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Poly[2-phenylene-(5-benzimidazole)] isophthalamide: macromolecular characterization

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Two different synthetic routes have been used to synthesize poly[2-phenylene-(5-benzimidazole)]isophthalamide (PABI), an aromatic polyamide that shows good compatibility with rigid chain polymers such as poly(*p*-benzamide). The influence of the conditions of synthesis in determining the molecular weight of PABI has been investigated in order to use this polymer for rigid–flexible copolymers with specific characteristics. Values of $[\eta]$ and M_w have been determined in 96% H_2SO_4 and dimethylacetamide, and conformational properties have been investigated by viscometry and molecular dynamics simulations.

(Keywords: polyamide benzimidazole; synthesis; conformational analysis)

INTRODUCTION

Polyamide benzimidazoles are quite a new class of aromatic polymers first synthesized by Serkov *et al.*[1]. A peculiar characteristic of one of these polyamides, poly[2-phenylene-(5-benzimidazole)]isophthalamide (PABI) (*Figure 1*), is its chemical compatibility with the liquid crystalline polymer poly(*p*-benzamide) (PBA), and for this reason PABI has been used to synthesize a new rigid–flexible diblock copolymer with potential mesogenic properties[2]. Rod–coil copolymers where the length of the flexible chain is much greater than that of the rigid one are of poor interest since in this particular case the formation of a liquid crystalline phase containing the whole copolymer is hardly feasible, as already seen in other systems[3] and theoretically predicted[4]. For this reason it appeared of great interest to synthesize PABI blocks of different molecular weights to study the phase behaviour of PBA–PABI copolymers with different lengths of the flexible block. For this purpose we have performed a further study on the synthesis of PABI to control its molecular weight and understand the dependence of the molecular weight on factors such as the stoichiometric imbalance. The persistence length of this polymer has been determined by an analysis of the dependence of its intrinsic viscosity on molecular weight using the Yamakawa–Fujii theory[5], and its conformational properties have been derived from light-scattering measurements and molecular dynamics (MD) simulations.

EXPERIMENTAL

Materials and methods

Isophthaloyl chloride (IPCl) was supplied by Fluka with a purity of >96%. Purification was performed by crystallization from boiling n-hexane. 5-Amino-2-(*p*-aminophenyl)benzimidazole (DAB) was synthesized at Moscow University and used after vacuum drying for 24 h at 100°C and storing over P_2O_5. *N*,*N*′-Dimethylacetamide (DMAc) was supplied by Fluka and vacuum distilled over CaH_2; it was then stored over Riedel type 4A molecular sieves. Lithium chloride (Riedel de Haen) was vacuum dried for 24 h at 200°C. Carbon tetrachloride and n-pentane were purchased from Fluka and used without further treatment.

The intrinsic viscosities $[\eta]$ of the polymer samples were measured in 96% H_2SO_4 and in DMAc at 25 ± 0.1°C using a suspended level Ubbelohde viscometer.

Light-scattering measurements were performed at 25°C with a Sofica 42000 photometer at 633 nm; d*n*/d*c* was determined using a KMX-16 Milton Roy diffractometer at the same wavelength. Light-scattering measurements were performed on solutions ranging in concentration from 0.60 to $9.40 \times 10^{-3}\,\mathrm{g\,ml^{-1}}$. The polymer density was determined on a density gradient column obtained using CCl_4 ($\delta = 1.59\,\mathrm{g\,ml^{-1}}$) and n-pentane ($\delta = 0.626\,\mathrm{g\,ml^{-1}}$).

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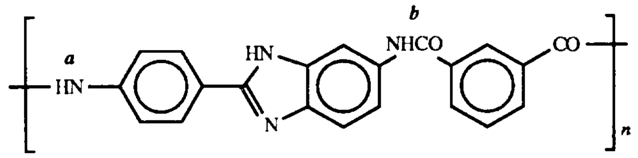

Figure 1 Repeat unit of PABI showing the 'a' and 'b' amino groups

Table 1 Influence of the stoichiometric imbalance on the intrinsic viscosity of samples synthesized according to the first synthetic route

Sample	*r* (moles DAB/ moles IPCl)	$[\eta]$ (dl g^{-1}) in H_2SO_4 at 25°C
1	0.69	0.32
2	0.75	0.71
3	0.86	0.82
4	0.96	1.44
5	1.00	2.00
6	1.07	0.33
7	1.14	0.17
8	1.22	0.21

The simulated behaviour of PABI chains was studied by molecular dynamics (MD) using the program Insight II/Discover by Biosym on a Silicon Graphics Iris workstation.

Polymer syntheses

PABI synthesis was performed according to two different methods. The first was a straightforward low temperature (−15°C) polycondensation between IPCl and DAB in DMAc containing 3% LiCl. After 5 h the reaction was considered to be complete and the system was slowly brought to room temperature. The second method required the addition in three different steps of IPCl to a cold suspension of DAB in DMAc containing 3% LiCl. During the first step, 60% of the total amount of IPCl was added to the system and left to react under mechanical stirring for 30 min. The reaction was then carried on at room temperature for 60 min more. The same procedure was then repeated adding, respectively, the remaining 30% and finally 10% of IPCl. This synthetic route allowed access to somewhat higher molecular weights and was developed from a synthesis described in the literature for other low temperature polycondensations[6]. After the synthesis the resulting polymer was precipitated in water, washed several times with hot water and finally vacuum dried for 24 h at 60°C.

RESULTS AND DISCUSSION

Eight polymer samples were synthesized according to the first synthetic route for various ratios between the equivalents of the reactants (r = moles DAB/moles IPCl) to study the influence of this ratio on the tailoring of the molecular weight. In *Table 1* the r values used to synthesize these eight samples and the intrinsic viscosities are reported.

It is important to remark that the samples synthesized with a stoichiometric imbalance r lower than 1 should mainly end with two COCl groups; this fact is of great interest when considering the synthesis of a block copolymer with PBA, where the acylic terminal group should provide the link between the two chains. Only in the case $r = 1$ are most of the chains supposed to end with one NH_2 group and one COCl; conversely, when r is higher than 1 the chains mainly end with NH_2 groups.

The intrinsic viscosities in 96% H_2SO_4 and DMAc, respectively, and the light-scattering data of the five samples obtained with the second synthetic route are reported in *Table 2*; the molecular weight M_w, the second virial coefficient A_2 and the dissymmetry ratio z were obtained assuming $dn/dc = 0.266$ ml g^{-1}. These samples were also used to obtain the Mark–Houwink coefficients in two different solvents. It can be seen that the values of z are always near to 1, indicating that the gyration radii $\langle R_G \rangle$ of our samples are too small to be evaluated with this technique. The M_w values can, therefore, be evaluated from extrapolation to $c = 0$ of the ratio $(c/H_\theta)_{90}$, where $H_\theta = (I - I_0)\sin\theta/(1+\cos^2\theta)$. Moreover, the second virial coefficient, determined from the slope of the plot of (c/H_{90}) vs. c (*Figure 2*), is always positive, decreasing, as expected, with M_w. These positive values confirm the absence of aggregation phenomena and their order of magnitude, about 10^{-3}, gives a first indication that this polymer tends to behave like a semirigid one; flexible polymers, in fact, have smaller second virial coefficients, usually ranging between 10^{-4} and 0. Viscometric and light-scattering data allow the determination of $[\eta]$–M_w relationships. Viscometry was performed on samples 9–13 in two different solvents, 96% H_2SO_4 and DMAc, and the corresponding values intepreted according to the Mark–Houwink relationship and the Yamakawa–Fujii theory[5], respectively, are reported in *Figures 3* and *4*. A linear fitting of the plot of log $[\eta]$ vs. log M_w (*Figure 3*) allows the determination of the parameters of the Mark–Houwink relationship $[\eta] = KM_w{}^a$. In our case the two resulting expressions are

$$[\eta] = 1.89 \times 10^{-4} M_w^{0.80} \text{ (in } H_2SO_4\text{)}$$

and

$$[\eta] = 6.56 \times 10^{-4} M_w^{0.68} \text{ (in DMAc)}$$

Table 2 Characteristic data for samples synthesized according to the second synthetic route

Sample	$[\eta]$ (dl g^{-1}) in H_2SO_4 at 25°C	$[\eta]$ (dl g^{-1}) in DMAc at 25°C	z^a	$10^{-3} M_w$	$10^3 A_2$
9	0.76	0.75	1.17	28.5	3.0
10	1.32	1.28	1.15	61.0	2.2
11	1.66	1.58	1.12	81.4	1.6
12	2.00	1.68	1.08	88.0	2.1
13	2.5	2.05	1.09	114.0	1.3

[a] The ratio between the intensities of the light scattered at 45° and 135° (I_{45}/I_{135})

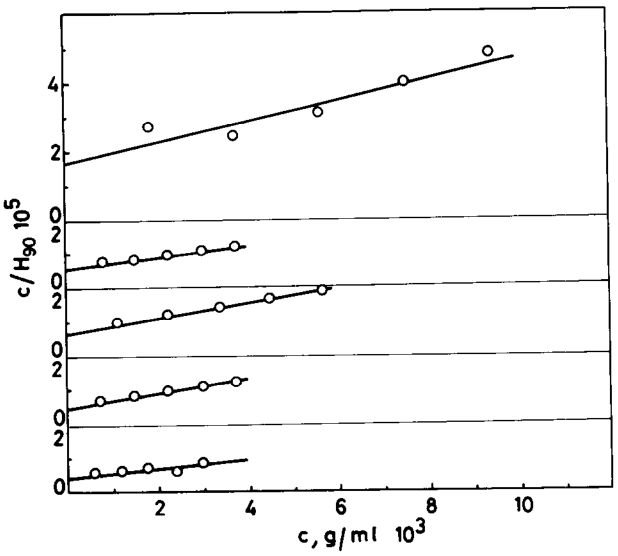

Figure 2 Concentration dependence of (c/H_{90}) for PABI samples 9–13

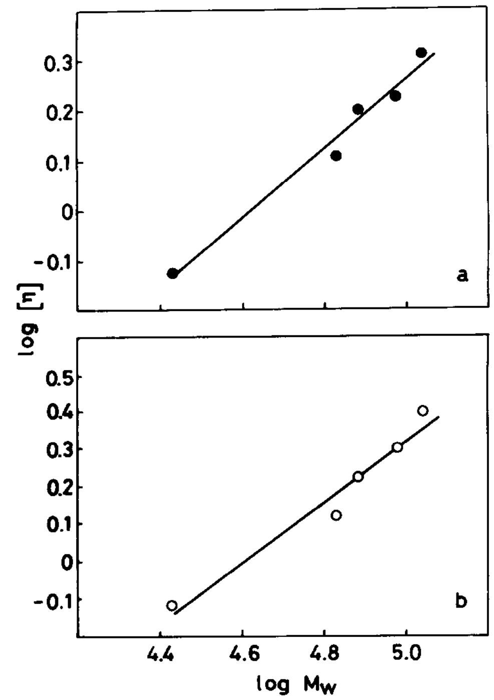

Figure 3 Molecular weight dependence of $[\eta]$ at 25°C for two different solvents (linear fitting): (a) DMAc; (b) 96% H_2SO_4

It can be seen that the coefficient a is rather higher than 0.5, the theoretical value for random coils under Θ conditions, for both solvents. This could be due to an expansion of the coil in a good solvent, with a remarkable excluded volume effect and consequent expansion coefficients α higher than 1. This effect could be due to a certain stiffness of the chain and could require a different model to fit the log $[\eta]$ vs. log M_w plots. In this case the polymer would be better represented by a worm-like model rather than by a random coil and the experimental values could be fitted by the Yamakawa–Fujii theory[5]. The dependence of $[\eta]$ on M_w for an unperturbed worm-like cylinder of diameter d is given by

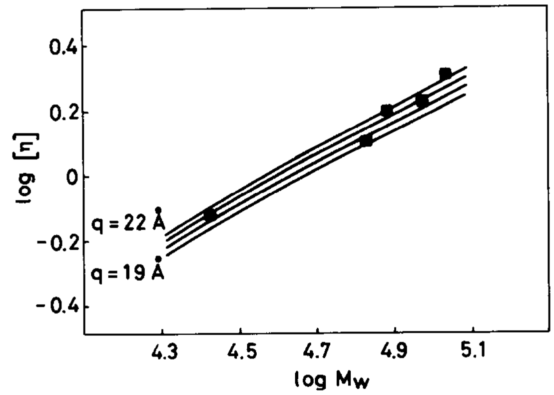

Figure 4 Molecular weight dependence of $[\eta]$. The lines are from the Yamakawa–Fujii theory for q ranging from 19 to 22 Å. The experimental data for DMAc are shown as filled squares

$$[\eta] = \Phi \frac{(L')^{3/2}}{\lambda^3 M}$$

where $L' = \lambda M/M_L$, $\lambda = 1/2q$, q is the persistence length of the chain, M_L is the mass per unit length of the chain and Φ is a tabulated function of L' and the reduced cylinder diameter $d' = d/2q$. In order to reproduce the theoretical curves for our polymer, we need to know the chain diameter d and M_L; the value of d was obtained from the density of the amorphous polymer (1.36 g ml^{-1}) using an appropriate equation[7] and turned out to be 5.2 Å; M_L is 22.34.

Figure 4 shows a good approximation to the experimental points from DMAc by a set of curves characterized by values of q between 19 and 22 Å. These values are sensibly lower than for analogous polymers[8] that have persistence lengths of about 40 Å. It must be taken into account that the $[\eta]$ values we have determined are probably overestimated, since we have obtained them in non-Θ solvents and the excluded volume effect can be substantial. In this case the q values would be lower than those determined.

In order to obtain further information about the chain conformation, we used MD simulations. This method has been successfully applied to describe the different behaviours of thermotropic polymers incorporating asymmetric moieties whose microstructures could not be easily determined experimentally because of their high melting temperatures and low solubilities[9]. In this case it was observed that although still far from giving 'true' equilibrium conformations for polymers in bulk, nevertheless this technique may be used to define the different rigidities of polymers with the same overall composition but incorporating reactants in a different orientational order. It seemed possible to extend, in a similar way, MD simulations to the determination of the conformational properties of polymers in solution with analogous structural characteristics, and in particular to PABI. In fact, 2-phenylene-5-benzimidazole, one of the two reactants constituting PABI, has two non-equivalent amino groups ('a' and 'b'), as shown *Figure 1*.

If 'I' stands for the isophthalic unit, the minimum energy conformations for the three possible dimers ab-I-ab, ab-I-ba and ba-I-ab can be determined. The first interesting fact to report is the tendency of the ab-I-ba dimers towards linearity through the compensating bond angles of the amide linkages between the isophthalic

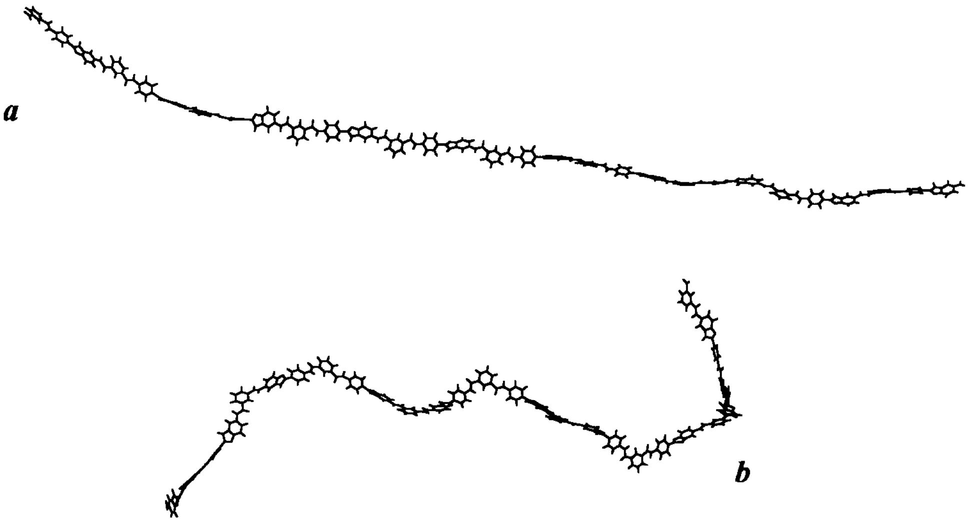

Figure 5 Conformations of regular model chains after 100 ps MD simulations: (*a*) ab-I-ab chain; (b) ab-I-ba-I-ab-I-ba chain

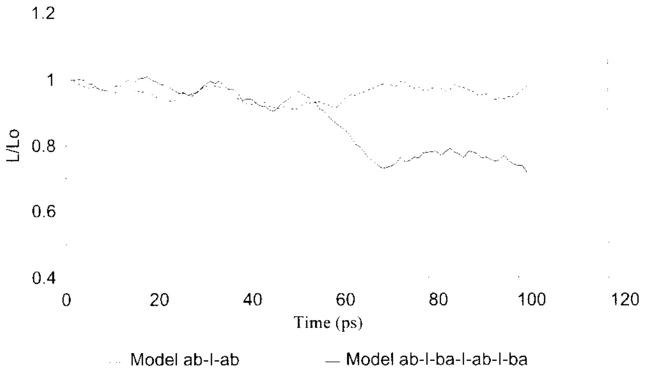

Figure 6 Normalized head–tail distances vs. time for the two model chains ab-I-ab and ab-I-ba-I-ab-I-ba

residue and the 'b' amino groups. Even the ab-I-ab sequence, in its minimized structure, is not far from linearity. On the other hand, the ba-I-ab group shows a central kink due to the double 'contribution' from the straight I-a linkages. In a second step we built two model polymer chains, connecting in a regular fashion, for the minimized structures of the dimers ba-I-ba and ba-I-ab. Of course, the latter chain should have a general composition of the kind ab-I-ba-I-ab-I-ba and so on, and can be considered as incorporating both ba-I-ab and ab-I-ba dimers. The behaviour of the two models proved to be very different. In the case of a regular ab-I-ab polymer, the model chain, as obtained by minimization techniques, is rather extended and our simulations show that it tends to maintain extended conformations (*Figure 5a*). A PABI polymer tailored in this way would be rather rigid. On the other hand, the regular ab-I-ba-I-ab-I-ba chain proved to be much more prone to coiling up, and, from our observations, it can be argued that a long chain of this kind would become rather flexible (*Figure 5b*). These results are summarized in *Figure 6*, normalized with respect to the initial extended conformation. In this plot we can observe the averaged time evolution of the chain conformations, expressed through their head–tail distances normalized with respect to the initial distances; it can be seen that whereas the ab-I-ab regular chain tends to maintain its head–tail distance with time, the ab-I-ba-I-ab-I-ba chain evolves towards coiled conformations. Of course, the simulations were performed only on short and regular model chains, but if we suppose, as seems reasonable, that the reactivities of the two amino groups of DAB are not so different as to influence strongly the orientation of the reactant sequence, a random connection may reasonably be foreseen. Therefore, we can conclude that the behaviour of PABI is strongly influenced by the presence of rigid segments and sparse abrupt kinks (*Figure 5b*).

CONCLUSIONS

In this paper we have reported the synthesis of the aromatic polyamide PABI. Its conformational properties have been investigated by several techniques; in addition, MD simulations have been performed on model PABI polymer chains. The collected data seem to point out that PABI can be properly represented as a polymer on the borderline between an expanded coil and a worm-like chain of low rigidity. In conclusion, PABI could represent a suitable chain to prepare rigid–flexible block copolymers having a predetermined length of the flexible moieties. Moreover, it would be highly interesting to synthesize PABI chains incorporating the asymmetric units linked in ordered sequences.

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