DFT Based Monte Carlo Simulations of Poly(9,9-dialkylfluorene-2,7-diyl) Polymers in Solution

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The dilute solution properties of poly(9,9-dihexylfluorene-2,7-diyl) (PDHF) were studied by coupled SEC/light scattering and MALDI–TOF over a large molecular weight (MW) span ranging from PDHF oligomers (1–8-mer) to high MW polymer. The results were compared with Monte Carlo simulations based on realistic PDHF models obtained from X-ray data and density functional theory (DFT) calculations and with a DFT based Kratky–Porod–Benoit–Doty (KPBD) worm-like chain. The simulations called “selective random walk” (SRW) and the corresponding “selective self-avoiding random walk” (SSAW) explicitly take into account the rotationally labile bonds between the fluorene units in that four distinct torsion angles (±37.5° and ±143°) between the units are chosen randomly. The simulations better account than the KPBD model for the experimental data obtained by us and others for various poly(9,9-dialkylfluorene-2,7-diyl) polymers but still give somewhat larger values for the radii of gyration and hydrodynamic volumes. The torsion angle selectivity of the SRW and SSAW simulations predict long chain sections punctuated by sudden sharp loops.

Introduction

The physical properties of poly(9,9-dialkylfluorene-2,7-diyl) (PDAF) and similar conjugated polymers are of considerable interest because of their promising luminescent and other optical properties.¹⁻¹⁶ However there have been few reports on the solution conformations of this interesting class of polymers. Grell et al.¹,² have reported on the chain dimensions of high solution conformations of this interesting class of polymers.

However, based on the KPBD lower MW polymers was not reported as the LS method was deemed unreliable in that case. However, based on the KPBD equation at lower MW there are deviations expected in the ($s^2$) vs MW plot.

Our emerging interest in the behavior of low MW poly(9,9′-dihexylfluorene-2,7-diyl) (PDHF) has prompted us to use density functional theory (DFT) to model their conformations. Here we report DFT optimized conformations of oligomers with degrees of polymerization (DP) values of up to 6 that have two methyl (PDMF), hexyl (PDHF), octyl (PDOF), and 2-ethylhexyl (PDEHF) groups at the 9-positions of fluorene. On the basis of these data, we simulate the conformational behavior of PDHF and other PDAF’s in highly dilute solutions and compare the resulting chains with experimental data (MALDI and SEC/LS) obtained by us and by others.

Experimental Section

Materials. The precursors, 2,7-dibromofluorene, 2-bromofluorene and 2-bromofluorene were alkylated with 1-bromohexane to obtain 2,7-dibromo-9,9′-dihexylfluorene (DBDHF) and 2-bromo-9,9′-dihexylfluorene (MBDHF).²⁰ Poly(9,9′-dihexylfluorene-2,7-diyl) (PDHF) was synthesized by Yamamoto coupling.²⁰⁻²² For the synthesis of the oligomers MBDHF was used to limit the degree of polymerization (DP) and obtain well-defined oligomers (DBDHF:MBDHF = 1:1.2).

Measurements. Coupled size exclusion chromatography/light scattering (SEC/LS) measurements were carried out in THF/triethylamine (90/10 w/w) on a Waters 510 HPLC module equipped with Beckman 156 refractive index (RI) detector and a Wyatt Dawn DSP multi angle light scattering detector using polystyrene standards (Pressure Chemicals) at a flow rate of 1.0 mL/min using three Polymer Laboratories columns (PLgel (5 µm 50 Å, MW ≤ 2,000), PLgel (5 µm 100 Å, 500 ≤ MW ≤ 600,000) and PLgel (10 µm 10 Å, 10,000 ≤ MW ≤ 600,000)) at 23 °C. For the case of low MW PDHF, a flow rate of 0.5 mL/min was used to optimize separation of oligomers. The data were analyzed using Wyatt Astra version 4.90.07 software. Values of the refractive increments (dρ/dn = 0.295 mL/g) were determined by the refractometer using an off-line method. Equation 1 was used to relate apparent hydrodynamic volumes with MW’s using the Mark–Houwink–Sakurada (MHS) based universal calibration method.

\[ \log V_h = (\alpha + 1) \log M + \log(0.40 \text{ K}) \]  

(1)

MALDI measurements were carried out on Voyager-DE STR mass spectrometer equipped with a N₂ laser emitting at 337 nm and 70 laser shots per spectrum using dithranol as the matrix. Spectra of PDHF for MW’s of 500–3,000 were acquired in positive-ion reflector mode using an acceleration voltage of 20 kV, a laser intensity of 1850 W/cm² and a delay time of 200 ns. All data were processed using “Voyager” software. Higher molecular weights could not be detected presumably due to low polymer volatilities.²³
Calculations. The geometry optimizations and energy calculations were carried out using the DFT B3LYP method with a 6-31G* basis set, that was found to be efficient and accurate for most calculations. These calculations were carried out using Gaussian 03. The calculations on the PM3 and MM2 methods were carried out using SPARTAN-04 software. A Monte Carlo simulation program was designed and run using MATLAB R14 software.

Results and Discussion

A number of PDHF polymers were synthesized by polymerization of DBDHF using Yamamoto conditions. In some cases MBDHF was used to limit degrees of polymerization (DP's) and give well-defined oligomers. At a MBDHF/DBDHF ratio of 1.2 mostly oligomers up to 8-mers were obtained. No oligomers containing bromine end groups were detected consistent with complete end-capping. The MALDI spectra of PDHF clearly showed well defined oligomers (n = 2–8, MW = 500–3000) with the expected 332 Da mass intervals. The SEC elution volumes of the oligomers were determined by curve resolution methods (Supporting Information, Figure SI-1). For PDHF with MW’s between 3000 and 10 000 no accurate MW’s could be determined by MALDI or light scattering. For higher MW PDHF (MW > 10 000) the online SEC/LS method gave both MW and radii of gyration, (were used to determine the molecular size. Multiple measurements were made for each sample to obtain an accurate average value.

DFT Calculations of Poly(9,9-dialkylfluorene-2,7-diyl) (PDAF’s) Oligomers. Conformations of the oligomers of PDHF, poly(9,9-dimethylfluorene-2,7-diyl) (PDMF), poly(9,9-diocetylfluorene-2,7-diyl) (PDOF) and poly(9,9-diethylhexylfluorene-2,7-diyl) (PDEHF) were evaluated by means of DFT (B3LYP/6-31G*) -based calculations and Monte Carlo simulations. The PDAF’s may be considered to consist of relatively rigid but internally “bent” fluorene units linked through rotationally labile bonds. The optimized geometries and energies of PDAF’s having hydrogen atoms at the terminal 2- and 7-positions were evaluated by DFT B3LYP/6-31G*, PM3 and

Table 1: Calculated (DFT BLYP/6-31G*) Torsion Angles (deg) between Adjacent Fluorene Units of Poly(9,9-dialkylfluorene-2,7-diyl) and Corresponding Energy Barriers (kJ/mol) of Rotation

<table>
<thead>
<tr>
<th>x-mer</th>
<th>PDHF</th>
<th>PDMF</th>
<th>PDOF</th>
<th>PDEHF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>36.9 (12.4)</td>
<td>37.9 (14.6)</td>
<td>39.2 (11.3)</td>
<td>38.4 (12.7)</td>
</tr>
<tr>
<td>3</td>
<td>38.6 (14.1)</td>
<td>37.1 (14.0)</td>
<td>36.7 (12.6)</td>
<td>36.8 (19.0)</td>
</tr>
<tr>
<td>4</td>
<td>36.6 (13.2)</td>
<td>37.1 (19.5)</td>
<td>34.4 (17.5)</td>
<td>79.1</td>
</tr>
<tr>
<td>5</td>
<td>38.1 (12.1)</td>
<td>79.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>37.3 (11.3)</td>
<td>79.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For methods used, see text. The PM3 and MM2 methods are given for comparison purposes. 

Figure 1. Hydrodynamic volumes (Vₐ) obtained by SEC as a function of PDHF MW. Molecular masses by MALDI-TOF (upward-triangles), molecular masses by LS (downward-triangles), SRW (solid line), SSAW (dashed line), DFT based KPBD (dotted line), DFT corrections (solid circles). Inset: Linear fit of experimental data.

Figure 2. Two optimized geometries of PDMF dimer having 2–7° torsion angles of 37.9° (A) and 143.1° (B), as well as PDHF dimer (C) with measured distances.
force field (MM2) methods (Table 1). It is clear that the results differ widely. However, there is general agreement that the B3LYP/6-31G* methods are superior and sufficient for the present systems with regard to both geometry and energies.26 This is also supported by X-ray data (see below).

Figure 2 shows the two DFT-optimized conformers of the PDMF dimer. The partial conjugation of the two fluorene units and the non bonded interactions of the aromatic hydrogens of the adjacent units results in C1−C2−C2′−C1′ torsion angles of 37.9° (“syn”) and 143.1° (“anti”). The torsion angles for the optimized syn conformers of the 2-mer to 6-mer of PDMF and PDHF were found to vary between 36 and 39° (Table 1). These results are in excellent agreement with recent DFT calculations on polyfluorene oligomers reported by Raos30 and Hannongbua31 but differ slightly from Hartree–Fock based calculations.32 X-ray data of PDOF33,34 and PDEHF35,36 indicate a 5/2 helix with a torsion angle of 144° for the anti conformer thus supporting the DFT based torsion angle restrictions see text.

Figure 3. Illustration of the polyfluorene conformations for Monte Carlo programming. The alkyl groups at 9,9-position are not entirely shown. The z-axis is the vector C2′−C2 and the x-axis is in the fluorene plane pointing the 9-position direction. The distances C2′−C2 and C2−C7 are 0.1484 and 0.6970 nm, respectively. For restrictions of fluorene geometry and torsion angle restrictions see text.

The DFT optimized geometries of the PDHF 3–6 mers are used to give average values for the angles between repeat units (C7′−C7−C7, Figure 3) of 21.2 ± 0.6° and torsion angles of the syn (±37.5°) and anti (±143°) conformers. The energies of formation of the PDMF and PDHF dimers as a function of torsion angle are illustrated in Figure 4. The syn and anti conformers have nearly identical energies of formation. Energies barriers corresponding to bond rotations of adjacent fluorene units between 11.3 and 14.6 kJ/mol were found at torsion angles of 0 and 90 degrees (Table 1).

Chain Conformation of PDHF and Similar Polyfluorenes. Dilute solutions of these polymers have been the subject of several studies1,6,10 using the Kratky–Porod–Benoit–Doty (KPBD) model.17,18 However, this model does not account explicitly for conformational effects due to rotation between adjacent fluorene units. Furthermore, intramolecular excluded volume interactions that are expected to become important at higher degrees of polymerization are not explicitly considered.

Figure 3 illustrates a more realistic, but more complex, alternative model. We start with the four DFT based torsion angles of 37.5, −37.5, 143.0, and −143.0 deg (see above) for the 2,7′ linkages of neighboring fluorene units and a fixed (C2′−C7′−C2) “internal” angle of 168.7° between the units.
Mean square radii of gyration \((\langle s^2 \rangle)\) obtained by light scattering versus weight-average molecular weight of PDHF in THF. Line represents linear fitting. The symbols refer to different PDHF samples.

A rigid C2′−C7′ fluorene fragment is followed by the C7′−C2 bond that is placed along the z-axis. Rotation of the next (C2′−C7′) unit now traces a cone corresponding to all possible conformations from which one of the above four torsion angles is chosen randomly for each successive unit (the two middle fluorene units in Figure 3 are shown in the anti conformation).

We refer to this model as the selective random walk (SRW). Based on these parameters, Monte Carlo (MC) simulations were carried out for PDHF’s (and similar polymers) with DP’s of up to 700 units using the simulated three-dimensional walk (Figure 5). A flowchart describing the computational methodology is shown in Figure SI-2 (Supporting Information). Thus, chain conformations were generated by adding successive fluorene units using the above bond length and angle parameters. In this process the coordinates of the 2- and 7-positions of every fluorene unit were recorded as a function of the degree of polymerization. The mean square end to end distance \(\langle h^2 \rangle\) and radii of gyration \(\langle s^2 \rangle\) were calculated for 25 000 chains with each chain containing up to 700 units. It should be stressed that no intermolecular excluded volume effects were considered as only one chain was calculated at the time, corresponding to a highly dilute solution consistent with the SEC measurements.

The distances of the pendant methyl end groups to the center of the fluorene units were evaluated as 0.25 nm for PDMF, 0.88 nm for PDHF and 1.03 nm for PDOF using the DFT calculations, and these were taken as the radii of “cylindrical” fluorene units for “selective self-avoiding walk” (SSAW) simulations, in which intramolecular excluded volume effects are taken into account implicitly. Chains with intramolecular distances between any of the fluorene units smaller than the above cylindrical diameters were discarded. The low MW PDAF chains (DP < 100) show no such effects but at a DP of 700 the number of excluded volume interactions is typically between 0 and 3.

The above procedures were used in calculating the mean square end-to-end distances \(\langle h^2 \rangle\) and mean square radii of gyration \(\langle s^2 \rangle\) of the polymer using every fluorene unit as a local center of mass. As expected the fractions of the SSAW chains showing one or more nonbonded interactions were found to increase with increasing DP’s. Error evaluation was done by repeating the MC program five times. The maximum errors of the \(\langle h^2 \rangle\) and \(\langle s^2 \rangle\) values were less than 1%.

**TABLE 2: Monte Carlo Simulated and Experimental Chain Dimensions for PDHF, PDMOF, PDOF, and PDEHF**

<table>
<thead>
<tr>
<th>PDAF</th>
<th>method</th>
<th>MW (\times 10^{-3})</th>
<th>solvent</th>
<th>temp (°C)</th>
<th>(b^0) (nm)</th>
<th>(q^c) (deg)</th>
<th>(a^0) (nm)</th>
<th>refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDHF</td>
<td>SSAW</td>
<td>0.33−233</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>(\pm 37.5, \pm 143)</td>
<td>9.2</td>
<td>f</td>
</tr>
<tr>
<td>PDHF</td>
<td>SRW</td>
<td>0.33−233</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>(\pm 37.5, \pm 143)</td>
<td>7.8</td>
<td>f</td>
</tr>
<tr>
<td>PDHF</td>
<td>KPBBD</td>
<td>0.33−233</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>all</td>
<td>12.5</td>
<td>f</td>
</tr>
<tr>
<td>PDHF</td>
<td>LS-F</td>
<td>50−130</td>
<td>THF</td>
<td>23</td>
<td>0.80(^a)</td>
<td>all</td>
<td>11</td>
<td>f</td>
</tr>
<tr>
<td>PDHF</td>
<td>viscosity(^c)</td>
<td>2−90</td>
<td>THF</td>
<td>80</td>
<td>0.80(^b)</td>
<td>all</td>
<td>8.0</td>
<td>11</td>
</tr>
<tr>
<td>PDOF</td>
<td>SSAW</td>
<td>0.39−272</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>(\pm 37.5, \pm 143)</td>
<td>9.4</td>
<td>f</td>
</tr>
<tr>
<td>PDOF</td>
<td>SRW</td>
<td>0.39−272</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>(\pm 37.5, \pm 143)</td>
<td>7.8</td>
<td>f</td>
</tr>
<tr>
<td>PDEHF</td>
<td>KPBBD</td>
<td>0.39−272</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>all</td>
<td>12.5</td>
<td>f</td>
</tr>
<tr>
<td>PDEHF</td>
<td>LS-F</td>
<td>40−260</td>
<td>THF</td>
<td>40</td>
<td>0.795(^b)</td>
<td>all</td>
<td>8.55</td>
<td>1</td>
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<tr>
<td>PDEHF(^d)</td>
<td>X-ray</td>
<td>0.39−272</td>
<td>e</td>
<td>e</td>
<td>0.837</td>
<td>6, 33, 34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDEHF</td>
<td>SRW</td>
<td>0.39−272</td>
<td>e</td>
<td>e</td>
<td>0.84</td>
<td>(\pm 37.5, \pm 143)</td>
<td>7.8</td>
<td>f</td>
</tr>
<tr>
<td>PDEHF(^d)</td>
<td>X-ray</td>
<td>89−253</td>
<td>toluene</td>
<td>20</td>
<td>0.75(^b)</td>
<td>all</td>
<td>7.0</td>
<td>10</td>
</tr>
<tr>
<td>PDEHF(^d)</td>
<td>X-ray/MO</td>
<td>89−253</td>
<td>toluene</td>
<td>20</td>
<td>0.75(^b)</td>
<td>all</td>
<td>7.0</td>
<td>10</td>
</tr>
<tr>
<td>PDEHF(^d)</td>
<td>X-ray</td>
<td>145.3</td>
<td>37.5</td>
<td>143</td>
<td>0.839</td>
<td>6, 36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDEHF(^d)</td>
<td>X-ray</td>
<td>145.3</td>
<td>37.5</td>
<td>143</td>
<td>0.839</td>
<td>6, 36</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDMOF</td>
<td>LS-F</td>
<td>24−193</td>
<td>THF</td>
<td>20</td>
<td>0.84(^d)</td>
<td>all</td>
<td>9.5</td>
<td>6</td>
</tr>
</tbody>
</table>

\(^a\) Simulation methods: selective self-avoiding walk model (SSAW), selective random walk model (SRW), DFT based KPBBD model; fitting of light scattering data using KPBBD equation (LS-F), and experimental results (X-ray). \(^b\) Lengths of repeat units from DFT calculations. \(^c\) Torsion angle between adjacent units; “all” indicates no torsion angle restrictions. \(^d\) Calculated and fitted persistence lengths (see text). Calculated values in vacuo. \(^f\) This paper. \(^\#\) Calculated from the KPBBD equation using \(a = b/(1 - \cos 21.2°)\). \(^\dagger\) Fitted value on the basis of KPBBD equation. Determined by SEC using viscosity detection see ref 11. 

**Figure 6.** \((\langle h^2 \rangle/\langle s^2 \rangle)\) ratio versus degree of polymerization of PDHF polymers. Solid line: SRW. Dashed line: SSAW. Dotted line: KPBBD.

**Figure 7.** Mean square radii of gyration \(\langle s^2 \rangle\) obtained by light scattering versus weight-average molecular weight of PDHF in THF. Line represents linear fitting. The symbols refer to different PDHF samples.
For the PDHF oligomers with DP’s of less than 5, the DFT based “end to end” distances of the terminal aromatic carbon atoms were found to be less than that between the corresponding methyl end groups as illustrated for a 2-mer in Figure 2C. Therefore, we calculated the mean square radii of gyration from every carbon atom of the PDHF oligomers obtained by DFT including the 9,9-alkyl group (Figure 5). These corrections to the mean square radii of gyration were shown to be only needed for the PDHF 1–4 mers.

We also evaluate a DFT based “worm-like” KPBD model by considering the chain as being composed of rigid units, C7’–C7”, of length, \( b = 0.843 \text{ nm} \) followed by the C7’–C7 unit and so on, and an angle of 21.2° between successive units (Figure 3).1,17,18 but no restrictions with regard to torsion angles. The resulting mean square end to end distances and radii of gyration are given by eqs 2a and 2b in which \( a = b(1-\cos 21.2^\circ) \) and \( L \) denote the persistence and contour lengths respectively. The persistence length \( a \) relative to that of the repeat unit \( b \) is an empirical measure of chain flexibility.

\[
\langle h^2 \rangle = 2aL \left[ 1 - \frac{a}{L} (1 - e^{-L/a}) \right]
\]

\[
\langle s^2 \rangle = a^2 \left[ \frac{2a}{L} \left( \frac{L}{a} - 1 + e^{-L/a} \right) - 1 + \frac{L}{3a} \right]
\]

The values of \( \langle s^2 \rangle \) of PDHF obtained from the DFT based SRW and SSAW simulations and that of the corresponding KPBD model are shown in Figure 5. The corresponding values of \( \langle h^2 \rangle \) (Supporting Information, Figure SI-3) and the \( \langle s^2 \rangle \) values of the SSAW and the SRW based simulations are nearly identical below DP values of 100. At higher DP’s the SSAW model shows the expected larger dimensions compared with the SRW model due to intramolecular excluded volume effects. Agreement of these simulations with the KPBD model is seen only at DP’s below about 40.

In contrast to the SRW and SSAW models that incorporate a rigid fluorene unit and a rotationally labile but restricted link to the next unit, the KPBD model does not consider this type of motion and in doing so requires a longer repeat unit that, hence, expands the chains.

The DFT based SRW, SSAW and KPBD models of PDHF generate persistence lengths of 7.8, 9.2 and 12.5 nm respectively (Table 2). The value of 12.5 nm seems much too large compared with the experimental values obtained for this and similar polymers (Table 2) and with that of the other models indicating again a lack of consistency with the DFT based KPBD model. The ratio \( \langle h^2 \rangle/\langle s^2 \rangle \) indicates a measure of conformity with the KPBD model and is calculated as 6 and 12 for “flexible” (L \( \gg a \)) and “rod-like” (L \( \ll a \)) chains, respectively (Figure 6).

A linear plot between MW’s of 40,000 and about 130,000 of \( \langle s^2 \rangle \) vs \( M_w \) of PDHF in THF at 23 °C by means of coupled SEC/light scattering (SEC/LS) was obtained by using eq 2b as reported by others (Figure 7).1,6,10 This linear fit (LS-F) gives a repeat unit length, \( b \), of 0.80 \( \pm \) 0.08 nm and a persistence length of 11 \( \pm \) 1 nm. The value of \( b \) is in good agreement with that determined using coupled SEC/viscosity measurements11 but smaller than the DFT calculated value (0.84 nm) and the nearly identical and more reliable value (0.837 nm) obtained by X-ray analysis of the structurally similar PDOF (Table 2).33,34 Deviations of this type also occur for PDOF and PDEHF (see below).1,10

At the \( \theta \) condition, the intrinsic viscosity, \( [\eta] \), of long and flexible PDHF chains should conform with the Flory equation 3a, where \( \Phi' = (4.2 \times 10^{24}) \) is the Flory parameter.37 Thus, the hydrodynamic volume (\( V_h \)) can be calculated from equation 3b that was extended to low molecular weight chains although the \( \Phi' \) value may need modification for short rigid PDHF oligomers.

\[
[\eta] = q'\langle s^2 \rangle^{1.5}/M \quad (3a)
\]

\[
V_h = 0.40[\eta]M = 0.40q'\langle s^2 \rangle^{1.5} \quad (3b)
\]

The dependence of the \( V_h \) of PDHF on MW for the KPBD, SRW and SSAW models and the SEC experimental values are summarized in Figure 1. For the PDHF oligomers there is satisfactory agreement of the SRW and SSAW models with the experimental results. At the higher MW’s the SRW and SSAW models more closely approximate the experimental \( V_h \) values than the KPBD model.

Because of the nature of the simulations solvation effects are not accounted for. Thus, intramolecular chain aggregation of the relatively rigid mostly “unit” sections of the chain may occur to give small liquid crystalline domains that could account for the above discrepancies (see below). The SRW model shows the best correspondence with the experimental results possibly because the intramolecular excluded volume effects that are neglected in this model are more than offset by intramolecular chain aggregation for which no simulation methods appear to be available. In order to see if the discrepancies in the MC simulated chains and experimental data could be improved we carried out additional calculations (both SSAW and SRW) using smaller torsion angles (20° and 160°). However, this gave larger differences with experimental data. (Supporting Information, Figure SI-4).

**Other PDAF’s.** The experimentally based values for the repeat unit, \( b \), and persistence lengths, \( a \), of poly(9,9’-dioctly-fluorene-2,7-diyl) (PDOF) based on fitting the KPBD (LS-F) model are 0.795 and 8.55 nm respectively.1 As also found for PDHF, the value for \( b \) differs from the more reliable PDOF X-ray data (\( b = 0.837 \text{ nm} \)) and the corresponding DFT values (Table 2). Like the case of PDHF the experimental DFT chain dimensions are smaller than predicted for the KPBD model and the SRW or SSAW simulations (Figure 8) with the KPBD model giving the poorest and the SRW the best approximation. A small increase in persistence length for PDOF compared with PDHF is seen for the SSAW simulations (Table 2). It is interesting to note that all four \( \langle s^2 \rangle \) vs DP plots are linear between DP’s of...
100 and 700 so that a single parameter could account for the solvent effects.

Light scattering studies of poly(9,9-bis-2-ethylhexylfluorene-2,7-diyl) (PDEHF) in toluene at 20 °C fitted using the KPBD model give a value of $b$ as 0.75 nm and a relatively small value of the persistence length of 7.0 nm (Table 2). The value of $b$ is too low compared with the X-ray data and the DFT calculations indicating that the KPBD model is not realistic in this case. Also the value of $V_h$ ($\langle s^2 \rangle$) is smaller than predicted by all DFT based models. This is probably due, at least in part, to toluene being a rather poor solvent for these polymers (see below). Only for poly[9,9-bis((S)-3,7-dimethyloctyl)fluorene-2,7-diyl] (PDMOF) are the LS based values of $b$ and persistence length, $a$, consistent with eq 2a. It is possible that in this case the presence of the very large alkyl groups expands the chains relative to the other PDAF’s. However the corresponding DFT calculations have not been carried out.

SRW and SSAW Models. The above indicates that the KPBD model is most at variance with the experimental data. This appears to be due to the simplification inherent in this model as indicated above. In contrast, the SRW and SSAW models better account for the PDOF and PDHF data. Given the support for torsion angle restrictions from X-ray data and the DFT calculations, a closer examination of the SRW (SSAW) models is of interest.

Figure 9 illustrates four representative PDHF chains with the same $\langle h^2 \rangle$ and $\langle s^2 \rangle$ values as the average value of 25 000 simulated chains. The chains consist of rod-like sections punctuated by loops that are associated with certain sequential torsion angle combinations as illustrated in Figure SI-5 (Supporting Information). The statistical probabilities for the loops are rather low thus explaining the long linear chain sections. These are lacking in the non selective random walk (NSRW) and KPBD models (see below). The long sections are consistent with possible intramolecular interactions that may account for the smaller than predicted chain dimensions.

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Conclusions

The dilute solution conformations of poly(9,9-dihexylfluororene-2,7-diyl) were studied by coupled SEC/light scattering and MALDI–TOF over a 0.30–233K molecular weight range and compared with density functional theory (DFT) based Monte Carlo simulations and with a fitted Kratky–Porod–Benoit–Doty (KPBD) worm-like chain. The “selective self-avoiding walk” (SSAW) and “selective random walk” (SRW) simulation models are restricted with respect to DFT based \( \pm 37.5^\circ \) and \( \pm 143^\circ \) torsion angles between adjacent fluorene units. Compared with the experimental results the KPBD model tends to significantly overestimate experimental chain dimensions obtained by us and others. The more realistic SRW and SSAW models better simulate the experimental data. Furthermore the SRW and SSAW models differ from the analogous non selective random walk (NSRW) and KPBD models in that they predict relatively long chain sections punctuated by rather sharp loops.

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Supporting Information Available: Figure SI-1, peak separation of SEC curves of PDHF oligomers, Figure SI-2, flow chart of Monte Carlo simulation program, Figure SI-3, mean square end-to-end distance \((\langle R^2 \rangle)\) of PDHF by SRW and SSAW Monte Carlo simulation and worm-like chain KPBD model, Figure SI-4, hydrodynamic volumes \( (V_h) \) obtained by SEC as a function of PDHF MW, Figure SI-5, examples of “straight” sections and typical 90° and 180° loops of PDAF chains generated by tetrad and octad torsion angle sequences, Figure SI-6, probabilities of chain direction changes for chain sections, and Figure SI-7, examples of Monte Carlo nonselective random walk (NSRW) PDHF chains having zero or two nonbonded interactions. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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