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Raman characterization of plastics: a DFT study of polystyrene

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SUPPLEMENTARY INFORMATION

Benchmark of computational parameters : BENZENE

Basis sets were taken from official crystal basis set library:
https://www.crystal.unito.it/basis_sets.html

The chosen basis sets are following (naming of atoms basis sets is consisted with nomenclature in the Crystal library):

Basis 1 : C_dovesi1990 and H_gatti1994

Basis 2 : C_dovesi1990 and H_dovesi1984

Basis 3 : C_DZVP and H_DZVP

Basis 4 : C_gatti1994 and H_gatti1994

Basis 5 : C_TZVP and H_TZVP

Basis 6 : C_valenzano2006 and H_gatti1994

Basis 7 : C_valenzano2006 and H_dovesi1984

Table S1. Raman vibrational frequencies for the benzene molecule calculated using PBE functional in combination with different basis sets. Theoretical values are compared to experimental ones measured for a benzene in a gas phase.

Vibrational frequencies [cm ⁻¹]							EXP. (gas)*
Basis 1	Basis 2	Basis 3	Basis 4	Basis 5	Basis 6	Basis 7	
601.15	600.24	595.09	598.65	602.18	602.15	602.06	606
819.74	815.67	826.68	828.87	828.15	821.12	824.16	849
1000.52	1002.45	1021.62	1003.56	1006.51	996.42	996.14	992
1165.32	1160.24	1156.29	1161.80	1157.11	1160.15	1155.24	1178
1599.52	1601.68	1637.43	1613.56	1606.57	1598.39	1597.77	1596
3116.33	3096.51	3150.77	3129.68	3116.67	3112.45	3086.10	3047
3143.24	3126.15	3176.69	3155.03	3142.83	3137.11	3112.06	3062

Table S2. Raman vibrational frequencies for the benzene molecule calculated using B3LYP functional in combination with different basis sets. Theoretical values are compared to experimental ones measured for a benzene in a gas phase.

Vibrational frequencies [cm^{-1}]						EXP. (gas)*
Basis 1	Basis 3	Basis 4	Basis 5	Basis 6	Basis 7	
623.31	617.48	619.92	624.39	624.51	624.59	606
857.58	862.88	864.24	863.67	857.04	861.19	849
1021.04	1041.10	1022.69	1025.03	1034.63	1014.05	992
1200.91	1192.34	1196.57	1192.81	1195.60	1191.42	1178
1644.69	1678.81	1655.98	1647.59	1639.61	1639.10	1596
3138.03	3216.84	3192.69	3178.16	3174.56	3149.95	3047
3209.49	3243.35	3218.49	3204.91	3192.32	3176.69	3062

*J. Mol. Model. (2013) 19:2865–2877, DOI 10.1007/s00894-012-1697-4

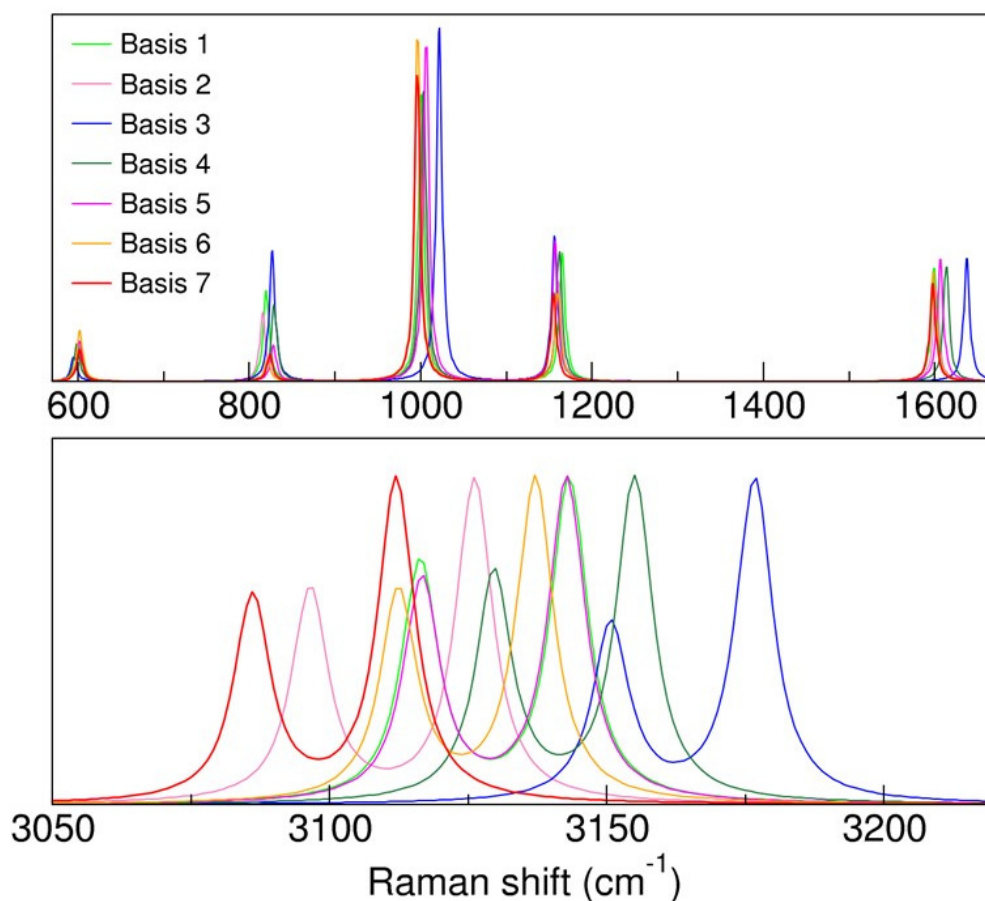


Figure S1. Calculated Raman spectra for benzene molecule obtained using PBE functional with different basis sets. The results show that though value of frequency varies with the basis set the overall shape of the spectra is preserved.

Benchmark of computational parameters : trans-planar and helical infinite polymers

Table S3. Structural parameters of trans-planar infinite polystyrene calculated with different functionals and basis sets. The measured repetition length along the *c*-axis for crystalline α/β sPST, is found to be in a range 5.06-5.1 Å.

	TRANS-PLANAR INFINITE POLYSTYRENE							
	PBE			PBE-D3			B3LYP	
	Basis_4	Basis_5	Basis_7	Basis_4	Basis_5	Basis_7	Basis_5	Basis_7
Repetition length [Å]	5.14	5.13	5.13	5.11	5.07	5.10	5.14	5.13
C ^{ch} -C ^{ch} bond [Å]	1.549	1.544	1.545	1.540-1.545	1.534-1.542	1.538-1.540	1.546	1.546
C ^{ch} -C ^{ph} bond [Å]	1.526	1.521	1.523	1.520	1.516	1.519	1.522	1.524
C-H bond in CH group [Å]	1.106	1.104	1.105	1.104-1.105	1.103-1.104	1.104-1.105	1.094	1.094
C-H bond in CH ₂ group [Å]	1.107	1.105	1.106	1.106 - 1.107	1.104-1.105	1.105-1.106	1.096	1.096
C-C-C angle for CH group [°]	~112.34	112.28	~112.2	112.98 / 111.1	110.7 /113.09	111.5 / 112.7	112.3	112.2
C-C-C angle for CH ₂ group [°]	~113 / 112.97	112.76	113	112.64 / 111.02 / 113.9	112.58 / 113.93 / 110.25	112.54 / 113.4 / 111.6	~113.06	113.32
C ^{ph} -C ^{ch} -H ^{ch} angle [°]	107.36	107.33	107.23	~107.25	106.99 / 107.27	107.14	107.3	107.22
H ^{ch} -C ^{ch} -H ^{ch} angle in CH ₂ [°]	~106.27	106.43	106.26	~106.4	106.3-106.9	~106.3	106.37	106.23
C ^{ph} -C ^{ph} bond [Å]	1.4-1.41	~1.4	~1.4	~1.4	~1.4	~1.4	~1.4	~1.4
C ^{ph} -H ^{ph} bond in ring [Å]	1.094- 1.096	1.091- 1.094	1.094	1.094-1.095	1.093	1.094	1.085	1.085- 1.086
Band gap [eV]	4.56	4.57	4.52	4.42	4.36	4.43	6.16	6.03

Table S4. Structural parameters of helical infinite polystyrene calculated with different functionals and basis sets. The experimental value of repetition length along the *c* direction for crystalline δ -sPST is equal to 7.7 Å.

	Helical infinite polystyrene			
	PBE		PBE-D3	
	Basis_5	Basis_7	Basis_5	Basis_7
Repetition length [Å]	7.8	7.9	7.6	7.7
C ^{ch} -C ^{ch} bond [Å]	1.544 / 1.546	1.545 / 1.549	1.541	1.541-1.543
C ^{ch} -C ^{ph} bond (chain-ring)	1.52	1.523	1.515	1.518
C-H bond in CH group [Å]	1.104	1.104	1.103	1.104
C-H bond in CH ₂ group [Å]	1.105	1.105	1.104	1.105
C-C-C angle for CH group [°]	112.4	112.25	111.92	111.96
C-C-C angle for CH ₂ group [°]	113.91 / 117.03	114.69 / 117.51	113.44 / 115.49	113.94 / 116
C ^{ph} -C ^{ch} -H ^{ch} angle [°]	106.81	106.6	106.96	106.78
H ^{ch} -C ^{ch} -H ^{ch} angle in CH ₂ [°]	105.73 / 106.34	105.89 / 105.61	106.60 / 106.05	105.93 / 106.20
C ^{ph} -C ^{ph} bond [Å]	1.395-1.404	1.397-1.403	1.395-1.402	1.396-1.403
C ^{ph} -H ^{ph} bond in ring [Å]	1.092-1.093	1.094-1.095	1.092-1.093	1.094
Band gap	4.52	4.45	4.48	4.42

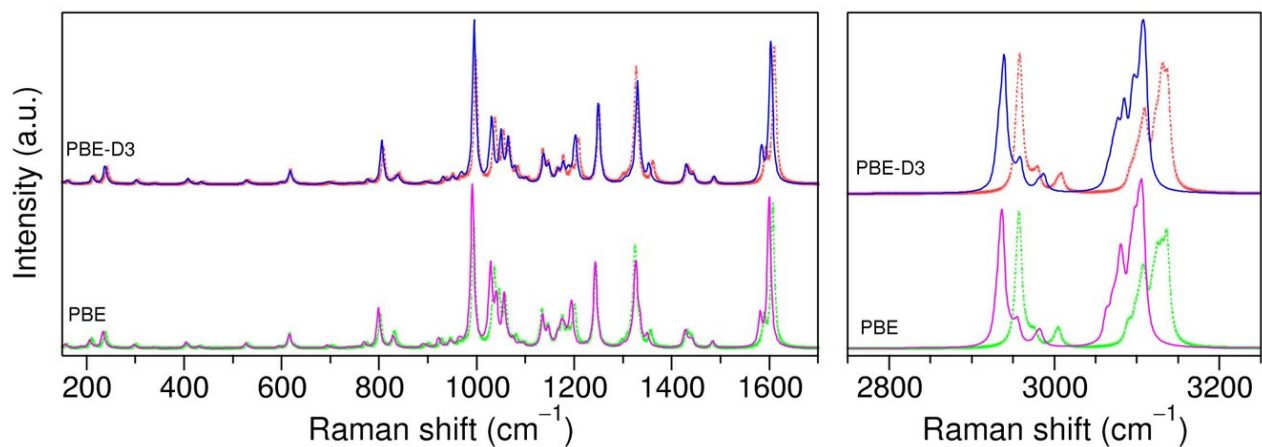


Figure S2. Raman spectra for helical infinite polystyrene chain calculated with PBE and PBE-D3 functional and two different basis sets: Basis 5 in dotted lines and Basis 7 in solid line.

Table S5. Table summarizes the number of atoms, the number of calculated frequencies, and values for negative frequencies (if present) for different polystyrene structures studied. Calculations were done with the PBE-D3 functional and basis set 7. Small negative frequencies are more related to computational parameters rather than structural instabilities (as explained in the main text).

Structure	Nr atoms	Nr of freq.	Negative freq. (cm^{-1})
Helical POLYMER	64	192	-19.5751
Trans-planar POLYMER	64	192	-
Spiral OLIGOMER	98	294	-15.6197
			-0.0127
Linear OLIGOMER	66	198	-15.7097
Bent OLIGOMER	98	294	-15.66
			-8.3

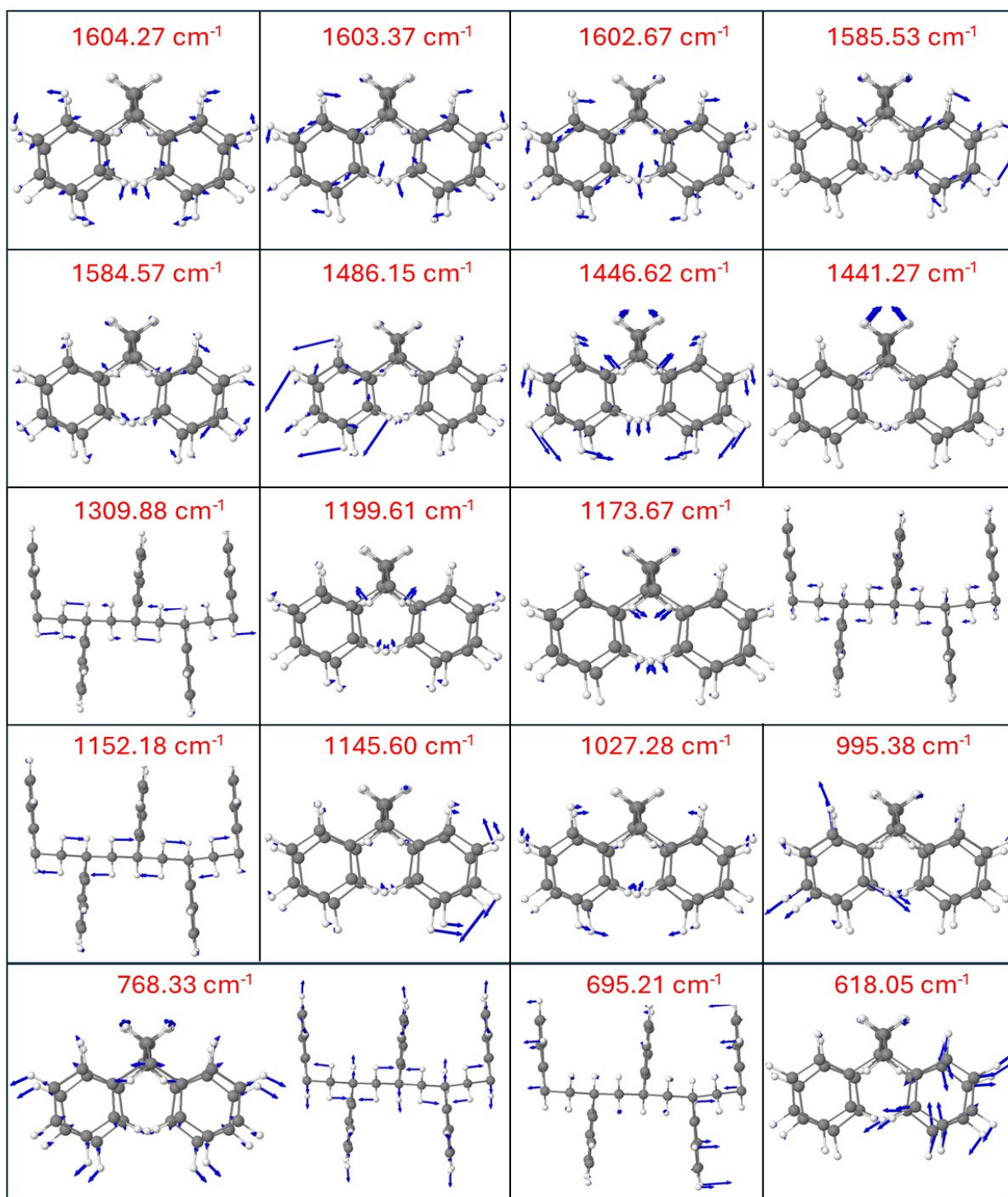


Figure S3. Schematic representation of chosen vibrational modes for trans-planar infinite polystyrene chain.

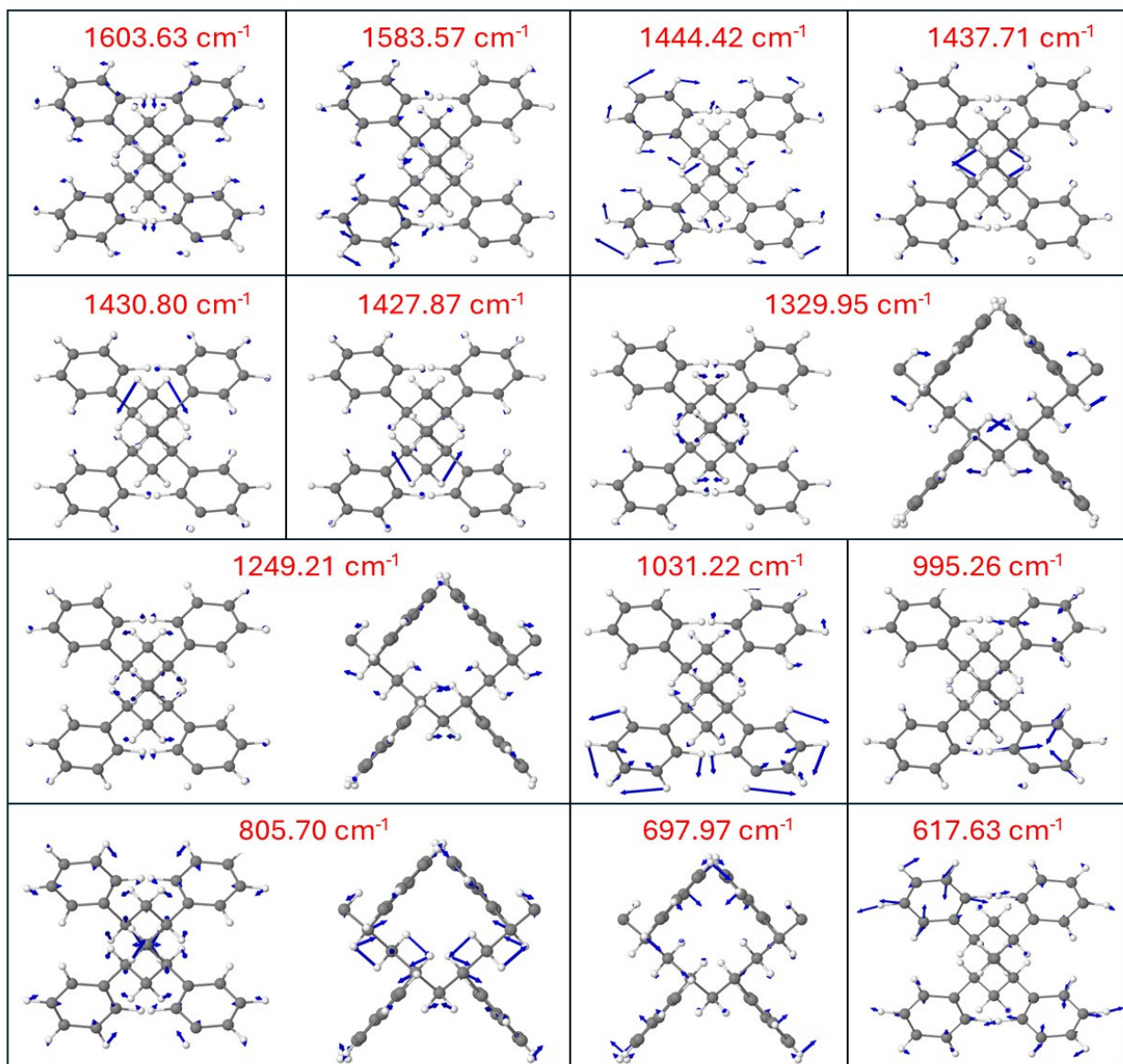


Figure S4. Schematic representation of chosen vibrational modes for helical infinite polystyrene chain.

Table S6. Raman vibrational frequencies in range 100-1700 cm⁻¹ calculated for trans-planar infinite polystyrene chain divided into modes described as pure phenyl ring modes, pure chain (backbone) modes or mixed modes. The modes in red (bolded) are visualized in Figure S3.

Infinite trans-planar polystyrene						
Ring		Backbone	Mixed			
1604.27	1027.28	1420.80	1446.62	1141.45	768.33	403.01
1603.37	995.57	1441.27	1444.30	1092.81	759.74	399.38
1602.90	995.38	1431.00	1443.90	1091.62	759.23	395.41
1602.67	995.29	1430.69	1442.72	1085.84	754.15	333.80
1585.53	994.91	1309.88	1367.79	1083.57	740.79	280.79
1584.57	965.38	1320.43	1361.25	1068.36	738.54	277.20
1584.29	961.12	1331.27	1358.45	1065.63	731.06	260.49
1584.08	960.72	1345.53	1356.32	1063.13	730.48	232.64
1487.03	957.45	1212.83	1342.90	1060.96	587.26	217.10
1486.15	951.84	1266.65	1342.40	1025.20	586.61	216.43
1484.30	942.72	1265.52	1336.19	987.40	575.73	214.23
1484.14	828.43	1152.18	1335.92	983.90	574.58	212.36
1170.53	826.97	1014.55	1330.47	976.86	552.76	169.34
1168.64	825.77		1305.03	949.69	548.82	126.43
1167.57	695.21		1293.72	948.84	546.20	123.74
1166.84	693.64		1292.69	930.06	529.30	
1147.21	692.67		1281.49	929.50	523.85	
1146.64	683.57		1199.61	897.98	463.48	
1145.60	618.51		1191.91	894.37	462.12	
1145.02	618.05		1190.99	893.32	448.92	
1032.09	617.30		1183.96	886.26	410.01	
1029.84	616.94		1173.67	840.08	408.97	
1029.05	411.69		1141.69	816.40	403.32	

Table S7. Raman vibrational frequencies in range 100-1700 cm^{-1} calculated for helical infinite polystyrene chain divided into modes described as pure phenyl ring modes, pure chain (backbone) modes or mixed modes. The modes in red (bolded) are visualized in Figure S4.

Infinite Helix polystyrene							
Ring		Backbone	Mixed				
1604.56	961.76	1437.71	1445.72	1225.57	966.72	597.43	193.47
1603.63	946.82	1430.80	1444.84	1202.77	964.13	572.89	161.16
1601.65	944.78	1428.09	1444.42	1198.99	963.41	562.69	156.40
1601.21	897.03	1427.87	1442.81	1190.71	955.86	539.18	144.97
1584.80	895.40	1255.86	1368.35	1187.48	951.82	529.58	118.27
1583.67	833.87	1064.33	1357.92	1177.35	950.31	526.94	
1583.57	829.04		1356.53	1177.20	936.03	496.93	
1583.26	828.91		1352.85	1167.81	931.08	494.50	
1486.97	823.91		1343.28	1167.59	890.85	445.79	
1486.43	749.11		1340.33	1161.28	890.60	434.50	
1486.14	697.97		1336.85	1137.08	846.30	411.24	
1485.62	693.63		1336.21	1101.16	838.60	408.23	
1166.60	691.96		1332.84	1093.34	823.60	406.27	
1149.06	687.94		1329.95	1078.78	805.70	400.86	
1148.22	618.69		1326.68	1077.52	775.88	337.91	
1146.16	618.11		1315.82	1071.46	765.41	302.03	
1145.71	617.63		1307.73	1066.66	759.82	265.91	
1031.22	617.38		1307.22	1049.93	742.75	248.63	
1030.21	405.66		1304.18	1039.06	741.21	245.49	
995.40	398.75		1302.18	1033.34	736.13	237.99	
995.26			1284.07	1027.00	627.60	234.35	
994.42			1270.68	1026.69	597.84	218.07	
994.09			1249.21	969.32	597.00	212.02	

Table S8. Raman vibrational frequencies in range 100-1700 cm⁻¹ calculated for finite “linear” trans-planar oligomer divided into modes described as pure phenyl ring modes, pure chain (backbone) modes or mixed modes.

Finite “linear” trans-planar oligomer						
Ring		Backbone	Mixed			
1604.64	962.66	1445.67	1449.52	1192.33	899.4	458.65
1603.54	962.31	1438.9958	1446.7	1191.09	898.54	430.5
1602.89	960.36	1433.2	1444.93	1186.63	892.83	410.19
1602.41	958.09	1429.76	1443.35	1163.24	889.3	407.16
1585.27	949.65	1423.96	1442.68	1149.1	887.08	402.49
1584.37	946.93	1360.26	1365.78	1146.76	872.01	401.09
1584.11	945.36	1250.93	1360.59	1144.05	833.55	396.8
1583.34	943.12		1352.7	1101.86	772.52	365.99
1485.97	827.44		1346.02	1088.68	756.35	333.37
1485.52	825.74		1341.63	1086.86	754.87	318.07
1485.4	822.53		1340.42	1081.61	751.18	273.25
1484.86	818.51		1337.36	1077.24	745.12	267.9
1169.84	694.24		1334.08	1066.3	733.95	244.44
1168.09	692.54		1330.74	1061.9	732.13	237
1167.58	689.69		1328.09	1055.99	718.77	221.6
1166.69	686.93		1324.71	1034.03	586.44	214.51
1147.56	618.06		1304.77	1031.93	583.25	213.36
1146.12	617.77		1302.23	1029.94	569.18	187.36
1145.64	616.73		1295.82	1026.16	553.47	177.43
1027.72	616.55		1289.87	1018.65	544.13	152.74
995.52	398.07		1282.7	983.76	537.72	135.81
995.09			1271.09	980.52	527.33	
994.71			1207.98	956.25	507.68	
994.69			1196.44	930.55	485.52	

Table S9. Raman vibrational frequencies in range 100-1700 cm⁻¹ calculated for finite “bent” trans-planar oligomer divided into modes described as pure phenyl ring modes, pure chain (backbone) modes or mixed modes.

Finite “bent” trans-planar oligomer									
Ring			Backbone	Mixed					
1604.43	1146	945.68	1457.31	1447.28	1327.1	1171.89	995.89	743.65	407.53
1603.98	1145.1	827.97	1451.81	1445.93	1323.64	1170.58	972.83	742.38	365.11
1603.48	1029.96	827.07	1433.98	1444.66	1320.6	1169.14	966.63	735.23	352.56
1603.38	1028.45	824.37	1426.11	1443.24	1313.22	1168.81	927.01	730.07	350.61
1602.98	1028.12	823.77	1248.65	1443.09	1307.97	1167.09	912.38	724.64	323.2
1601.15	1027.27	822.49		1442.2	1307.17	1157.84	903.62	639.39	321.94
1583.9	995.31	695.23		1441.47	1304.2	1141	899.46	629.19	310.78
1583.65	994.26	693.31		1440.77	1297.38	1103.82	897.46	622.19	303.87
1583.48	993.49	692.25		1438.69	1296.79	1099.59	892.1	607.97	275.19
1582.24	992.98	691.07		1436.01	1292.4	1091.12	890.55	597.73	262.1
1581.91	992.83	689.45		1373.12	1282.49	1086.1	889.18	562.41	255.53
1581.08	992.47	688.69		1368.89	1272.91	1082.51	883.61	555.5	242.22
1487.01	964.09	618.59		1364.96	1258.45	1078.02	879.31	543.34	225.57
1486.13	962.37	617.81		1360.75	1238.19	1074.39	862.69	542.12	216.61
1485.84	960.88	617.35		1356.61	1226.72	1071.17	844.2	527.95	209.23
1485.59	959.93	616.61		1350.15	1218	1065.14	834.68	525.51	206.26
1485.47	959.83	616.3		1347.84	1203.98	1064.69	830.33	514.26	204.89
1483.55	959.32	402.84		1345.39	1200.63	1049.8	818.05	504.65	196.55
1168.38	950.69	401.67		1342.76	1198.35	1045.22	783.83	490.1	180.38
1147.19	949.68	401.37		1340.16	1192.37	1033.7	769.35	476.12	152.3
1146.93	947.77	398.94		1339.49	1186.92	1030.55	760.8	452.36	134.26
1146.68	947.51	398.13		1337.35	1181.47	1025.38	752.42	441.41	130.69
1146.29	946.43	397.4		1332.84	1174.16	1011.65	751.44	432.76	115.39
				1330.71	1172.53	999.17	747.21	411.06	

Table S10. Comparison of experimental Raman frequencies used for the calibration with values calculated theoretically for different polystyrene structures.

Exp. (cm ⁻¹) ASTM E1840-96	Theo. Trans-planar PST			
	Infinite	"Linear" oligomer	"Bent" oligomer	
620.9	618.51	618.06	618.59	616.61
	618.05	617.77	617.81	616.3
	617.3	616.73	617.35	
	616.94	616.55		
795.8	768	772.52	769.35	
1001.4	995.57	995.52	995.31	992.83
	995.38	995.09	994.26	992.47
	995.29	994.71	993.49	
	994.91	994.69	992.98	
1031.8	1032.09	1027.72	1029.96	
	1029.84	1029.94	1028.45	
	1029.05	1026.16	1028.12	
	1027.28	1031.93	1027.27	
1155.3	1147.21	1147.56	1147.19	1146
	1146.64	1146.12	1146.93	1145.1
	1145.6	1145.64	1146.68	
	1145.02	1146.76	1146.29	
1450.5	1446.62	1445.67	1457.31	1441.47
	1444.3	1438.996	1451.81	1440.77
	1443.9	1433.2	1433.98	1438.69
	1442.72	1429.76	1426.11	1436.01
	1441.27	1423.96	1447.28	
	1420.8	1449.52	1445.93	
	1431	1446.7	1444.66	
	1430.69	1444.93	1443.24	
		1443.35	1443.09	
	1442.68	1442.2		
1583.1	1585.53	1585.27	1583.9	1581.91
	1584.57	1584.37	1583.65	1581.08
	1584.29	1584.11	1583.48	
	1584.08	1583.34	1582.24	
1602.3	1604.27	1604.64	1604.43	1602.98
	1603.37	1603.54	1603.98	1601.15
	1602.9	1602.89	1603.48	
	1602.67	1602.41	1603.38	
2852.4	-	-	-	
2904.5	-	-	-	
3054.3	3105.9	3106.1	3101.6	3110.2
	3107.8	3107.1	3104.9	3110.3
	3109.5	3110.9	3107.5	3114.1
	3110.4	3111.3	3109.1	

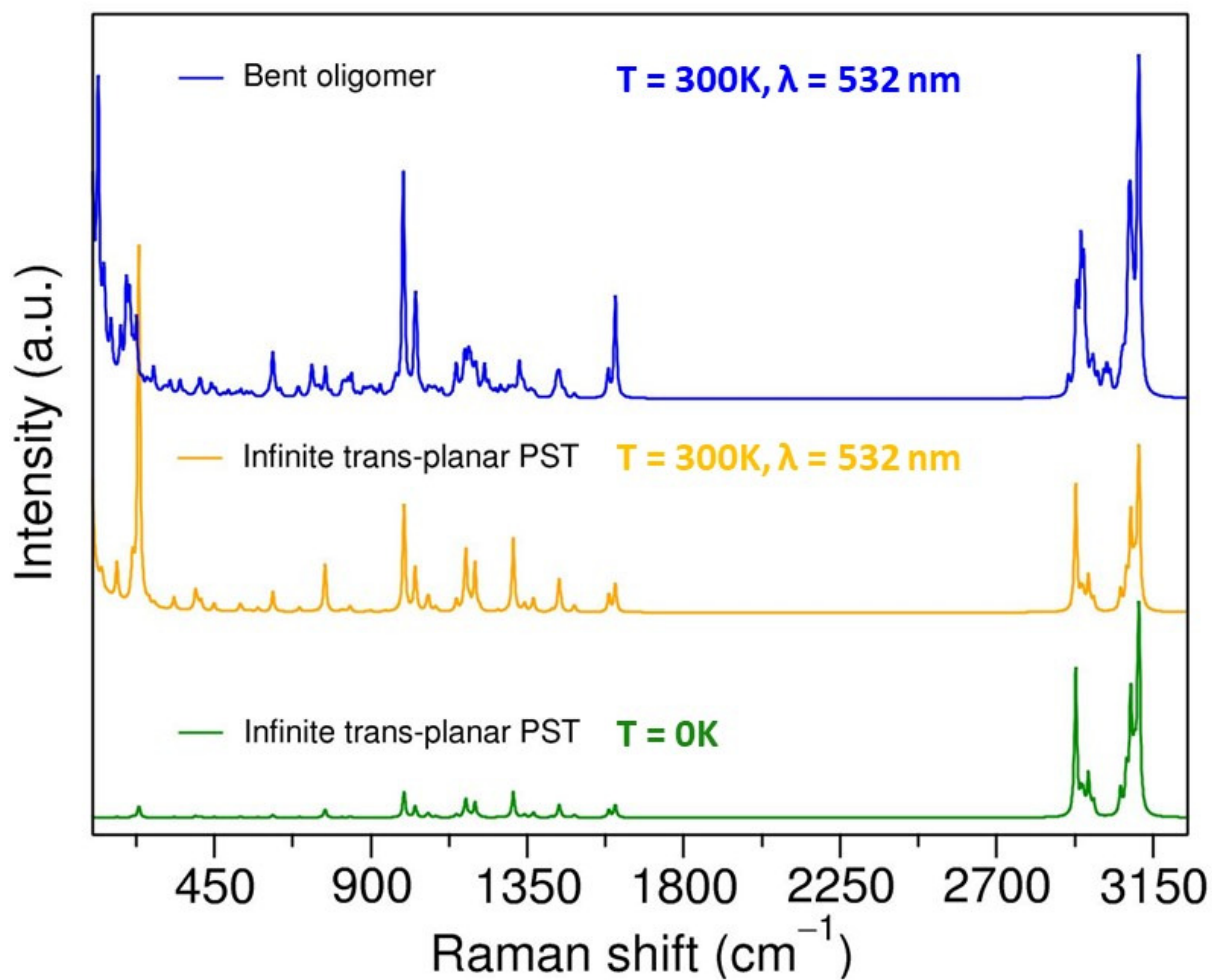


Figure S5. Raman spectra of infinite trans-planar sPST and a bent oligomer with or without temperature and laser correction for intensities.

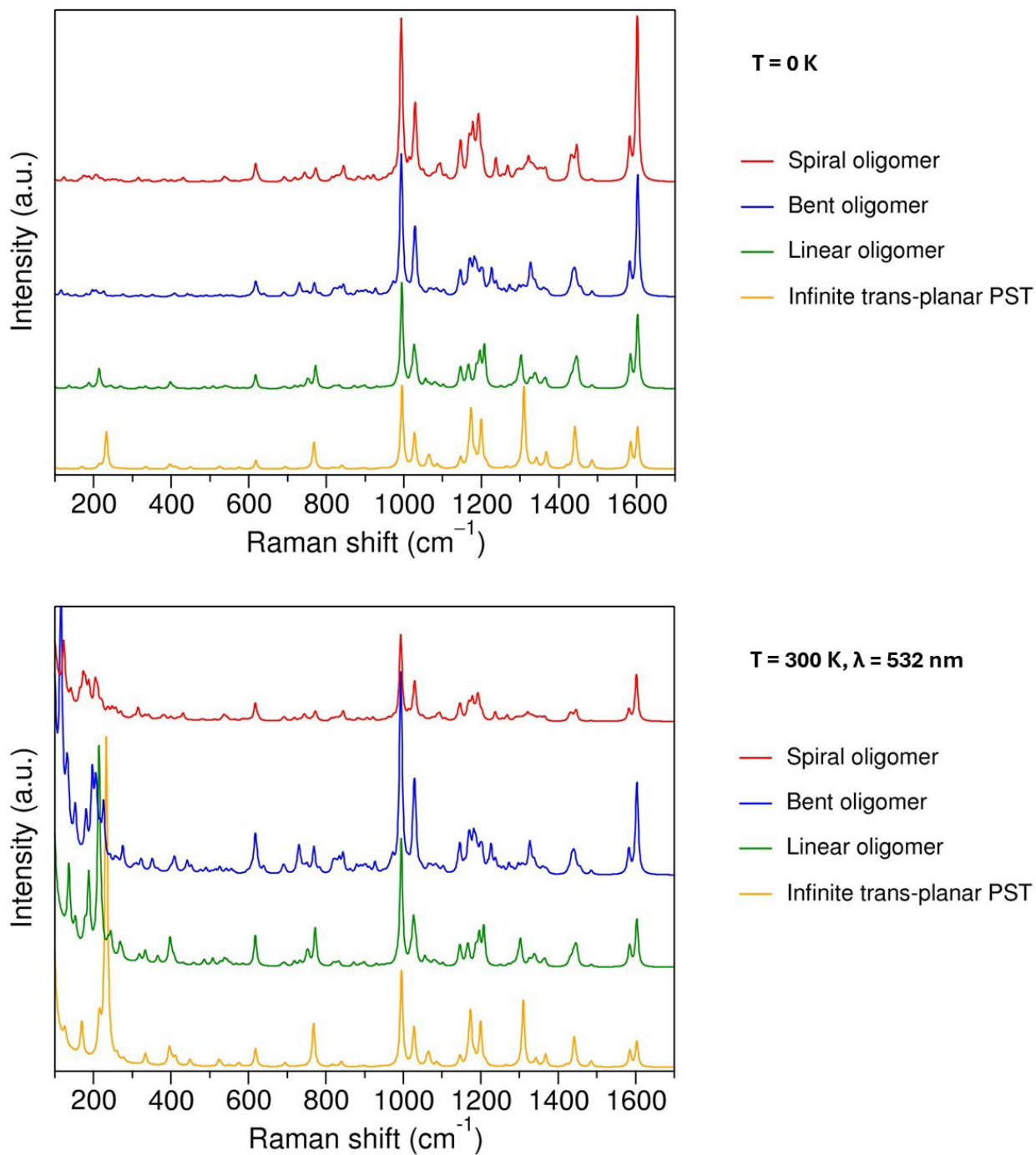


Figure S6. Comparison of Raman spectra, in the lower frequency region, for distinct sPST models that were considered without (left) and with (right) temperature and laser correction for intensity.