Electronic Supplementary Information

Donor-Acceptor type conjugated copolymers based on alternating BNBP and oligothiophene units: from electron acceptor to electron donor and from amorphous to semicrystalline

Junhui Miao,[ab] Hongxiang Li,[ab] Tao Wang,[ac] Yanchun Han,*[ab] Jun Liu,*[ab] and Lixiang Wang[ab]

[a]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, 130022, P. R. China

[b]School of Applied Chemistry and Engineering, University of Science and Technology of China, Hefei 230026, P. R. China

[c]University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, P. R. China

Contents

1. Estimating the persistence length (l_p) for the polymers

(1) Estimating the persistence length (l_p) for P-1T

Firstly, the dihedral potential of P-1T was computed via density functional theory (DFT) calculation, the subsequent operation was done on a workstation using Mathematica.

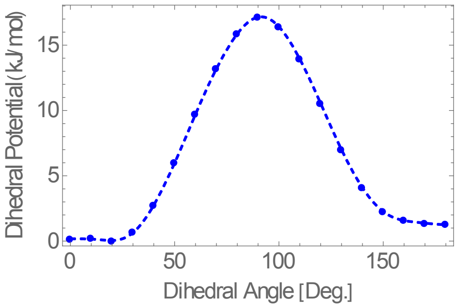
PFTdihedral = {{0, 0.14230}, {10, 0.21529}, {20, 0.0}, {30, 0.68499}, {40, 2.73288}, {50, 5.99375}, {60, 9.71094}, {70, 13.19576}, {80, 15.86590}, {90, 17.14241}, {100, 16.40307}, {110, 13.94718}, {120, 10.53377}, {130, 6.99302}, {140, 4.08974}, {150, 2.25084}, {160, 1.59289}, {170, 1.34872}, {180, 1.28229}};

fitf[x_] = Fit[PFTdihedral, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out = 17.144 - 1.8494 Cos[([Pi] x)/180] - 35.0774 Cos[([Pi] x)/180]^2 + 10.6905 Cos[([Pi] x)/180]^3 + 58.091 Cos[([Pi] x)/180]^4 - 47.3438 Cos[([Pi] x)/180]^5 - 223.878 Cos[([Pi] x)/180]^6 + 120.768 Cos[([Pi] x)/180]^7 + 592.221 Cos[([Pi] x)/180]^8 - 180.757 Cos[([Pi] x)/180]^9 - 862.41 Cos[([Pi] x)/180]^10 + 140.591 Cos[([Pi] x)/180]^11 + 651.263 Cos[([Pi] x)/180]^12 - 42.6464 Cos[([Pi] x)/180]^13 - 196.632 Cos[([Pi] x)/180]^14

Show[ListPlot[{PFTdihedral}, PlotMarkers → Automatic, PlotStyle → {Blue}, PlotRange → All, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {"Dihedral Angle [Deg.]", "Dihedral Potential (kJ/mol)"}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] & /@ {"Dihedral BNBP-fT"})], Plot[{fitf[x]}, {x, 0, 180}, PlotStyle → {{Blue, Thickness[0.004], Dashed}, {Purple, Thickness[0.004], Dashed}}, PlotRange → All, Frame → True, Axes → False, FrameLabel → {"Dihedral Angle [deg.]", "Dihedral Potential (kJ/mol)"}, FrameTicks → {True, True, True, True}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]]

out =



According to the dihedral potential, we compute the dihedral distribution of P-1T p(Φ) using Boltzmann Factors.

kTval = 2.43652

normVal = 2 NIntegrate[Exp[-fitf[x]/kTval], {x, 0, 180}];

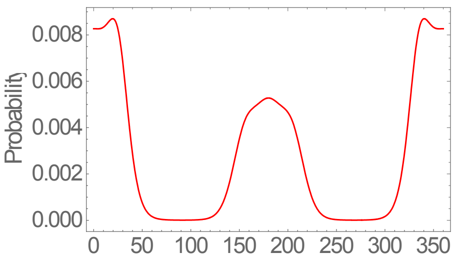
Clear[prob]

prob[x_] := Exp[-fitf[x]/kTval]/normVal /; 0 ≤ x ≤ 180;

prob[x_] := prob[360 - x] /; 180 < x ≤ 360;

Plot[prob[x], {x, 0, 360}, PlotStyle → {Thickness[0.004], Red}, PlotRange → All, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {None, "Probability"}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]

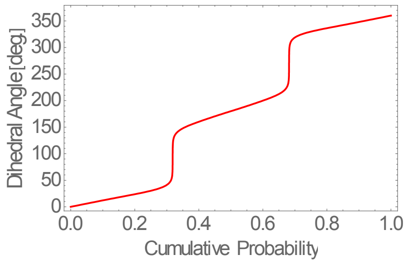
out=



Here we compute the table of cumulative probability for P-1T $p^c(\Phi)$.

pIntTable = Quiet[Table[{NIntegrate[prob[xp], {xp, 0, x}], x}, {x, 0, 360}]]; ListLinePlot[pIntTable, PlotStyle → {PointSize[.004], Red}, Frame → True, Axes → False, FrameLabel → {"Cumulative Probability", "Dihedral Angle [deg.]"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]

out =



Then, we interpolate the table of cumulative probability to construct a function for later calculations.

th[prob_] = Interpolation[pIntTable][prob];

We construct the P-1T chain:

Length of C-C (across the BNBP unit) is 7.03942 Å;

Length of C-C bond (between the BNBP unit and fluoro-thiophene) is 1.45982 Å;

Length of C-S-C (across fluoro-thiophenering) is 2.55872 Å;

Length of C-C bond (between fluoro-thiophene and the BNBP unit) is 1.45965 Å;

Deflection angles (the angle corresponding to the deflection of P-1T backbone bond from Z-axis) are listed below from angle 1 to angle 4.

lbb = 7.03942;

lcc1 = 1.45982;

lcsc1 = 2.55872;

lcc2 = 1.45965;

l = {lbb, lcc1, lcsc1, lcc2};

Angle1 = 2.87882/180 Pi;

Angle2 = -15.10907/180 Pi;

Angle3 = -14.94322/180 Pi;

Angle4 = 2.94505/180 Pi;

Angle = {Angle1, Angle2, Angle3, Angle4};

v[i_] := If[i > 1, RotationMatrix[Angle[[Mod[i - 1, 4, 1]]]].v[i - 1](l[[Mod[i, 4, 1]]])/(l[[Mod[i - 1, 4, 1]]]), l[[1]] {1, 0}]*

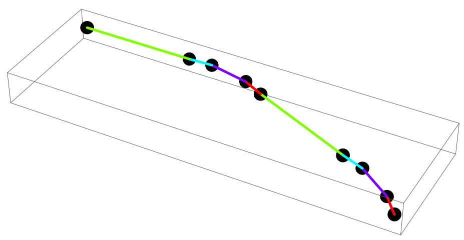
Now we can construct an initial conformation for P-1T.

chain[n_] := Append[#, 0] & /@ Prepend[Accumulate[Table[v[k], {k, 1, n}]], {0, 0}]; drawChain[pts_] := Graphics3D[{PointSize[.03], Point /@ pts, Thick, *Table[{Hue[(1/4) Mod[i, 4]], Line[{pts[[i]], pts[[i + 1]]}]}, {i, 1, Length[pts] - 1}]}];*

A drawing of P-1T dimer is obtained.

drawChain[chain[8]]

out =



We rotate a backbone dihedral angle by certain degree. Only the tangent vectors with even index (corresponding to the inter-moiety bond) will be rotated.

dihedralRotate[pts_, nb_?EvenQ, theta_] := Module[{}, vec = pts[[nb + 1]] - pts[[nb]]; origin = pts[[nb]]; rot = RotationMatrix[theta, vec]; Join[Take[pts, nb], origin + (rot.(# - origin)) & /@ Drop[pts, nb]]]

The function below computing the tangent correlation between the 1st inter-moiety vector in the monomer and the 1st inter-moiety vector in the 1st monomer.

cosVals[pts_] : = Table[(pts[[k]] - pts[[k - 1]]).(pts[[3]] - pts[[2]])/(Norm[pts[[k]] - pts[[k - 1]]] Norm[pts[[3]] - pts[[2]]]), {k, 3, Length[pts], 4}]

randomRotate[pts_] := Module[{}, newpts = pts; Do[If[(k - 4 Floor[k/4]) == 2, newpts = dihedralRotate[newpts, k, th[RandomReal[]] Degree], If[(k - 4 Floor[k/4]) == 0, newpts = dihedralRotate[newpts, k, th[RandomReal[]] Degree]]], {k, 2, Length[pts], 2}]; newpts]

We rotate a P-1T 20mer over 10,000 times to compute tangent-tangent correlation function.

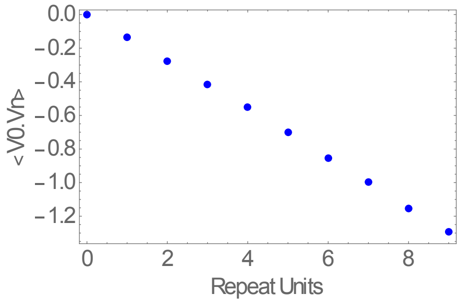
Clear[ch]

ch = chain[40];

cosList2 = ParallelTable[cosVals[randomRotate[ch]], {10000}]; corr2 = Plus @@ cosList2/10000; ListPlot[Table[{i - 1, Log[corr2[[i]]]}, {i, 1, 10}],

PlotStyle→ {Blue, PointSize[0.02]}, Frame → True, FrameLabel → {"Repeat Units", "<V0.Vn>"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, *LabelStyle → Directive[FontFamily → "Helvetica", 16]]*

out =



logFitP-1T[x_] = Fit[Log[corr2[[1 ;; 10]]], {1, x}, x]

out =

0.156401 - 0.144447 x

The number of repeat units (N_p) of P-1T is compute as the following: *-1/logFitP-1T'[x]*

out =

6.92294

(2) Estimating the persistence length (l_p) for P-2T

Type A dihedral is the dihedral angle between fluoro-thiophene and fluoro-thiophene. Type B dihedral is the dihedral angle between fluoro-thiophene and the BNBP unit.

dihedralA = {{180, 0.0}, {170, 0.80839}, {160, 3.06212}, {150, 5.96645}, {140, 9.14304}, {130, 12.41336}, {120, 15.63354}, {110, 18.38454}, {100, 20.43925}, {90, 21.47396}, {80, 21.15969}, {70, 19.32473}, {60, 16.66142}, {50, 13.85083}, {40, 12.48294}, {30, 12.23667}, {20, 13.49454}, {10, 15.80315}, {0, 17.65229}};

dihedralB = {{180, 0.78240}, {170, 0.44030}, {160, 0.0}, {150, 0.18851}, {140, 1.53802}, {130, 4.14068}, {120, 7.74575}, {110, 11.51203}, {100, 14.43789}, {90, 15.78477}, {80, 15.01366}, {70, 12.19098}, {60, 8.54784}, {50, 5.26518}, {40, 2.95185}, {30, 1.66562}, {20, 1.43904}, {10, 2.04973}, {0, 2.64834}};

The dihedral potentials were fitted by the following equations.

fitfA[x_] = Fit[dihedralA, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi *(x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]*

out =

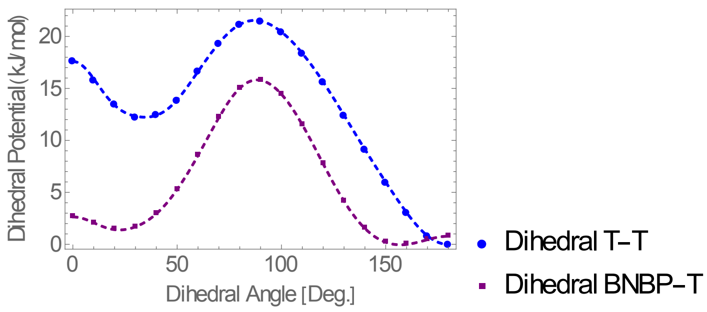
21.4813 + 2.43265 Cos[([Pi] x)/180] - 23.0884 Cos[([Pi] x)/180]^2 - 14.2836 Cos[([Pi] x)/180]^3 + 5.14481 Cos[([Pi] x)/180]^4 + 65.1001 Cos[([Pi] x)/180]^5 + 22.4405 Cos[([Pi] x)/180]^6 - 202.357 Cos[([Pi] x)/180]^7 - 130.314 Cos[([Pi] x)/180]^8 + 405.221 Cos[([Pi] x)/180]^9 + 345.295 Cos[([Pi] x)/180]^10 - 396.137 Cos[([Pi] x)/180]^11 - 384.079 Cos[([Pi] x)/180]^12 + 148.822 Cos[([Pi] x)/180]^13 + 151.912 Cos[([Pi] x)/180]^14

fitfB[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

15.7833 + 2.10384 Cos[([Pi] x)/180] - 35.2977 Cos[([Pi] x)/180]^2 - 17.132 Cos[([Pi] x)/180]^3 + 5.3483 Cos[([Pi] x)/180]^4 + 87.4049 Cos[([Pi] x)/180]^5 + 109.303 Cos[([Pi] x)/180]^6 - 224.811 Cos[([Pi] x)/180]^7 - 317.55 Cos[([Pi] x)/180]^8 + 319.316 Cos[([Pi] x)/180]^9 + 476.497 Cos[([Pi] x)/180]^10 - 239.633 Cos[([Pi] x)/180]^11 - 368.608 Cos[([Pi] x)/180]^12 + 73.68 Cos[([Pi] x)/180]^13 + 116.23 Cos[([Pi] x)/180]^14

Show[ListPlot[{dihedralA, dihedralB}, PlotMarkers → Automatic, PlotStyle → {{Blue}, {Purple}}, PlotRange → All, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {"Dihedral Angle [Deg.]", "Dihedral Potential (kJ/mol)"}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})], Plot[{fitfA[x], fitfB[x]}, {x, 0, 180}, PlotStyle → {{Blue, Thickness[0.004], Dashed}, {Purple, Thickness[0.004], Dashed}}, PlotRange → All, Frame → True, Axes → False, FrameLabel → {"Dihedral Angle [deg.]", "Dihedral Potential (kJ/mol)"}, FrameTicks → {True, True, True, True}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]]



kTval = 2.43652

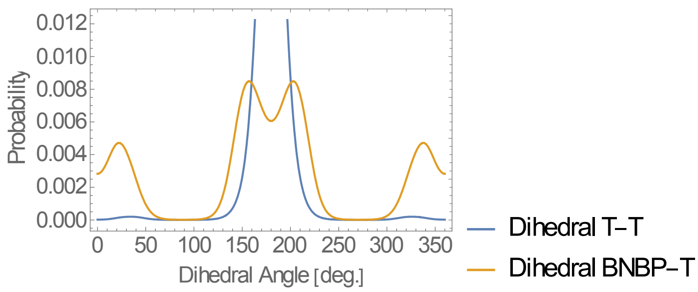
normValA = 2 NIntegrate[Exp[-fitfA[x]/kTval], {x, 0, 180}];

normValB = 2 NIntegrate[Exp[-fitfB[x]/kTval], {x, 0, 180}];

probA[x_] := Exp[-fitfA[x]/kTval]/normValA /; 0 ≤ 180; probA[x_] := probA[360 - x] /; 180 < x ≤ 360; probB[x_] := Exp[-fitfB[x]/kTval]/normValB /; 0 ≤ x ≤ 180; probB[x_] := probB[360 - x] /; 180 < x ≤ 360;

Plot[{probA[x], probB[x]}, {x, 0, 360}, PlotStyle → Automatic, PlotRange → Automatic, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {"Dihedral Angle [deg.]", "Probability"}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})]

out =



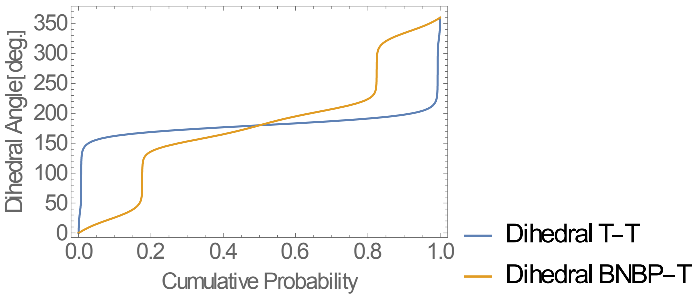
Here we compute the cumulative probability for both A and B types of dihedral angles.

pIntTableA = Quiet[Table[{NIntegrate[probA[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableB = Quiet[Table[{NIntegrate[probB[xp], {xp, 0, x}], x}, {x, 0, 360}]]; ListLinePlot[{pIntTableA, pIntTableB}, PlotStyle → Automatic, Frame → True, Axes → False, FrameLabel → {"Cumulative Probability", "Dihedral Angle [deg.]"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily →

"Helvetica", FontSize → 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})]

out =



thA[prob_] = Interpolation[pIntTableA][prob];

thB[prob_] = Interpolation[pIntTableB][prob];

We construct the P-2T chain:

Length of C-C (across the 1st fluoro-thiophene) is 2.52980 Å;

Length of C-C bond (between the 1st fluoro-thiophene and the 2nd fluoro-thiophene) is 1.43818 Å;

Length of C-C (across the 2nd fluoro-thiophenering) is 2.53079 Å;

Length of C-C bond (between the 2nd fluoro-thiophene and the BNBP unit) is 1.46141 Å;

Length of C-C (across the BNBP unit) is 7.03842 Å;

Length of C-C bond (between the BNBP unit and the 3rd fluoro-thiophene) is 1.46057 Å;

Deflection angles (the angle corresponding to the deflection of P-2T backbone bond from Z-axis) are listed below from angle 1 to angle 6.

lbb = 2.52980;

lcc1 = 1.43818;

lcsc1 = 2.53079;

lcc2 = 1.46141;

lcsc2 = 7.03842;

lcc3 = 1.46057;

l = {lbb, lcc1, lcsc1, lcc2, lcsc2, lcc3};

Angle1 = -13.00995/180 Pi;

Angle2 = 13.01544/180 Pi;

Angle3 = 14.93897/180 Pi;

Angle4 = -2.42596/180 Pi;

Angle5 = 2.74260/180 Pi;

Angle6 = -15.00185/180 Pi;

Angle = {Angle1, Angle2, Angle3, Angle4, Angle5, Angle6};

v[i_] := If[i > 1, RotationMatrix[Angle[[Mod[i - 1, 6, 1]]]].v[i - 1](l[[Mod[i, 6, 1]]])/(l[[Mod[i - 1, 6, 1]]]), l[[1]] {1, 0}]*

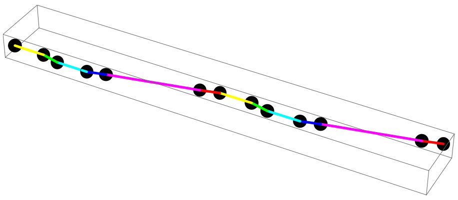
Now we can construct an initial conformation for P-2T.

chain[n_] := Append[#, 0] & /@ Prepend[Accumulate[Table[v[k], {k, 1, n}]], {0, 0}]; drawChain[pts_] := Graphics3D[{PointSize[.03], Point /@ pts, Thick, Table[{Hue[(1/6) Mod[i, 6]], Line[{pts[[i]], pts[[i + 1]]}]}, {i, 1, Length[pts] - 1}]}];

A drawing of P-2T dimer is obtained.

drawChain[chain[12]]

out =



Then, we rotate a backbone dihedral angle by certain degree. Only the tangent vectors with even index (corresponding to the inter-moiety bond) will be rotated.

dihedralRotate[pts_, nb_?EvenQ, theta_] := Module[{}, vec = pts[[nb + 1]] - pts[[nb]]; origin = pts[[nb]]; rot = RotationMatrix[theta, vec]; Join[Take[pts, nb], origin + (rot.(# - origin)) & /@ Drop[pts, nb]]]

The function below computing the tangent correlation between the 1st inter-moiety vector in the monomer and the 1st inter-moiety vector in the 1st monomer.

cosVals[pts_] := Table[(pts[[k]] - pts[[k - 1]]).(pts[[3]] - pts[[2]])/(Norm[pts[[k]] - pts[[k - 1]]] Norm[pts[[3]] - pts[[2]]]), {k, 3, Length[pts], 6}]randomRotate[pts_] := Module[{}, newpts = pts;

Do[If[(k - 6 Floor[k/6]) == 2, newpts = dihedralRotate[newpts, k, *thA[RandomReal[]] Degree], If[(k - 6 Floor[k/6]) == 4, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree], If[(k - 6 Floor[k/6]) == 0, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree]]]], {k, 2, Length[pts], 2}]; newpts]*

We rotate a P-2T 10mer over 10,000 times to compute tangent-tangent correlation function.

Clear[ch]

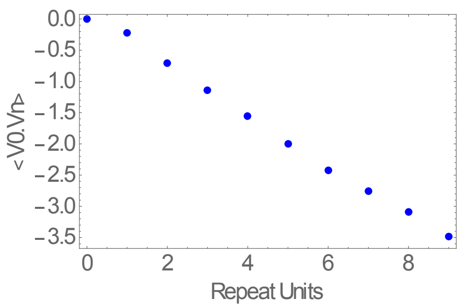
ch = chain[60];

cosList2 = ParallelTable[cosVals[randomRotate[ch]], {10000}];

corr2 = Plus @@ cosList2/10000;

ListPlot[Table[{i - 1, Log[corr2[[i]]]}, {i, 1, 10}], PlotStyle → {Blue, PointSize[0.02]}, Frame → True, FrameLabel → {"Repeat Units", "<V0.Vn>"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]

out =



logFitP-2T[x_] = Fit[Log[corr2[[1 ;; 10]]], {1, x}, x]

out =

0.463386 - 0.400209 x

The number of repeat units (N_p) of P-2T is compute as the following: *-1/logFitP-2T'[x]*

out =

2.4987

(3) Estimating the persistence length (l_p) for P-3T

Type A dihedral is the dihedral angle between fluoro-thiophene and thiophene.

Type B dihedral is the dihedral angle between fluoro-thiophene and the BNBP unit.

dihedralA = {{180, 0.0}, {170, 0.53560}, {160, 1.68583}, {150, 3.41840}, {140, 5.88716}, {130, 8.93825}, {120, 11.95784}, {110, 14.99581}, {100, 17.48215}, {90, 18.27427}, {80, 17.59164}, {70, 15.52668}, {60, 12.60109}, {50, 9.41846}, {40, 6.60917}, {30, 4.49276}, {20, 3.11069}, {10, 2.60528}, {0, 2.73026}};

dihedralB = {{180, 0.86248}, {170, 0.54505}, {160, 0.0}, {150, 0.27358}, {140, 1.80398}, {130, 4.57467}, {120, 8.15612}, {110, 11.79768}, {100, 15.09059}, {90, 16.55693}, {80, 15.57027}, {70, 12.94739}, {60, 9.61616}, {50, 6.27127}, {40, 3.74370}, {30, 2.36295}, {20, 2.29968}, {10, 3.13774}, {0, 3.80409}};

The dihedral potentials were fitted by the following equations.

fitfA[x_] = Fit[dihedralA, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

18.2894 + 0.0185695 Cos[([Pi] x)/180] - 24.644 Cos[([Pi] x)/180]^2 + 12.3216 Cos[([Pi] x)/180]^3 - 34.4943 Cos[([Pi] x)/180]^4 - 63.2679 Cos[([Pi] x)/180]^5 + 296.315 Cos[([Pi] x)/180]^6 + 108.741 Cos[([Pi] x)/180]^7 - 852.548 Cos[([Pi] x)/180]^8 - 35.094 Cos[([Pi] x)/180]^9 + 1222.8 Cos[([Pi] x)/180]^10 - 67.4607 Cos[([Pi] x)/180]^11 - 866.185 Cos[([Pi] x)/180]^12 + 46.0912 Cos[([Pi] x)/180]^13 + 241.833 Cos[([Pi] x)/180]^14

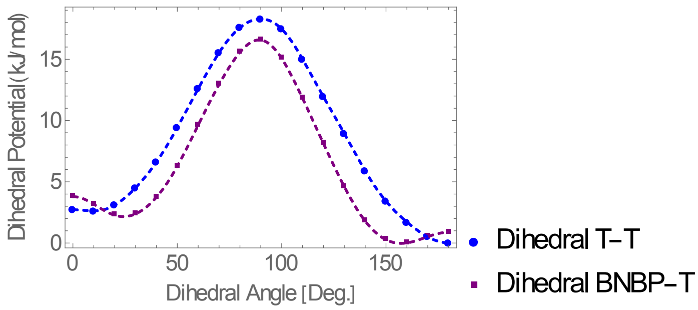
fitfB[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

16.5674 + 1.22343 Cos[([Pi] x)/180] - 44.0116 Cos[([Pi] x)/180]^2 + 8.41646 Cos[([Pi] x)/180]^3 + 95.2529 Cos[([Pi] x)/180]^4 - 56.6009 Cos[([Pi] x)/180]^5 - 261.765 Cos[([Pi] x)/180]^6 + 149.081 Cos[([Pi] x)/180]^7 + 473.503 Cos[([Pi] x)/180]^8 - 186.502 Cos[([Pi] x)/180]^9 - 463.847 Cos[([Pi] x)/180]^10 + 107.194

Cos[([Pi] x)/180]^11 + 223.863 Cos[([Pi] x)/180]^12 - 21.3573 Cos[([Pi] x)/180]^13 - 37.2334 Cos[([Pi] x)/180]^14

Show[ListPlot[{dihedralA, dihedralB}, PlotMarkers -> Automatic, PlotStyle -> {{Blue}, {Purple}}, PlotRange -> All, Frame -> True, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, FrameLabel -> {"Dihedral Angle [Deg.]", "Dihedral Potential (kJ/mol)"}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})], Plot[{fitfA[x], fitfB[x]}, {x, 0, 180}, PlotStyle -> {{Blue, Thickness[0.004], Dashed}, {Purple, Thickness[0.004], Dashed}}, PlotRange -> All, Frame -> True, Axes -> False, FrameLabel -> {"Dihedral Angle [deg.]", "Dihedral Potential (kJ/mol)"}, FrameTicks -> {True, True, True, True}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16]]]



kTval = 2.43652

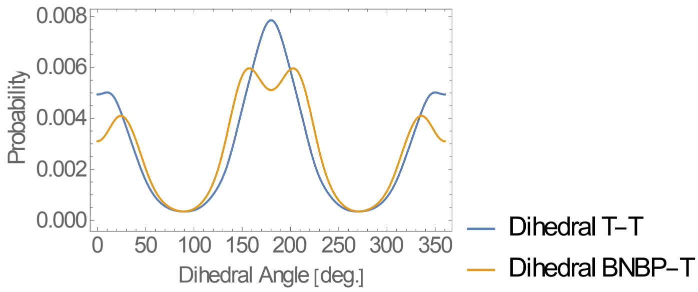
normValA = 2 NIntegrate[Exp[-fitfA[x]/kTval], {x, 0, 180}];

normValB = 2 NIntegrate[Exp[-fitfB[x]/kTval], {x, 0, 180}];

probA[x_] := Exp[-fitfA[x]/kTval]/normValA /; 0 ≤ x ≤ 180; probA[x_] := probA[360 - x] /; 180 < x ≤ 360; probB[x_] := Exp[-fitfB[x]/kTval]/normValB /; 0 ≤ x ≤ 180; probB[x_] := probB[360 - x] /; 180 < x ≤ 360;

Plot[{probA[x], probB[x]}, {x, 0, 360}, PlotStyle -> Automatic, PlotRange -> Automatic, Frame -> True, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, FrameLabel -> {"Dihedral Angle [deg.]", "Probability"}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})]

out =



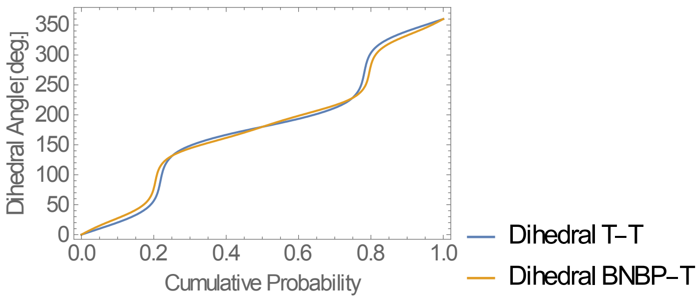
Here we compute the cumulative probability for both A and B types of dihedral angles.

pIntTableA = Quiet[Table[{NIntegrate[probA[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableB = Quiet[Table[{NIntegrate[probB[xp], {xp, 0, x}], x}, {x, 0, 360}]];

ListLinePlot[{pIntTableA, pIntTableB}, PlotStyle → Automatic, Frame → True, Axes → False, FrameLabel → {"Cumulative Probability", "Dihedral Angle [deg.]"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] & /@ {"Dihedral T-T", "Dihedral BNBP-T"})]

out =



thA[prob_] = Interpolation[pIntTableA][prob];

thB[prob_] = Interpolation[pIntTableB][prob];

We construct the P-3T chain:

Length of C-C (across the BNBP unit) is 7.04271 Å;

Length of C-C bond (between the BNBP unit and the) is 1.46076 Å;

Length of C-C (across the 1st fluoro-thiophene) is 2.52059 Å;

Length of C-C bond (between the 1st fluoro-thiophene and the thiophene) is 1.43939 Å;

Length of C-C (across the thiophene) is 2.55595 Å;

Length of C-C bond (between the thiophene and the 2nd fluoro-thiophene) is

1.43982 Å;

Length of C-C (across the 2nd fluoro-thiophene) is 2.51898 Å;

Length of C-C bond (between the 2nd fluoro-thiophene and the 2nd BNBP unit) is 1.46163 Å;

Deflection angles (the angle corresponding to the deflection of P-3T backbone bond from Z-axis) are listed below from angle 1 to angle 8.

lbb = 7.04271;

lcc1 = 1.46076;

lcsc1 = 2.52059;

lcc2 = 1.43939;

lcsc2 = 2.55595;

lcc3 = 1.43982;

lcsc3 = 2.51898

lcc4 = 1.46163

l = {lbb, lcc1, lcsc1, lcc2, lcsc2, lcc3, lcsc3, lcc4};

Angle1 = 3.57929/180 Pi;

Angle2 = -14.72266/180 Pi;

Angle3 = -14.45890/180 Pi;

Angle4 = 14.65067/180 Pi;

Angle5 = 14.63730/180 Pi;

Angle6 = -14.40836/180 Pi;

Angle7 = -14.38586/180 Pi;

Angle8 = -2.90725/180 Pi;

Angle = {Angle1, Angle2, Angle3, Angle4, Angle5, Angle6, Angle7, Angle8};

v[i_] := If[i > 1, RotationMatrix[Angle[[Mod[i - 1, 8, 1]]]].v[i - 1](l[[Mod[i, 8, 1]]])/(l[[Mod[i - 1, 8, 1]]]), l[[1]] {1, 0}]*

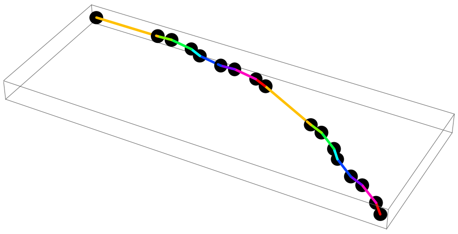
We can construct an initial conformation for P-3T.

chain[n_] := Append[#, 0] & /@ Prepend[Accumulate[Table[v[k], {k, 1, n}]], {0, 0}]; drawChain[pts_] := Graphics3D[{PointSize[.03], Point /@ pts, Thick, Table[{Hue[(1/8) Mod[i, 8]], Line[{pts[[i]], pts[[i + 1]]}]}, {i, 1, Length[pts] - 1}]}];

A drawing of P-3T dimer is obtained.

drawChain[chain[16]]

out =



Then, we rotate a backbone dihedral angle by certain degree. Only the tangent vectors with even index (corresponding to the inter-moiety bond) will be rotated.

dihedralRotate[pts_, nb_?EvenQ, theta_] := Module[{}, vec = pts[[nb + 1]] - pts[[nb]]; origin = pts[[nb]]; rot = RotationMatrix[theta, vec]; Join[Take[pts, nb], origin + (rot.(# - origin)) & /@ Drop[pts, nb]]]

The function below computing the tangent correlation between the 1st inter-moiety vector in the monomer and the 1st inter-moiety vector in the 1st monomer.

cosVals[pts_] := Table[(pts[[k]] - pts[[k - 1]]).(pts[[3]] - pts[[2]])/(Norm[pts[[k]] - pts[[k - 1]]] Norm[pts[[3]] - pts[[2]]]), {k, 3, Length[pts], 8}]randomRotate[pts_] := Module[{}, newpts = pts;

Do[If[(k - 8 Floor[k/8]) == 2, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree], If[(k - 8 Floor[k/8]) == 4, newpts = dihedralRotate[newpts, k, thA[RandomReal[]] Degree], If[(k - 8 Floor[k/8]) == 6, newpts = dihedralRotate[newpts, k, thA[RandomReal[]] Degree], If[(k - 8 Floor[k/8]) == 0, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree]]]]], {k, 2, Length[pts], 2}]; newpts]

We rotate a P-3T 10mer over 10,000 times to compute tangent-tangent correlation function.

Clear[ch]

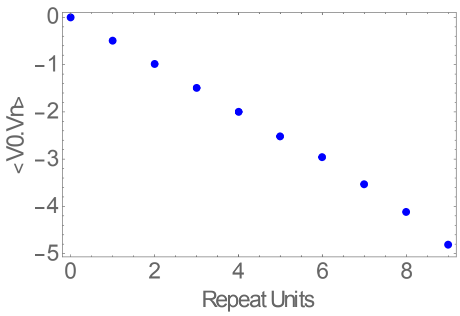
ch = chain[80];

cosList2 = ParallelTable[cosVals[randomRotate[ch]], {10000}];

corr2 = Plus @@ cosList2/10000;

ListPlot[Table[{i - 1, Log[corr2[[i]]]}, {i, 1, 10}], PlotStyle → {Blue, *PointSize[0.02]}, Frame → True, FrameLabel → {"Repeat Units", "<V0.Vn>"}, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]*

out =



logFitP-3T[x_] = Fit[Log[corr2[[1 ;; 10]]], {1, x}, x]

out =

0.585085 - 0.522835 x

The number of repeat units (N_p) of P-3T is compute as the following: *-1/logFitP-3T'[x]*

out =

1.91265

(4) Estimating the persistence length (l_p) for P-4T

Type A dihedral is the dihedral angle between fluoro-thiophene and fluoro-thiophene. Type B dihedral is the dihedral angle between thiophene and the BNBP unit. Type C dihedral is the dihedral angle between fluoro-thiophene and thiophene.

dihedralA = {{180, 0.0}, {170, 0.63905}, {160, 2.69508}, {150, 5.75903}, {140, 9.30871}, {130, 12.49029}, {120, 15.51592}, {110, 18.34516}, {100, 20.8974}, {90, 21.98252}, {80, 21.506}, {70, 19.69046}, {60, 17.23142}, {50, 14.50904}, {40, 12.71818}, {30, 12.5617}, {20, 13.94692}, {10, 15.89478}, {0, 17.11248}};

dihedralB = {{180, 0.92916}, {170, 0.44423}, {160, 0.0}, {150, 0.37203}, {140, 1.93998}, {130, 4.78366}, {120, 9.05903}, {110, 13.1296}, {100, 16.2059}, {90, 17.44724}, {80, 16.32457}, {70, 13.20154}, {60, 9.35229}, {50, 5.81601}, {40, 3.16714}, {30, 1.7709}, {20, 1.53172}, {10, 2.19807}, {0, 2.75861}};

dihedralC = {{180, 0.33528}, {170, 0.01339}, {160, 0.0}, {150, 0.53193}, {140, *1.76617}, {130, 3.53629}, {120, 5.47207}, {110, 7.49607}, {100, 9.04669}, {90, 9.63191}, {80, 8.95558}, {70, 7.26108}, {60, 4.94539}, {50, 2.73918}, {40, 1.27416}, {30, 0.74223}, {20, 1.44192}, {10, 2.29705}, {0, 2.81112}};*

The dihedral potentials were fitted by the following equations.

fitfA[x_] = Fit[dihedralA, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

22.0073 + 1.71111 Cos[([Pi] x)/180] - 28.3251 Cos[([Pi] x)/180]^2 + 3.34896 Cos[([Pi] x)/180]^3 + 25.3447 Cos[([Pi] x)/180]^4 - 9.36824 Cos[([Pi] x)/180]^5 + 22.1851 Cos[([Pi] x)/180]^6 - 53.9623 Cos[([Pi] x)/180]^7 - 223.63 Cos[([Pi] x)/180]^8 + 213.483 Cos[([Pi] x)/180]^9 + 467.426 Cos[([Pi] x)/180]^10 - 230.91 Cos[([Pi] x)/180]^11 - 414.619 Cos[([Pi] x)/180]^12 + 84.2418 Cos[([Pi] x)/180]^13 + 138.15 Cos[([Pi] x)/180]^14

fitfB[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

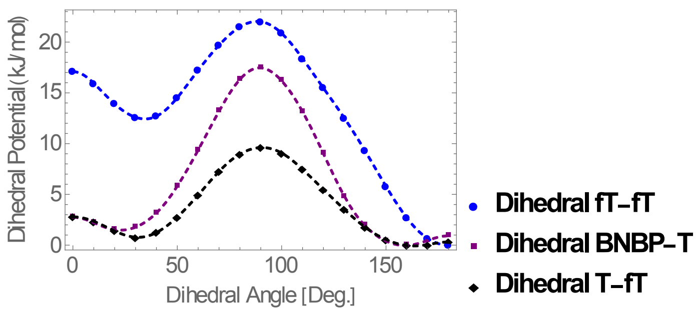
17.4574 + 0.769079 Cos[([Pi] x)/180] - 41.3535 Cos[([Pi] x)/180]^2 - 14.6934 Cos[([Pi] x)/180]^3 + 52.261 Cos[([Pi] x)/180]^4 + 97.9877 Cos[([Pi] x)/180]^5 - 123.982 Cos[([Pi] x)/180]^6 - 250.559 Cos[([Pi] x)/180]^7 + 237.526 Cos[([Pi] x)/180]^8 + 310.513 Cos[([Pi] x)/180]^9 - 197.836 Cos[([Pi] x)/180]^10 - 187.988 Cos[([Pi] x)/180]^11 + 36.7978 Cos[([Pi] x)/180]^12 + 44.886 Cos[([Pi] x)/180]^13 + 20.9635 Cos[([Pi] x)/180]^14

fitfC[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

9.60992 - 0.425669 Cos[([Pi] x)/180] - 19.3169 Cos[([Pi] x)/180]^2 + 5.70692 Cos[([Pi] x)/180]^3 - 11.2036 Cos[([Pi] x)/180]^4 - 61.1007 Cos[([Pi] x)/180]^5 + 147.514 Cos[([Pi] x)/180]^6 + 218.86 Cos[([Pi] x)/180]^7 - 431.386 Cos[([Pi] x)/180]^8 - 366.086 Cos[([Pi] x)/180]^9 + 630.147 Cos[([Pi] x)/180]^10 + 299.857 Cos[([Pi] x)/180]^11 - 454.061 Cos[([Pi] x)/180]^12 - 95.5734 Cos[([Pi] x)/180]^13 + 130.244 Cos[([Pi] x)/180]^14

Show[ListPlot[{dihedralA, dihedralB, dihedralC}, PlotMarkers -> Automatic, PlotStyle -> {{Blue}, {Purple}, {Black}}, PlotRange -> All, Frame -> True, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, FrameLabel -> {"Dihedral Angle [Deg.]", "Dihedral Potential (kJ/mol)"}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] &/{"Dihedral fT-fT", "Dihedral BNBP-T" , "Dihedral T-fT"})], Plot[{fitfA[x], fitfB[x], fitfC[x]}, {x, 0, 180}, PlotStyle -> {{Blue, Thickness[0.004], Dashed}, {Purple, Thickness[0.004], Dashed}, {Black, Thickness[0.004], Dashed}}, PlotRange -> All, Frame -> True, Axes -> False, FrameLabel -> {"Dihedral Angle [deg.]", "Dihedral Potential (kJ/mol)"}, FrameTicks -> {True, True, True, True}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16]]]



kTval = 2.43652

normValA = 2 NIntegrate[Exp[-fitfA[x]/kTval], {x, 0, 180}];

normValB = 2 NIntegrate[Exp[-fitfB[x]/kTval], {x, 0, 180}];

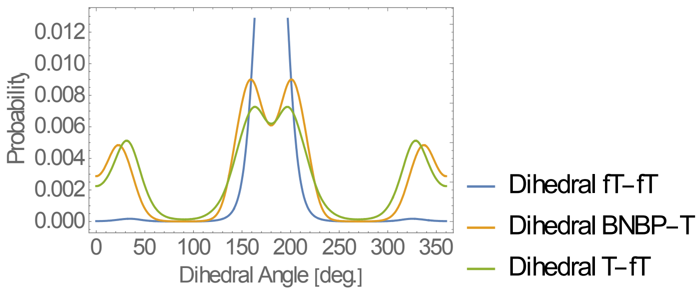
normValC = 2 NIntegrate[Exp[-fitfC[x]/kTval], {x, 0, 180}];

probA[x_] := Exp[-fitfA[x]/kTval]/normValA /; 0 ≤ x \[LessSlantEqual] 180;

probA[x_] := probA[360 - x] /; 180 < x ≤ 360; probB[x_] := Exp[-fitfB[x]/kTval]/normValB /; 0 ≤ x ≤ 180; probB[x_] := probB[360 - x] /; 180 < x ≤ 360; probC[x_] := Exp[-fitfC[x]/kTval]/normValC /; 0 ≤ x ≤ 180; probC[x_] := probC[360 - x] /; 180 < x ≤ 360;

Plot[{probA[x], probB[x], probC[x]}, {x, 0, 360}, PlotStyle → Automatic, PlotRange → Automatic, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {"Dihedral Angle [deg.]", "Probability"}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] & /@ {"Dihedral fT-fT", "Dihedral BNBP-T", "Dihedral T-fT"})]

out =



Here we compute the cumulative probability for A, B and C types of dihedral angles.

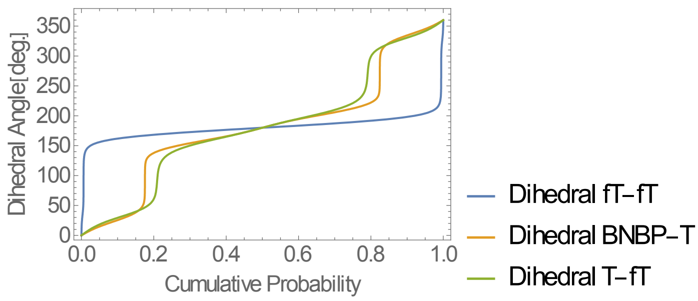
pIntTableA = Quiet[Table[{NIntegrate[probA[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableB = Quiet[Table[{NIntegrate[probB[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableC = Quiet[Table[{NIntegrate[probC[xp], {xp, 0, x}], x}, {x, 0, 360}]];

ListLinePlot[{pIntTableA, pIntTableB, pIntTableC}, PlotStyle -> Automatic, Frame -> True, Axes -> False, FrameLabel -> {"Cumulative Probability", "Dihedral Angle [deg.]"}, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] & /@ {"Dihedral fT-fT", "Dihedral BNBP-T", "Dihedral T-fT"})]

out =



thA[prob_] = Interpolation[pIntTableA][prob];

thB[prob_] = Interpolation[pIntTableB][prob];

thC[prob_] = Interpolation[pIntTableC][prob];

We construct the P-4T chain:

Length of C-C (across the 1st thiophene) is 2.52516 Å;

Length of C-C bond (between the 1st thiophene and the 1st fluoro-thiophene) is 1.44576 Å;

Length of C-C (across the 1st fluoro-thiophenering) is 2.54194 Å;

Length of C-C bond (between the 1st fluoro-thiophene and the 2nd fluoro-thiophene) is 1.43589 Å;

Length of C-C (across the 2nd fluoro-thiophene) is 2.54363 Å;

Length of C-C bond (between the 2nd fluoro-thiophene and the 2nd thiophene) is 1.44457 Å;

Length of C-C (across the 2nd thiophene) is 2.52686 Å;

Length of C-C bond (between the 2nd thiophene and the BNBP unit) is 1.45992 Å;

Length of C-C (across the BNBP unit) is 7.04278 Å;

Length of C-C bond (between the BNBP unit and the 3rd thiophene) is 1.45939 Å;

Deflection angles (the angle corresponding to the deflection of P-4T backbone bond from Z-axis) are listed below from angle 1 to angle 10.

lbb = 2.52516;

lcc1 = 1.44576;

lcsc1 = 2.54194;

lcc2 = 1.43589;

```
lcsc2 = 2.54363;
lcc3 = 1.44457;
lcsc3 = 2.52686;
lcc4 = 1.45992;
lcsc4 = 7.04278;
lcc5 = 1.45939;
l = {lbb, lcc1, lcsc1, lcc2, lcsc2, lcc3, lcsc3, lcc4, lcsc4, lcc5};
Angle1 = -17.96605/180 Pi;
Angle2 = 14.26171/180 Pi;
Angle3 = 13.21406/180 Pi;
Angle4 = -13.05738/180 Pi;
Angle5 = -13.83939/180 Pi;
Angle6 = 18.04276/180 Pi;
Angle7 = 14.3615/180 Pi;
Angle8 = -3.62208/180 Pi;
Angle9 = 3.76038/180 Pi;
Angle10 = -14.26547/180 Pi;
Angle = {Angle1, Angle2, Angle3, Angle4, Angle5, Angle6, Angle7, Angle8, Angle9, Angle10};
v[i_] := If[i > 1, RotationMatrix[Angle[[Mod[i - 1, 10, 1]]]].v[i - 1]*(l[[Mod[i, 10, 1]]])/(l[[Mod[i - 1, 10, 1]]]), l[[1]] {1, 0}]
```

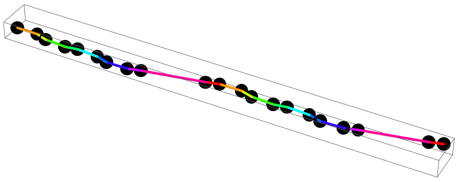
Now we can construct an initial conformation for P-4T.

```
chain[n_] := Append[#, 0] & /@ Prepend[Accumulate[Table[v[k], {k, 1, n}]], {0, 0}]; drawChain[pts_] := Graphics3D[{PointSize[.03], Point /@ pts, Thick, Table[{Hue[(1/10) Mod[i, 10]], Line[{pts[[i]], pts[[i + 1]]}]}, {i, 1, Length[pts] - 1}]}];
```

A drawing of P-4T dimer is obtained.

```
drawChain[chain[20]]
```

out =



Then, we rotate a backbone dihedral angle by certain degree. Only the tangent vectors with even index (corresponding to the inter-moiety bond) will be rotated.

dihedralRotate[pts_, nb_?EvenQ, theta_] := Module[{}, vec = pts[[nb + 1]] - pts[[nb]]; origin = pts[[nb]]; rot = RotationMatrix[theta, vec]; Join[Take[pts, nb], origin + (rot.(# - origin)) & /@ Drop[pts, nb]]]

The function below computing the tangent correlation between the 1^{st} inter-moiety vector in the monomer and the 1^{st} inter-moiety vector in the 1^{st} monomer.

cosVals[pts_] := Table[(pts[[k]] - pts[[k - 1]]).(pts[[3]] - pts[[2]])/(Norm[pts[[k]] - pts[[k - 1]]] Norm[pts[[3]] - pts[[2]]]), {k, 3, Length[pts], 10}] randomRotate[pts_] := Module[{}, newpts = pts;

Do[If[(k - 10 Floor[k/10]) == 2, newpts = dihedralRotate[newpts, k, thC[RandomReal[]] Degree], If[(k - 10 Floor[k/10]) == 4, newpts = dihedralRotate[newpts, k, thA[RandomReal[]] Degree], If[(k - 10 Floor[k/10]) == 6, newpts = dihedralRotate[newpts, k, thC[RandomReal[]] Degree], If[(k - 10 Floor[k/10]) == 8, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree], If[(k - 10 Floor[k/10]) == 0, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree]]]]]], {k, 2, Length[pts], 2}]; newpts]

We rotate a P-4T 10mer over 10,000 times to compute tangent-tangent correlation function.

Clear[ch]

ch = chain[100];

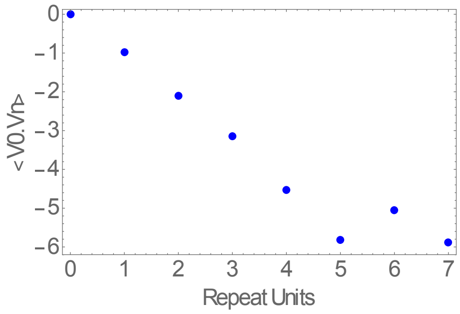
cosList2 = ParallelTable[cosVals[randomRotate[ch]], {10000}];

corr2 = Plus @@ cosList2/10000;

ListPlot[Table[{i - 1, Log[corr2[[i]]]}, {i, 1, 8}], PlotStyle -> {Blue, PointSize[0.02]}, Frame -> True, FrameLabel -> {"Repeat Units", "<V0.Vn>"}, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, LabelStyle ->

Directive[FontFamily -> "Helvetica", 16]]

out =



logFitP-4T[x_] = Fit[Log[corr2[[1 ;; 8]]], {1, x}, x]

out =

0.530046 - 0.88161 x

The number of repeat units (N_p) of P-4T is compute as the following: *-1/logFitP-4T'[x]*

out =

1.13429

(5) Estimating the persistence length (l_p) for P-5T

Type A dihedral is the dihedral angle between thiophene and the BNBP unit. Type B dihedral is the dihedral angle between thiophene and thiophene. Type C dihedral is the dihedral angle between thiophene and fluoro-thiophene.

dihedralA = {{180, 0.94387}, {170, 0.50751}, {160, 0.0}, {150, 1.21114}, {140, 2.68904}, {130, 5.35156}, {120, 8.91226}, {110, 12.66121}, {100, 15.53403}, {90, 16.77721}, {80, 15.80262}, {70, 13.16531}, {60, 9.54921}, {50, 6.04548}, {40, 3.29316}, {30, 1.862}, {20, 1.68977}, {10, 2.74181}, {0, 2.94135}};

dihedralB = {{180, 0.08349}, {170, 0.06774}, {160, 0.0}, {150, 0.64193}, {140, 1.84704}, {130, 3.32887}, {120, 5.34237}, {110, 7.47375}, {100, 9.3263}, {90, 9.83013}, {80, 9.06874}, {70, 7.48399}, {60, 5.1003}, {50, 3.02746}, {40, 1.78271}, {30, 1.51203}, {20, 2.06417}, {10, 3.06028}, {0, 3.37981}};

dihedralC = {{180, 0.0}, {170, 0.30692}, {160, 1.35817}, {150, 3.16924}, {140, 5.67318}, {130, 8.67308}, {120, 11.93053}, {110, 15.06354}, {100, 17.4853}, {90, 18.39031}, {80, 17.66725}, {70, 15.57998}, {60, 12.66016}, {50, 9.44812}, {40, *6.50861}, {30, 4.20133}, {20, 2.86836}, {10, 2.39839}, {0, 2.32488}};*

The dihedral potentials were fitted by the following equations.

fitfA[x_] = Fit[dihedralA, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

16.7798 + 0.555475 Cos[(\[Pi] x)/180] - 38.8102 Cos[(\[Pi] x)/180]^2 + 7.94713 Cos[(\[Pi] x)/180]^3 + 73.7003 Cos[(\[Pi] x)/180]^4 - 83.6977 Cos[(\[Pi] x)/180]^5 - 292.406 Cos[(\[Pi] x)/180]^6 + 344.241 Cos[(\[Pi] x)/180]^7 + 763.514 Cos[(\[Pi] x)/180]^8 - 676.608 Cos[(\[Pi] x)/180]^9 - 1013.31 Cos[(\[Pi] x)/180]^10 + 625.07 Cos[(\[Pi] x)/180]^11 + 647.789 Cos[(\[Pi] x)/180]^12 - 216.503 Cos[(\[Pi] x)/180]^13 - 155.257 Cos[(\[Pi] x)/180]^14

fitfB[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

9.84288 - 1.14705 Cos[(\[Pi] x)/180] - 22.6943 Cos[(\[Pi] x)/180]^2 + 20.1382 Cos[(\[Pi] x)/180]^3 + 34.8859 Cos[(\[Pi] x)/180]^4 - 130.145 Cos[(\[Pi] x)/180]^5 - 167.26 Cos[(\[Pi] x)/180]^6 + 371.937 Cos[(\[Pi] x)/180]^7 + 573.688 Cos[(\[Pi] x)/180]^8 - 534.667 Cos[(\[Pi] x)/180]^9 - 946.456 Cos[(\[Pi] x)/180]^10 + 387.031 Cos[(\[Pi] x)/180]^11 + 738.875 Cos[(\[Pi] x)/180]^12 - 111.506 Cos[(\[Pi] x)/180]^13 - 219.133 Cos[(\[Pi] x)/180]^14

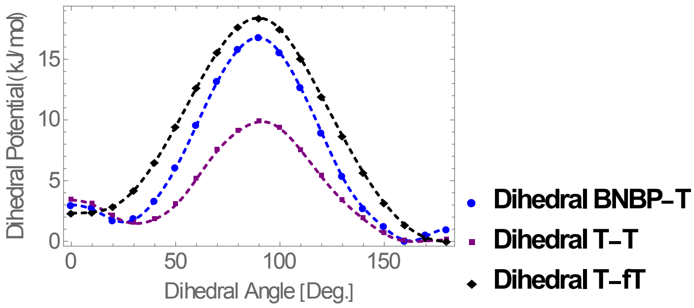
fitfC[x_] = Fit[dihedralB, {1, Cos[Pi (x)/180], Cos[Pi (x)/180]^2, Cos[Pi (x)/180]^3, Cos[Pi (x)/180]^4, Cos[Pi (x)/180]^5, Cos[Pi (x)/180]^6, Cos[Pi (x)/180]^7, Cos[Pi (x)/180]^8, Cos[Pi (x)/180]^9, Cos[Pi (x)/180]^10, Cos[Pi (x)/180]^11, Cos[Pi (x)/180]^12, Cos[Pi (x)/180]^13, Cos[Pi (x)/180]^14}, (x)]

out =

18.3981 + 0.331787 Cos[(\[Pi] x)/180] - 27.9415 Cos[(\[Pi] x)/180]^2 +

7.50761 Cos[(\[Pi] x)/180]^3 + 14.3842 Cos[(\[Pi] x)/180]^4 - 45.0382 Cos[(\[Pi] x)/180]^5 + 5.49387 Cos[(\[Pi] x)/180]^6 + 120.939 Cos[(\[Pi] x)/180]^7 - 40.5556 Cos[(\[Pi] x)/180]^8 - 170.885 Cos[(\[Pi] x)/180]^9 + 60.7542 Cos[(\[Pi] x)/180]^10 + 122.998 Cos[(\[Pi] x)/180]^11 - 41.0609 Cos[(\[Pi] x)/180]^12 - 34.6891 Cos[(\[Pi] x)/180]^13 + 11.6892 Cos[(\[Pi] x)/180]^14

Show[ListPlot[{dihedralA, dihedralB, dihedralC}, PlotMarkers → Automatic, PlotStyle → {{Blue}, {Purple}, {Black}}, PlotRange → All, Frame → True, FrameTicks → {Automatic, Automatic, Automatic, Automatic}, FrameLabel → {"Dihedral Angle [Deg.]", "Dihedral Potential (kJ/mol)"}, LabelStyle → Directive[FontFamily → "Helvetica", 16], PlotLegends → (Style[#, FontFamily → "Helvetica", FontSize → 16] &/{"Dihedral BNBP-T", "Dihedral T-T" , "Dihedral T-fT"})], Plot[{fitfA[x], fitfB[x], fitfC[x]}, {x, 0, 180}, PlotStyle → {{Blue, Thickness[0.004], Dashed}, {Purple, Thickness[0.004], Dashed}, {Black, Thickness[0.004], Dashed}}, PlotRange → All, Frame → True, Axes → False, FrameLabel → {"Dihedral Angle [deg.]", "Dihedral Potential (kJ/mol)"}, FrameTicks → {True, True, True, True}, LabelStyle → Directive[FontFamily → "Helvetica", 16]]]



kTval = 2.43652

normValA = 2 NIntegrate[Exp[-fitfA[x]/kTval], {x, 0, 180}];

normValB = 2 NIntegrate[Exp[-fitfB[x]/kTval], {x, 0, 180}];

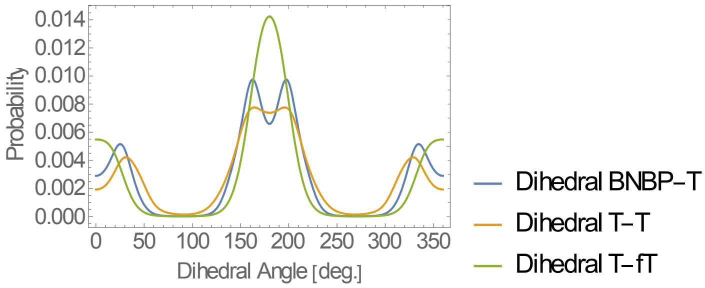
normValC = 2 NIntegrate[Exp[-fitfC[x]/kTval], {x, 0, 180}];

probA[x_] := Exp[-fitfA[x]/kTval]/normValA /; 0 ≤ x \[LessSlantEqual] 180; probA[x_] := probA[360 - x] /; 180 < x ≤ 360; probB[x_] := Exp[-fitfB[x]/kTval]/normValB /; 0 ≤ x ≤ 180; probB[x_] := probB[360 - x] /; 180 < x ≤

360; probC[x_] := Exp[-fitfC[x]/kTval]/normValC /; 0 ≤ x ≤ 180; probC[x_] := probC[360 - x] /; 180 < x ≤ 360;

Plot[{probA[x], probB[x], probC[x]}, {x, 0, 360}, PlotStyle -> Automatic, PlotRange -> Automatic, Frame -> True, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, FrameLabel -> {"Dihedral Angle [deg.]", "Probability"}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] & /@ {"Dihedral BNBP-T", "Dihedral T-T", "Dihedral T-fT"})]

out =



Here we compute the cumulative probability for A, B and C types of dihedral angles.

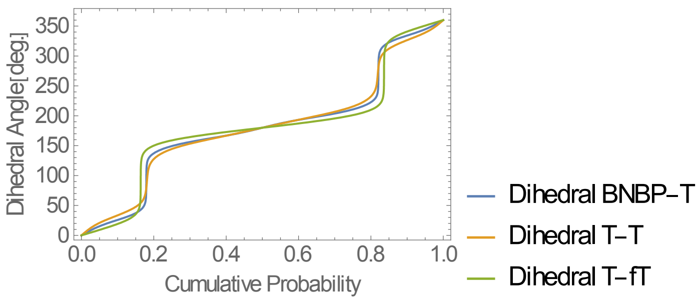
pIntTableA = Quiet[Table[{NIntegrate[probA[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableB = Quiet[Table[{NIntegrate[probB[xp], {xp, 0, x}], x}, {x, 0, 360}]];

pIntTableC = Quiet[Table[{NIntegrate[probC[xp], {xp, 0, x}], x}, {x, 0, 360}]];

ListLinePlot[{pIntTableA, pIntTableB, pIntTableC}, PlotStyle -> Automatic, Frame -> True, Axes -> False, FrameLabel -> {"Cumulative Probability", "Dihedral Angle [deg.]"}, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16], PlotLegends -> (Style[#, FontFamily -> "Helvetica", FontSize -> 16] & /@ {"Dihedral BNBP-T", "Dihedral T-T", "Dihedral T-fT"})]

out =



thA[prob_] = Interpolation[pIntTableA][prob];

thB[prob_] = Interpolation[pIntTableB][prob];

thC[prob_] = Interpolation[pIntTableC][prob];

We construct the P-5T chain:

Length of C-C (across the 1st thiophene) is 2.52763 Å;

Length of C-C bond (between the 1st thiophene and the 2nd thiophene) is 1.44552 Å;

Length of C-C (across the 2nd thiophenering) is 2.53028 Å;

Length of C-C bond (between the 2nd thiophene and the fluoro-thiophene) is 1.43793 Å;

Length of C-C (across the fluoro-thiophene) is 2.55995 Å;

Length of C-C bond (between the fluoro-thiophene and the 3rd thiophene) is 1.43793 Å;

Length of C-C (across the 3rd thiophene) is 2.53039 Å;

Length of C-C bond (between the 3rd thiophene and the 4th thiophene) is 1.44550 Å;

Length of C-C (across the 4th thiophene) is 2.52769 Å;

Length of C-C bond (between the 4th thiophene and the BNBP unit) is 1.45965 Å;

Length of C-C (across the BNBP unit) is 7.04349 Å;

Length of C-C bond (between the BNBP unit and the 5th thiophene) is 1.45926 Å;

Deflection angles (the angle corresponding to the deflection of P-5T backbone bond from Z-axis) are listed below from angle 1 to angle 12.

v[i_] := If[i > 1, RotationMatrix[Angle[[Mod[i - 1, 12, 1]]]].v[i - 1](l[[Mod[i, 12, 1]]])/(l[[Mod[i - 1, 12, 1]]]), l[[1]] {1, 0}]*

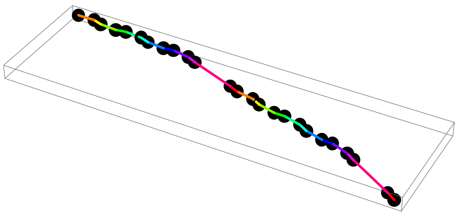
Now we can construct an initial conformation for P-5T.

chain[n_] := Append[#, 0] & /@ Prepend[Accumulate[Table[v[k], {k, 1, n}]], {0, 0}]; drawChain[pts_] := Graphics3D[{PointSize[.03], Point /@ pts, Thick, Table[{Hue[(1/12) Mod[i, 12]], Line[{pts[[i]], pts[[i + 1]]}]}, {i, 1, Length[pts] - 1}]}];

A drawing of P-5T dimer is obtained.

drawChain[chain[24]]

out =



Then, we rotate a backbone dihedral angle by certain degree. Only the tangent vectors with even index (corresponding to the inter-moiety bond) will be rotated.

dihedralRotate[pts_, nb_?EvenQ, theta_] := Module[{}, vec = pts[[nb + 1]] - pts[[nb]]; origin = pts[[nb]]; rot = RotationMatrix[theta, vec]; Join[Take[pts, nb], origin + (rot.(# - origin)) & /@ Drop[pts, nb]]] cosVals[pts_] := Table[(pts[[k]] - pts[[k - 1]]).(pts[[3]] - pts[[2]])/(Norm[pts[[k]] - pts[[k - 1]]] Norm[pts[[3]] - pts[[2]]]), {k, 3, Length[pts], 12}] randomRotate[pts_] := Module[{}, newpts = pts;

Do[If[(k - 12 Floor[k/12]) == 2, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree], If[(k - 12 Floor[k/12]) == 4, newpts = dihedralRotate[newpts, k, thC[RandomReal[]] Degree], If[(k - 12 Floor[k/12]) == 6, newpts = dihedralRotate[newpts, k, thC[RandomReal[]] Degree], If[(k - 12 Floor[k/12]) == 8, newpts = dihedralRotate[newpts, k, thB[RandomReal[]] Degree], If[(k - 12 Floor[k/12]) == 10, newpts = dihedralRotate[newpts, k, thA[RandomReal[]] Degree], If[(k - 12 Floor[k/12]) == 0, newpts = dihedralRotate[newpts, k, thA[RandomReal[]] Degree]]]]]]], {k, 2, Length[pts], 2}]; newpts]

We rotate a P-5T 10mer over 10,000 times to compute tangent-tangent correlation function.

Clear[ch]

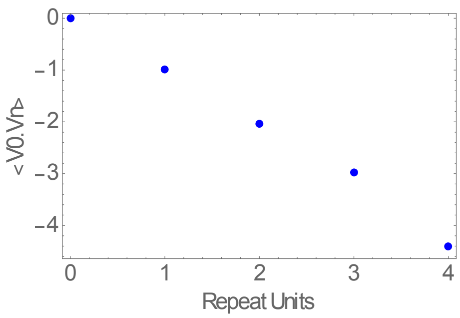
```
ch = chain[120];

cosList2 = ParallelTable[cosVals[randomRotate[ch]], {10000}];

corr2 = Plus @@ cosList2/10000;

ListPlot[Table[{i - 1, Log[corr2[[i]]]}, {i, 1, 5}], PlotStyle -> {Blue, PointSize[0.02]}, Frame -> True, FrameLabel -> {"Repeat Units", "<V0.Vn>"}, FrameTicks -> {Automatic, Automatic, Automatic, Automatic}, LabelStyle -> Directive[FontFamily -> "Helvetica", 16]]
```

out =




```
logFitP-5T[x_] = Fit[Log[corr2[[1 ;; 5]]], {1, x}, x]
```

out =

1.15648 - 1.07923 x

The number of repeat units (N_p) of P-5T is compute as the following: *-1/logFitP-5T'[x]*

out =

0.926587

Table S1. The persistence length l_p of the polymers P-1T, P-2T, P-3T, P-4T and P-5T.

Polymer	The number of repeat units (N_p)	The length of a repeat unit[a] (h/Å)	The persistence length[b] (l_p/nm)
P-1T	6.9	12.51	8.6
P-2T	2.5	16.43	4.1
P-3T	1.9	20.34	3.9
P-4T	1.1	24.27	2.7
P-5T	0.9	28.21	2.5

[a]The length of a repeat unit (h) was measured from the geometry structure in DFT. [b]The persistence length (l_p) was calculated by $l_p = N_p \times h$.