BUTTERWORTH HEINEMANN

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Characterization of a stiff-chain polyimide in solution

L. Schmitz and M. Ballauff*
Polymer-Institut, Universität (T.H.) Karlsruhe, Kaiserstrasse 12, 76128 Karlsruhe, Germany
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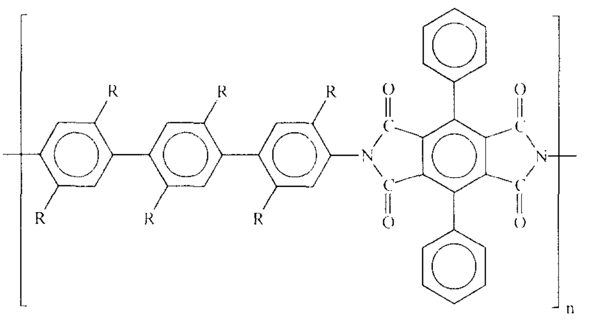
An analysis of the conformation of a stiff-chain polyimide in solution is given. It is shown that these polyimides exhibit the rather low persistence length of 13 nm despite the fact that the repeating unit consists of stiff and fully linear building blocks. A comparison with recent experimental and theoretical findings on similar systems corroborates the present analysis and suggests the bending fluctuations of the bonds as the main reason for the rather high flexibility.

(Keywords: polyimide; stiff chain; characterization)

INTRODUCTION

Polyimides based on *p*-terphenylene diamine and substituted pyromellitic anhydride units should present nearly ideal model compounds for the study of rigid-rod polymers since the molecular structure of their repeat unit suggests an almost fully extended shape of these macromolecules. Recently we have presented[1,2] a new and efficient synthetic route to these polyimides. The main advantage of the synthesis lies in the fact that the crucial step of the imide formation is relegated to the synthesis of the monomer; the polycondensation is effected through the Pd-catalysed coupling of substituted benzeneboronic acid with the suitable diimide moiety. In this context it could be shown[2] that polyimides (PI) of the structure:



R = n-Dodecyl

exhibit a much better solubility in common organic solvents than the respective polymers with unsubstituted pyromellitic units. Preliminary measurements, furthermore, indicated that the PI exhibit rather high degrees of polymerization. In this communication we present the results of a comprehensive investigation of these polyimides in solution. The objective is the determination of molecular weights and of the conformation and persistence length in solution.

MATERIALS AND METHODS

Chloroform, cyclohexene, *o*-dichlorobenzene and bromobenzene were used as received. Polyimides PI with varying degree of polycondensation were prepared as described elsewhere[2]. To close possible boronic acid end-groups, a few millilitres of bromobenzene were added after completion of polycondensation with vigorous exclusion of oxygen. After 1 day of stirring at room temperature the mixture was poured into a 8–10-fold excess of acetone. The polymers, which precipitated together with inorganic salts, were purified by stirring the precipitate in dilute aqueous HCl with slight warming to remove inorganic material. The precipitate was filtered off, washed with H_2O and acetone and dried. Subsequently, the dried polymer was extracted with chloroform in a Soxhlet apparatus followed by precipitation into acetone. Finally, the polymer was dissolved in benzene, which was removed by freeze-drying. In some cases the resulting polymer contained minute amounts of colloidal palladium originating from the catalyst. To remove this impurity, solutions in benzene were subjected to centrifugation (25 000*g*) for 2 h prior to freeze-drying.

Intrinsic viscosities were determined at 50°C in *o*-dichlorobenzene using an Ubbelohde viscometer. Membrane osmometry was done using a Knauer 0100 membrane osmometer at 50°C in *o*-dichlorobenzene. Knauer Y1245-membranes (regenerated cellulose) were used, which proved to be stable under these conditions.

Light-scattering intensities were determined using a SOFICA-P6D-42000 apparatus equipped with a laser operating at 633 nm. All measurements were done using an equimolar mixture of chloroform and cyclohexene at a temperature of 28.5°C. To remove dust particles all solutions were centrifuged at 25 000*g* for at least 2 h. The solutions were carefully transferred into cuvettes (1 cm diameter). Prior to all measurements the solutions were centrifuged again at 2000*g* for 6 min in the cuvettes and subsequently transferred into the light-scattering photometer.

The refractive index increment (d*n*/d*c*) was measured with a Brice–Phoenix differential refractometer at two

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* To whom correspondence should be addressed

different wavelengths and extrapolated to 633 nm. The value obtained for the PI in $CHCl_3$/cyclohexene is $dn/dc = 0.096$ at 28.5°C.

Gel-permeation chromatography (g.p.c.) was done on a 5 μm Styragel column in chloroform at a flow rate of 1 ml min^{-1} with u.v. detection (254 nm).

RESULTS AND DISCUSSION

Membrane osmometry

As already reported for a number of stiff-chain polyesters, osmometry can be done without major difficulties at 50°C using a membrane made from regenerated cellulose. The respective degrees of polymerization for all samples under consideration here are given in *Table 1*. The error is estimated to be 5% at most and the determination of molecular weights could be well reproduced for all samples under consideration here.

Light scattering

A series of experiments was done to determine the optimal solvent for the light-scattering experiments. Aromatic solvents, for example toluene, dissolve the PI quite readily but the solutions have a dn/dc value much too small for accurate measurements. Chloroform, on the other hand, is an excellent solvent with the highest dn/dc value but its high density presented difficulties when trying to remove the dust or any other kind of particles remaining from synthesis. Finally, the equimolar mixture of cyclohexene and $CHCl_3$ successfully applied recently[3] to a series of stiff-chain polyesters proved to be the best choice. This mixture of isorefractive solvents dissolves the PI without problems but its density, which is low compared with $CHCl_3$, allows removal of dust by prolonged centrifugation. Also, the PIs under consideration here are composed of polar main chains and non-polar side chains. Use of a mixed solvent consisting of a polar and a non-polar component therefore might be helpful to avoid association.

Measurements on samples with open end-groups, however, showed clearly that use of the mixed solvent did not fully suppress association. In particular, light-scattering measurements done on samples with end-groups point to the existence of large associates through exceedingly high molecular weights and second virial coefficients lower by two orders of magnitude than those measured by osmometry. Closure of end-groups in the manner indicated above removed this problem at once and led to molecular weights compatible with other information.

Figure 1 displays the light-scattering intensities of PI-10 (see *Table 1*) in a Zimm plot. Evaluation of the pertinent data was done in the usual manner[4] to yield the weight-average molecular weight, M_w (see *Table 1*), the radius of gyration R_g and the second virial coefficient A_2.

In order to check the internal consistency of the present set of M_n and M_w data collected in *Table 1*, all PIs were subjected to an analysis by g.p.c. using chloroform as a solvent. For this purpose intrinsic viscosities have been measured in *o*-dichlorobenzene at 50°C and in chloroform at 25°C. Under these conditions the influence of possible association should be negligible, as suggested by osmometry (see above). The intrinsic viscosities obtained by Huggins plots[4] of the respective specific viscosities are given in *Table 1*. The respective Mark–Houwink plot is shown in *Figure 2*. Good agreement of the intrinsic viscosities obtained from both solvents can be seen, which points to the absence of excluded volume effects due to chain stiffness.

The Mark–Houwink coefficients K ($=4.07\times10^{-4}$ ml g^{-1}) and α ($=1.11$) taken from this plot served for the universal calibration of the g.p.c. calibrated previously

Table 1 Properties of polyimides

Polyimide	$M_{n,os}$[a] (g mol^{-1})	$P_{n,os}$[a]	$P_{w,ls}$[b]	$[\eta]_{o\text{-DCB}}$[a] (m g^{-1})	$[\eta]_{CHCl_3}$[d] (ml g^{-1})
PI-1	10 500	7	17	34.3	
PI-2	12 000	8	15	27.8	26.4
PI-3	16 400	10	18	35.5	-
PI-4	21 800	13	22	50.5	53.0
PI-5	22 400	14	35	77.7	73.1
PI-6	23 500	15	28	69.2	-
PI-7	25 000	16	29	69.8	76.1
PI-8	31 000	19	57	115.0	-
PI-9	31 100	19	46	118.5	-
PI-10	39 100	24	50	150.0	147.2
PI-11	40 200	25	61	130.0	--
PI-12	73 600	46	111	280.0	268.0

[a] Measured in *o*-dichlorobenzene at 50°C

[b] Measured at 25°C in an equimolar mixture of chloroform and cyclohexene

[c] Measured at 25°C in chloroform

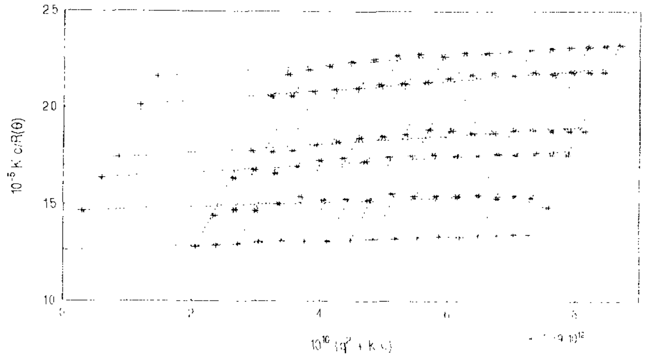

Figure 1 Zimm plot of the light-scattering intensities of polyimide PI-10 in an equimolar mixture of chloroform and cyclohexene at 25°C

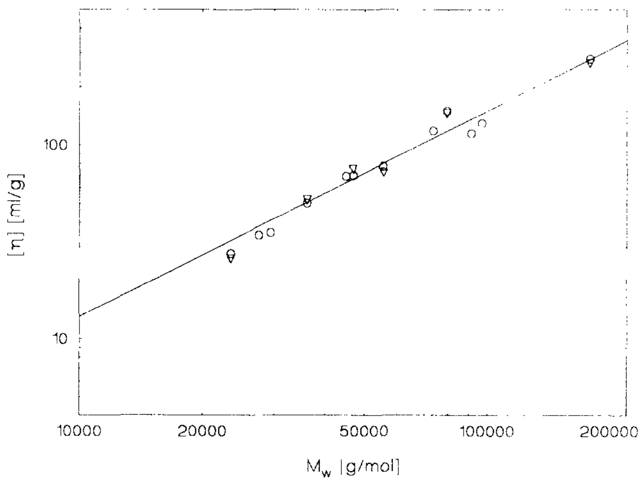

Figure 2 Mark–Houwink plot of the intrinsic viscosities of the polyimides PI measured in *o*-dichlorobenzene at 50°C (○) and in chloroform at 25°C (▽). The weight-average molecular weights have been determined by light-scattering measurements

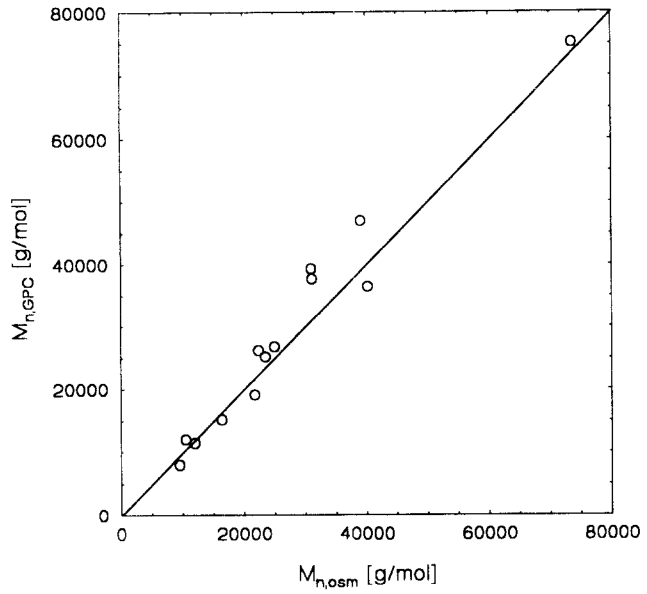

Figure 3 Correlation of directly measured (osmometry) and calculated (from g.p.c. measurements) number-average molecular weights (see text for further explanation)

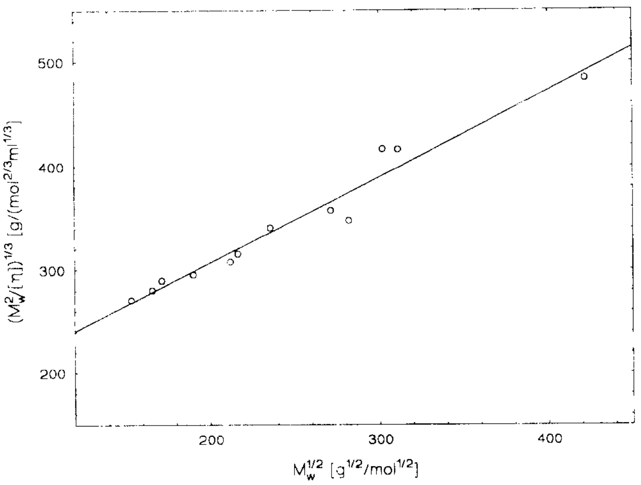

Figure 4 Bohdanecky plot[8] of the intrinsic viscosities of the polyimides PI

with narrowly distributed polystyrene samples. Using this calibration, the M_n values for all PIs can be determined and compared with the data measured directly by osmometry (cf. ref. 5). *Figure 3* shows that the correlation of the osmometric molecular weights with the light-scattering data through the above g.p.c. analysis is satisfactory.

The consistency of the molecular weights determined by different methods within given limits of error suggests that the problem of association in solution has been overcome by closure of the end-groups and that the molecular weights determined by light scattering are reliable.

In principle, the radius of gyration together with the polydispersity of the samples (cf. *Table 1*) should lead directly to the persistence length by applying the procedure of Wenz *et al.*[6]. It turned out, however, that the radii of gyration determined for the smaller molecular weight are not accurate enough to allow for a meaningful determination of chain stiffness. Thus, for the highest molecular weight under consideration here (sample PI-12), evaluation of the light-scattering data gives a radius of gyration $\langle s^2\rangle^{1/2} = 37.8$ nm which, together with $P_w/P_n = 2.4$ (cf. *Table 1*), leads to a persistence length of 13 nm by applying the procedure given in ref. 6. It is clear that this figure is subject to considerable error, necessitating the application of another procedure for the determination of the persistence length.

As in previous investigations[3,6,7] we apply for this purpose the procedure developed by Bohdanecky[8,9]. Thus, the determination of the persistence length can be done using the following plot:

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

where A_η is a quantity depending on the hydrodynamic diameter of the chains and B_η can be expressed as

$$B_\eta = B_0 \Phi_{0,\infty}^{-1/3} \cdot (\langle r^2\rangle_0/M)_\infty^{-1/2} \tag{2}$$

where $\langle r^2\rangle_0$ is the unperturbed mean-square end-to-end distance and the subscript ∞ indicates that the ratio of $\langle r^2\rangle_0$ and M is taken in the random-coil limit. The quantity $\Phi_{0,\infty}$ is the viscosity function for infinite chain length. The value used by Bohdanecky[8] ($\Phi_{0,\infty} = 2.86 \times 10^{23}$) was taken for all calculations. The quantity B_0 varies between 1.10 and 1.00 and can be approximated by the mean value of 1.05 at the present level of accuracy.

The Bohdanecky plot displayed (*Figure 4*) shows that equation (1) is fulfilled within given limits of error. Hence the slope may be used to evaluate the Kuhn length $l_K = \langle r^2\rangle_0/Nl_u$ where $N = M/M_u$ with M_u (1604.6 g mol^{-1}) and l_u being the mass per unit length and the length of the monomer unit ($l_u = 20.9$ Å), respectively. The resulting persistence length is 13.6 nm. Given the limits of error, this figure is in very good agreement with the persistence length determined by light scattering (see above).

The hydrodynamic diameter d of the chains was evaluated from the intercept A_η. According to Bohdanecky[8]

$$\frac{d_r^2}{A_0} = (4\Phi_{0,\infty}/1.215\pi N_A)(\bar{v}/A_\eta)B_\eta^4 \tag{3}$$

with $d_r = d/l_K$ being the reduced hydrodynamic diameter of the chain and $\bar{v}$ the partial specific volume of the polymer in solution. The quantity A_0 is related to d_r by

$$\log\left(\frac{d_r^2}{A_0}\right) = 0.173 + 2.158 \log(d_r) \tag{4}$$

The partial specific volume $\bar{v}$ was approximated by 1.00 cm^3 g^{-1}. From these data the hydrodynamic diameter could be estimated to be of the order of 1.2 nm. Values of similar magnitude have been obtained previously for related systems[3,5,6] and compare favourably with the average lateral dimensions of such systems (cf. the discussion of this point in ref. 10).

CONCLUSION

The foregoing analysis of the polyimides PI in solution by two independent methods shows clearly that the polyimide main chains under consideration here cannot be regarded as rigid rods despite the presence of the terphenyl moiety and the pyromellitic imide linkage in the repeating unit. Similar observations have been made when investigating stiff-chain polyesters having similar building blocks[3,5,7]. The main reason for the rather low stiffness of all these chains seems to be located in out-of-plane fluctuations of single bonds within the chain[11-13]. These small deviations will add up to produce a considerable curvature of the macromolecule even when the repeating unit consists of stiff units, as is the case for the polyimides PI under consideration here. Thus, the present findings as well as previous results[3,5,7,11-13] unambiguously demonstrate that it is virtually impossible to construct a truly rigid-rod polymer with repeating units containing single covalent bonds. Rigid objects will only result from three-dimensional building blocks with sufficient diameter, such as, for example, helical structures.

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