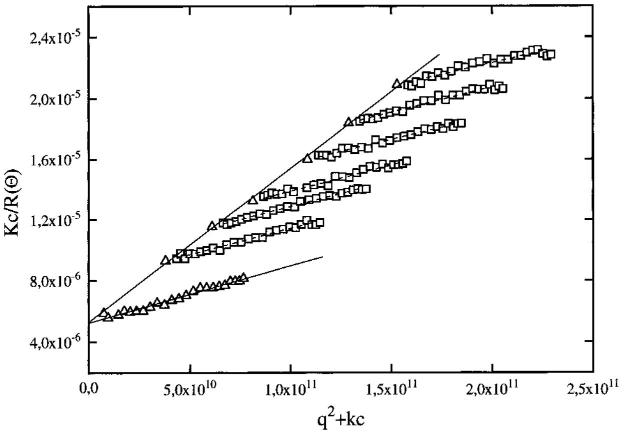

Figure 3. Zimm plot of polymer P1 in trichloroethylene.

The determination of M_w through the construction of a Zimm plot is allowed when the depolarization of the scattered light is negligible.[9] This depolarization can be important for anisotropic molecules like PP with different polarizabilities in different directions. In order to determine the depolarization, the ratio of the intensities of the horizontally and vertically polarized components of the scattered light was measured. The low value (0.02) indicates that for PP the depolarization of the scattered light need not be considered.

Zimm plots were determined in trichloroethylene and toluene, giving an identical molar mass for both solvents. The best results were obtained in trichloroethylene, which might be explained by the larger value of d*n*/d*c* in trichloroethylene (d*n*/d*c* = 0.095 mL/g) compared to toluene (d*n*/d*c* = 0.078 mL/g). Moreover, decreasing the temperature to 15 °C does not affect the results obtained in trichloroethylene, while for certain samples measured in toluene (e.g. P5) a determination of the molar mass is no longer possible due to aggregation phenomena. A typical Zimm plot of PP in trichloroethylene is shown in Figure 3. M_w, A_2, and $\langle R_g^{\ 2}\rangle_z$ are obtained by linear regression. The values measured in trichloroethylene for the different samples are given in Table 2. Weight average molar masses between 27 and 189 kg/mol are obtained. Because of the low scattering intensity, an accurate determination of A_2 and $\langle R_g^{\ 2}\rangle_z$ has

Table 2. Light Scattering, Osmometry, and Viscometry Results (Respectively Measured in Trichloroethylene, Toluene, and THF) for the Different Samples

	light scattering			osmometry		
no.	M_w/kg mol^{-1}	$\langle R_g^2\rangle_z^{1/2}$/nm	$A_2 \times 10^4$/mol cm^3 g^{-2}	M_n/kg mol^{-1}	$A_2 \times 10^4$/mol cm^3 g^{-2}	$[\eta]$/mL g^{-1}
P1	189	45.6	11.3	99	5.91	331
P2	157	40.2	10.9	76	9.95	275
P3	113	29.7	9.45	54	8.28	180
P4	101	33.0	10.8	48	7.95	176
P5	90	29.4	6.78	36	8.40	127
P6	64	19.4	9.76	39	9.95	125
P7	40	15.7	8.27	22	10.9	67
P8	38		9.53	23	11.4	78
P9	27			16.5	9.87	45

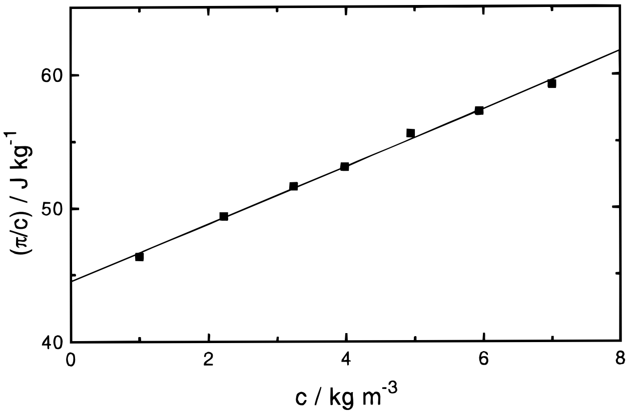

Figure 4. Osmometry measurement of polymer P3 in toluene.

not been possible for the samples with the lowest molar mass.

Membrane Osmometry. The number average molar mass M_n was determined by membrane osmometry in toluene:

$$\lim_{c\to 0}\frac{\pi}{c} = RT\left(\frac{1}{M_n} + A_2c\right) \qquad (4)$$

π is the osmotic pressure, T is the temperature, and R is the gas constant.

The extrapolation of π/c to zero concentration gives M_n (Figure 4). Table 2 shows M_n and A_2 for the different samples.

The values of A_2 measured with osmometry in toluene are comparable to those measured with light scattering in trichloroethylene. A_2 fluctuates considerably for the different samples, but for both toluene and trichloroethylene a mean value of 1×10^{-3} mol cm^3 g^{-2} is obtained.

Size Exclusion Chromatography. SEC measurements in THF were used to determine the molar mass distribution and the averages M_n and M_w. Columns 2 and 3 of Table 3 give these molar masses as obtained from polystyrene (PS) calibration. With this calibration the SEC results are clearly too large when compared to the molar masses determined by light scattering or osmometry (Table 2), a finding which already indicates the stiffness of the polymer chains.

Therefore, universal calibration is used to transform the PS calibration curve into one that can be used for different polymer types.[10] Universal calibration is based on the assumption that SEC fractionates strictly according to the hydrodynamic volume V_h, which is proportional to the product of the molar mass M and the intrinsic viscosity $[\eta]$:[11]

$$\frac{5}{2}N_AV_h = [\eta]M \qquad (5)$$

N_A is Avogadro's number. Usually, the Mark–Houwink–Sakurada equation

$$[\eta] = KM^{\alpha} \qquad (6)$$

is used to express the intrinsic viscosity as a function of the molar mass. K and α are constants for a given polymer–solvent system at a given temperature. The exponent α is characteristic for the polymer topology and reaches from $\alpha = 0$ (solid spheres) over $\alpha = 0.5$ (random coil under θ conditions) to $\alpha = 2$ (rigid rod).

For the description of the $[\eta]$–M relation over a broad molar mass range, the wormlike chain model is used.[12] A wormlike chain can be modeled starting from a chain with contour length L consisting of n elements of length ΔL, where the angle between the neighboring elements $\Delta\phi$ is identical for all chain elements. The wormlike chain is obtained from this model in the limit as ΔL and $\Delta\phi$ tend to zero.

When ϕ is the angle between two elements separated by a chain segment of contour length l, the persistence length a is defined by

$$\langle\cos\phi\rangle = e^{-l/a} \qquad (7)$$

A wormlike chain can be pictured as a chain with a constant curvature. The value of this curvature, and therefore the stiffness of the polymer chain, is determined by a.

An approximate $[\eta]$–M relation for the wormlike chain model has been given by Bohdanecky:[13]

$$[\eta] = M^2(A_\eta + B_\eta M^{1/2})^{-3} \qquad (8)$$

From A_η and B_η the persistence length a and the hydrodynamic diameter of the chain d can be calculated:

$$a = \frac{M_0}{2l_0}\frac{B_0^{\,2}}{B_\eta^{\,2}\,\Phi_{0\infty}^{\,2/3}} \qquad (9)$$

$$\frac{d_r^{\,2}}{A_0} = \frac{4\Phi_{0\infty}\bar{v}B_\eta^{\,4}}{1.215\pi N_A A_\eta} \qquad (10)$$

with

$$\log\left(\frac{d_r^{\,2}}{A_0}\right) = 0.173 + 2.158\log(d_r) \qquad (11)$$

$\Phi_{0\infty} = 2.86 \times 10^{23}$ mol^{-1} is the viscosity constant for infinite chain length, $B_0 = 1.05$, M_0 and l_0 are the molar mass (947 g mol^{-1}) and the length (1.28×10^{-7} cm) of the monomer, $d_r = d/(2a)$ is the reduced hydrodynamic diameter, and $\bar{v}$ is the partial specific volume of the polymer (approximated by unity).

Table 3. SEC Results for the Different Samples with PS Calibration, and Universal Calibration Based on Both the Mark–Houwink–Sakurada Equation and the Wormlike Chain Model

	PS calibration		Mark–Houwink–Sakurada eq		wormlike chain	
no.	M_n/kg mol^{-1}	M_w/kg mol^{-1}	M_n/kg mol^{-1}	M_w/kg mol^{-1}	M_n/kg mol^{-1}	M_w/kg mol^{-1}
P1	164	393	89	171	93	179
P2	121	347	69	153	73	160
P3	79	230	48	106	51	109
P4	83	223	49	104	53	106
P5	52	157	34	77	38	77
P6	62	152	38	75	41	75
P7	29	72	20	39	23	39
P8	31	83	22	44	25	44
P9	21	51	15	29	18	30

Obviously, a simple scaling law according to eq 6 is not sufficient to describe a wormlike chain polymer over the entire molar mass range, since for $L/a \ll 1$ rigid rod ($\alpha = 2$) and for $L/a \gg 1$ random coil ($\alpha = 0.5$) behavior is expected. However, it will be shown later that eq 6 can be used as a local approximation for moderately polydisperse polymers.

The calibration of the SEC apparatus in terms of hydrodynamic volume in THF at room temperature is obtained from a PS calibration and eq 6 with $K_{PS} = 0.0136$ mL/g and $\alpha_{PS} = 0.714$.[14]

To establish an $[\eta]-M$ relation for universal calibration and with the aim to determine the persistence length, a series of polymers with different molar masses has been synthesized and characterized as described in the preceding sections. The respective light scattering, osmometry, and viscometry results are summarized in Table 2.

Both eqs 6 and 8 are two-parameter models that can be used for a parameterization of the measured $[\eta]-M$ relation. While, as already mentioned, eq 6 is only approximately valid for the wormlike chain model, it is much easier to handle, and it will be shown that the errors introduced by using eq 6 instead of eq 8 are negligible.

Usually, for eq 6 a linear representation is obtained by plotting log $[\eta]$ versus log M:

$$\log [\eta] = \log K + \alpha \log M \qquad (12)$$

For eq 8 a linearizing plot has been given by Bohdanecky:[13]

$$\left(\frac{M^2}{[\eta]}\right)^{1/3} = A_\eta + B_\eta M^{1/2} \qquad (13)$$

The evaluation of the measured $[\eta]-M_w$ data according to eq 12 is shown in Figure 5. From a linear regression $K_{PP} = 0.00267$ mL/g and $\alpha_{PP} = 0.961$ are obtained. The corresponding linear regression of eq 13 is shown in Figure 6, yielding $A_\eta = 111$ g mol$^{-2/3}$ mL$^{-1/3}$ and $B_\eta = 0.866$ g$^{1/2}$ mol$^{-1/6}$ mL$^{-1/3}$.

Strictly speaking, for polydisperse samples the viscosity average molar mass, $M_v = ([\eta]/K)^{1/\alpha}$, and not M_w, should be used in eqs 6 and 12. $[\eta]$ is the measured weight average intrinsic viscosity. Since $\alpha \approx 1$, however, M_w and M_v are almost identical. A similar argument holds for eqs 8 and 13, where a more complicated averaging is involved.

The $[\eta]-M_w$ relation as obtained from the Bohdanecky equation (eq 13) is also plotted in Figure 5 (dashed line) and vice versa. Both dashed lines show a slight curvature, but they equally well fit the measured data. Hence, while not strictly applicable for the wormlike chain model, the Mark–Houwink–Sakurada equation serves as a reasonable approximation within a certain molar mass range for universal calibration of SEC.

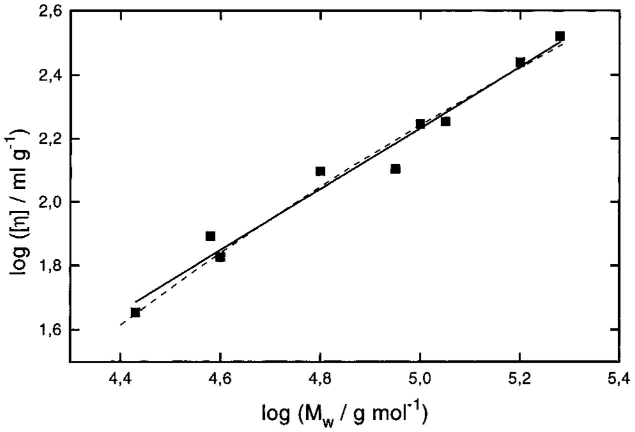

Figure 5. Plot of log $[\eta]$ versus log M_w: experimental data (■); linear regression of the experimental data using the Mark–Houwink–Sakurada equation (solid line); the $[\eta]-M_w$ relation calculated from the wormlike chain model (dashed line).

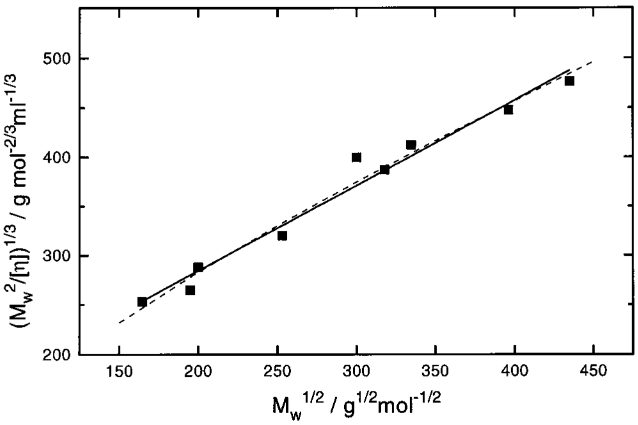

Figure 6. $[\eta]$ and M_w data plotted according to the Bohdanecky procedure: experimental data (■); linear regression of the experimental data using the wormlike chain model (solid line); the $[\eta]-M_w$ relation based on the Mark–Houwink–Sakurada equation (dashed line).

Once K and α are known, the wormlike chain parameters A_η and B_η can be calculated:

$$A_\eta = \frac{2\alpha - 1}{3} K^{-1/3} M^{(2-\alpha)/3} \qquad (14)$$

$$B_\eta = \frac{2(2\alpha - 1)}{3} K^{-1/3} M^{(1-2\alpha)/6} \qquad (15)$$

The slight molar mass dependence of A_η and B_η reflects the only local validity of the Mark–Houwink–Sakurada equation.

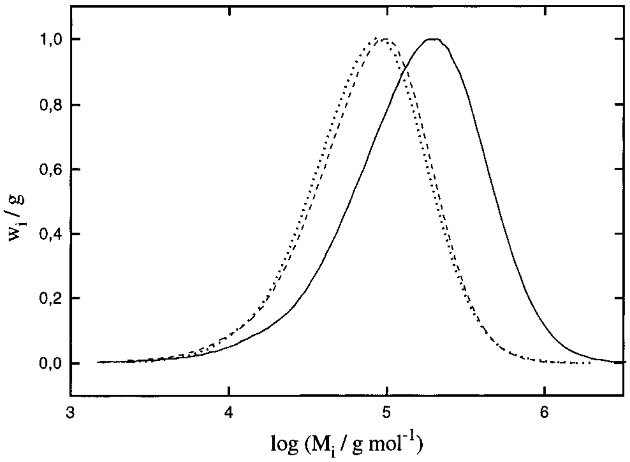

Figure 7. SEC elugram of polymer P3 in THF, with w_i the mass of the ith slice of molar mass M_i: PS calibration (solid line); universal calibration based on the Mark–Houwink–Sakurada equation (dashed line); the wormlike chain model (dotted line).

Figure 7 shows the molar mass distributions as obtained from SEC with PS calibration and with universal calibration according to eqs 6 and 8. In the case of the Mark–Houwink–Sakurada equation, the correct molar mass of the ith slice $M_{i,\mathrm{PP}}$ is obtained in the usual way from

$$\log M_{i,\mathrm{PP}} = \frac{1}{\alpha_{\mathrm{PP}} + 1}\left[\log \frac{K_{\mathrm{PS}}}{K_{\mathrm{PP}}} + (1 + \alpha_{\mathrm{PS}})\log M_{i,\mathrm{PS}}\right] \tag{16}$$

When the wormlike chain model is used, $M_{i,\mathrm{PP}}$ is numerically determined, using the Newton–Raphson method,[15] as the root of

$$M_{i,\mathrm{PP}}^{3}(A_\eta + B_\eta M_{i,\mathrm{PP}}^{1/2})^{-3} - K_{\mathrm{PS}} M_{i,\mathrm{PS}}^{1+\alpha_{\mathrm{PS}}} = 0 \tag{17}$$

Universal calibration causes M_n and M_w (calculated from eqs 18 and 19 below) to decrease considerably, when compared to PS calibration, whereas the difference between both $[\eta]$–M relations is almost completely negligible, and both M_n and M_w agree well with the corresponding numbers measured by membrane osmometry and light scattering (Tables 2 and 3).

Persistence Length. From the A_η and B_η values determined with eq 13 and Figure 6, together with eqs 9–11, a hydrodynamic diameter of 1.3 nm and a persistence length of 12.6 nm are obtained. The persistence length exceeds by 1 order of magnitude the value for typical flexible chain polymers (1–2 nm) which clearly demonstrates the rigid character of PP. Nevertheless, the persistence length is smaller than the value that might be expected for a polymer with a poly(p-phenylene) backbone, although recently some indications have been found that poly(p-phenylene) might be relatively flexible with $a \approx 20$ nm.[16,17]

Data Evaluation Using a Single Polydisperse Sample. Hydrodynamic Properties. Up to now the $[\eta]$–M relation has been determined from a series of samples with different molar masses. In this section it will be shown that a reasonable SEC calibration and persistence length determination can also be obtained from a single polydisperse sample, which reduces the experimental effort considerably.[18,19] To demonstrate its feasibility, the procedure has been applied to all nine samples separately. The input parameters that have been determined experimentally are the molar mass distribution as obtained from SEC with PS calibration, M_n as obtained from membrane osmometry, M_w as obtained from light scattering, and $[\eta]$ as obtained from viscosity measurements.

Employing universal calibration the molar mass averages and the intrinsic viscosity can be calculated from the SEC elugram for a given $[\eta]$–M relation:

$$M_{\mathrm{n,calc}} = \left(\sum_i w_i/M_{i,\mathrm{PP}}\right)^{-1} \tag{18}$$

$$M_{\mathrm{w,calc}} = \sum_i w_i M_{i,\mathrm{PP}} \tag{19}$$

$$[\eta]_{\mathrm{calc}} = \sum_i w_i [\eta]_i \tag{20}$$

The summation index i extends over all SEC slices of mass fraction w_i with $\sum_i w_i = 1$. $M_{i,\mathrm{PP}}$ is obtained from eq 16 or 17, depending on the model used for the $[\eta]$–M relation, and $[\eta]_i$ is given by

$$[\eta]_i = K_{\mathrm{PS}} M_{i,\mathrm{PS}}^{1+\alpha_{\mathrm{PS}}} M_{i,\mathrm{PP}}^{-1} \tag{21}$$

Both $[\eta]$–M relations are two-parameter models and the calculated quantities in eqs 18–20 are functions of the unknown parameters (K_PP, α_PP) or (A_η, B_η), depending on whether the Mark–Houwink–Sakurada equation or the wormlike chain model is used. Since there are three measured quantities, the two unknown parameters are overdetermined, and for every sample a solution is found from a nonlinear least squares regression, which minimizes $\epsilon_\mathrm{n}^2 + \epsilon_\mathrm{w}^2 + \epsilon_\eta^2$,[20] with

$$\epsilon_\mathrm{n} = \frac{M_{\mathrm{n,calc}}}{M_\mathrm{n}} - 1 \tag{22}$$

$$\epsilon_\mathrm{w} = \frac{M_{\mathrm{w,calc}}}{M_\mathrm{w}} - 1 \tag{23}$$

$$\epsilon_\eta = \frac{[\eta]_{\mathrm{calc}}}{[\eta]} - 1 \tag{24}$$

The quantities in the denominator are the respective measured ones.

The results for the nine samples are summarized in Table 4 for the Mark–Houwink–Sakurada equation and in Table 5 for the wormlike chain model. Both (K_PP, α_PP) and (A_η, B_η), which are obtained from a single sample, agree reasonably with the corresponding values determined from the molar mass series (Figure 8). Also given in the two tables are $M_{\mathrm{n,calc}}/M_\mathrm{n}$, $M_{\mathrm{w,calc}}/M_\mathrm{w}$, and $[\eta]_{\mathrm{calc}}/[\eta]$, which allow us to judge the quality of the measured values. For M_n the agreement is almost perfect, and for M_w and $[\eta]$ the error is of the order of a few percent. The calculated average values are almost identical for both $[\eta]$–M relations.

Also listed in Table 4 are the wormlike chain model parameters (A_η, B_η) as calculated from (K_PP, α_PP) according to eqs 14 and 15. Since the right side of these two equations depends on the molar mass, and it is not obvious which average should be used for polydisperse samples, both M_n and M_w have been tried and the corresponding numbers are indicated in Table 4 by subscripts. As can be seen, a slightly better agreement with (A_η, B_η) from Table 5 is found in the case of M_n.

Table 4. Parameters of the Mark–Houwink–Sakurada Equation (K_{PP}, α_{PP}) and the Wormlike Chain Model (A_η, B_η) As Calculated from the Mark–Houwink–Sakurada Equation and Experimental Data of a Single Sample (details in the text)

no.	$K_{PP} \times 10^4$/mL g^{-1}	α_{PP}	$[\eta]_{calc}/[\eta]$	$M_{n,calc}/M_n$	$M_{w,calc}/M_w$	A_{η,M_n}[a]	B_{η,M_n}[b]	A_{η,M_w}[a]	B_{η,M_w}[b]
P1	1.7	1.19	0.89	1.01	0.88	185	0.69	213	0.61
P2	3.9	1.12	0.95	1.00	0.95	152	0.77	185	0.67
P3	5.4	1.09	0.97	1.00	0.97	132	0.87	163	0.76
P4	33.2	0.94	1.02	1.00	1.02	88	0.95	115	0.85
P5	32.0	0.93	0.94	1.00	0.94	82	1.08	111	0.95
P6	6.8	1.09	1.10	1.00	1.10	110	0.85	131	0.76
P7	6.1	1.09	1.00	1.00	0.99	96	0.99	114	0.88
P8	2.9	1.18	1.06	1.00	1.07	107	0.85	125	0.74
P9	9.4	1.05	1.11	1.00	1.11	80	1.07	97	0.96

[a] g mol$^{-2/3}$ mL$^{-1/3}$. [b] g$^{1/2}$ mol$^{-1/6}$ mL$^{-1/3}$.

Table 5. A_η and B_η Calculated from the Wormlike Chain Model and Experimental Data of a Single Sample (details in the text)

no.	$[\eta]_{calc}/[\eta]$	$M_{n,calc}/M_n$	$M_{w,calc}/M_w$	A_η[a]	A_η[b]
P1	0.88	1.00	0.88	177	0.68
P2	0.95	1.00	0.95	150	0.73
P3	0.97	1.00	0.97	129	0.82
P4	1.02	1.00	1.02	86	0.91
P5	0.94	1.00	0.94	76	1.04
P6	1.10	1.00	1.10	110	0.81
P7	1.00	1.00	0.99	94	0.95
P8	1.06	1.00	1.07	105	0.81
P9	1.11	1.00	1.11	80	1.03

[a] g mol$^{-2/3}$ mL$^{-1/3}$. [b] g$^{1/2}$ mol$^{-1/6}$ mL$^{-1/3}$.

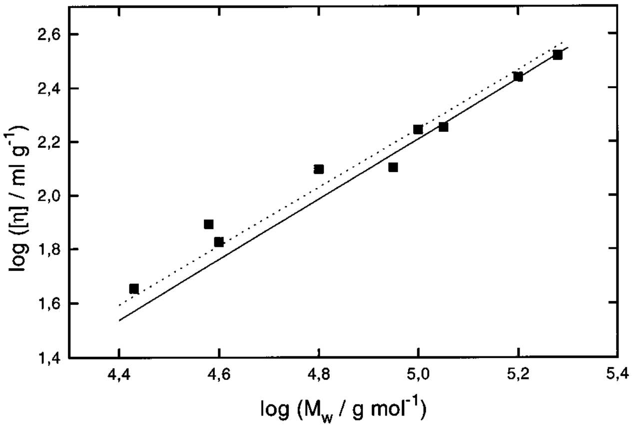

Figure 8. log $[\eta]$ as a function of log M_w: experimental data (■); calculated $[\eta]$–M_w relation using the K_{PP} and α_{PP} values determined from a single sample (Table 4) for polymer P2 (solid line) and P7 (dotted line).

The persistence length a can be calculated from eq 9, and the B_η values listed in Tables 4 and 5. Figure 9 shows the considerable fluctuation of the persistence length for the different samples. Nevertheless, when the large persistence length of polymer P1 is neglected, the mean values of 12.4 nm when the wormlike chain model is used (Table 5) and 11.3 and 14.5 nm when the Mark–Houwink–Sakurada equation is used (respectively from B_{η,M_n} and B_{η,M_w} of Table 4) agree well with the persistence length calculated before.

Since there are only two unknown parameters in both models, the measurement of only two of the three quantities M_n, M_w, and $[\eta]$ is, at least in principle, sufficient. If the SEC elugram, $[\eta]$, and one of the molar mass averages are measured, the evaluation within the framework of the Mark–Houwink–Sakurada equation gives

$$K = \left\{[\eta]\left[\frac{1}{c}\sum_i c_i\left(\frac{5}{2}N_A V_{hi}\right)^{\alpha/(1+\alpha)}\right]^{-1}\right\}^{1+\alpha} \qquad (25)$$

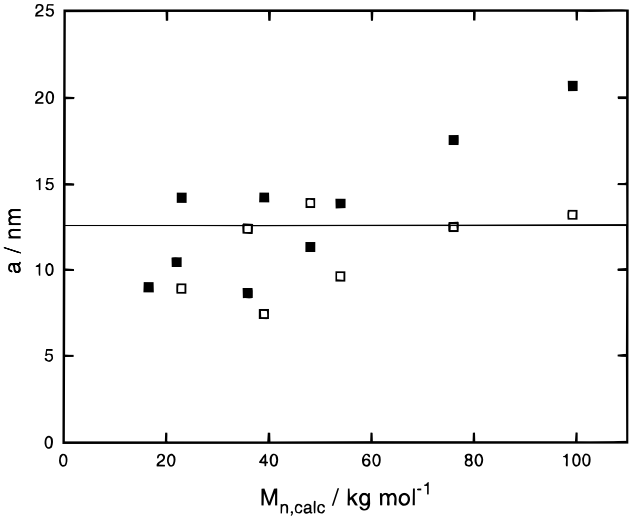

Figure 9. Persistence length a calculated for every sample separately from the B_η values of Table 5 according to eq 9 (■) and from the $\langle R_g^2\rangle_z$ values according to eq 27 (□). The solid line gives the persistence length which was determined from eq 13 using all the samples (a = 12.6 nm).

and α is obtained from $M_{n,calc}(\alpha) = M_n$ or $M_{w,calc}(\alpha) = M_w$. It turns out, however, that the persistence length becomes much more susceptible to experimental noise.

Summarizing this section, it has been shown that the correct wormlike chain parameters (A_η, B_η) and the persistence length a can be determined from a single polydisperse sample, and the Mark–Houwink–Sakurada equation can be employed for data evaluation in order to simplify the mathematical treatment.

Geometric Properties. Besides from the hydrodynamic properties, the persistence length for a single polydisperse sample may also be obtained from purely geometric considerations.

For a wormlike chain, the mean square radius of gyration $\langle R_g^2\rangle$ is given by

$$\langle R_g^2\rangle = \frac{aL}{3} - a^2 + \frac{2a^3}{L}\left[1 - \frac{a}{L}(1 - e^{-L/a})\right] \qquad (26)$$

This equation reduces to $\langle R_g^2\rangle = aL/3$ for flexible coils ($L/a \rightarrow \infty$), and to $\langle R_g^2\rangle = L^2/12$ for rigid rod polymers ($L/a \rightarrow 0$).

The z-average mean square radius of gyration, $\langle R_g^2\rangle_z$, for a polydisperse sample with a Schulz–Flory molar mass distribution ($M_w/M_n = 2$) has been given in ref 21:

$$\langle R_g^{\,2}\rangle_z = \frac{\sum_P \langle R_g^{\,2}\rangle P^3 (1 - 2/P_w)^P}{\sum_P P^3 (1 - 2/P_w)^P} \qquad (27)$$

$P_w = M_w/M_0$ is the weight average of the degree of polymerization P. Equation 27 is an implicit equation for the persistence length a and is numerically solved. The persistence lengths calculated for the individual samples according to eq 27 from the measured M_w and $\langle R_g^2\rangle_z$ values are plotted in Figure 9 as open squares together with the respective values obtained from the hydrodynamic properties. The data evaluation from purely geometric considerations suffers from the problem that the true molar mass distribution is replaced by an idealized Schulz−Flory distribution. Nevertheless, there is a reasonable agreement with the results obtained from the hydrodynamic considerations.

Summary and Conclusions

The rodlike polymer PP, which consists of a poly(*p*-phenylene) backbone with sulfonate ester and dodecyl side groups, was synthesized by a Pd-catalyzed coupling of the 1,3-propanediol diester of 2-dodecyl-5-methyl-1,4-benzenediboronic acid with 2,2′-bis(3,5-di-*tert*-butylbenzenesulfonato)-4,4′-dibromobiphenyl. Several molar masses (M_w between 27 and 189 kg mol^{-1}) were obtained by varying the ratio of the two monomers.

This polymer is soluble without aggregation in conventional organic solvents like THF and toluene, which allows the accurate determination of the molar mass by light scattering, osmometry, and SEC where the universal calibration technique was used. The $[\eta]-M$ relation, necessary for universal calibration, was determined from both the Mark−Houwink−Sakurada equation and the wormlike chain model.

In order to determine the stiffness of the polymer chain, the wormlike chain model was used to calculate the persistence length. The relative low persistence length (13 nm), although far from the value for a flexible polymer coil, indicates that this polymer is more flexible than might be expected from a naive picture of its molecular structure. Molecular dynamics calculations on poly(*p*-phenylene), giving $a \approx 20$ nm, indicate that the flexibility of this polymer is of dynamic origin and can be explained by out of plane bending of the phenyl repeat units.[16] In addition, the steric hindrance between the bulky side groups of the polymer PP might cause a static bending and hence a further decrease of the persistence length.

An approximate value of the persistence length and the parameters of the Mark−Houwink−Sakurada equation (K_{PP}, α_{PP}) and the wormlike chain model (A_η, B_η) can be calculated using $[\eta]$, M_n, M_w, and the SEC elugram of a single polydisperse sample. These parameters, which were determined from only one sample, can describe the $[\eta]-M$ relation for a wide molar mass range. The results are further supported by the comparable persistence lengths determined from the measured $\langle R_g^2\rangle_z$ and M_w together with the approximation of a Schulz−Flory molar mass distribution. While the experimental effort is greatly reduced for the evaluation of the persistence length from a single polydisperse sample, the experimental error increases when compared to the values obtained from a molar mass series.

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