Supporting Information: Development of a systematic coarse-grained model for poly(caprolactone) in melt

Petra Bačová,[*,†] Gonzalo González Huarte,[†] Vagelis Harmandaris,[‡,¶,§] and Sergio I. Molina[†]

†*Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, IMEYMAT, Campus Universitario Río San Pedro s/n., Puerto Real, Cádiz 11510, Spain*

‡*Computation-based Science and Technology Research Center, The Cyprus Institute, 20 Constantinou Kavafi Str., Nicosia 2121, Cyprus*

¶*Institute of Applied and Computational Mathematics (IACM), Foundation for Research and Technology Hellas (FORTH), GR-70013 Heraklion, Crete, Greece*

§*Department of Mathematics and Applied Mathematics, University of Crete, GR-71409 Heraklion, Crete, Greece*

E-mail: petra.bacova@uca.es

Comparison of the solvated PCL with the literature data

System preparation

First, the initial configuration of PCL was prepared using the software AVOGADRO.[S1] A trimer was designed, which is the shortest chain that includes the three types of monomer: the initial monomer, the central monomer and the terminal monomer. Next, a home-made code available elsewhere[S2] has been used to copy and translate the central monomer to achieve a fully extended structure with the desired number of monomers, i.e., $N = 10, 30, 50, 100, 125$. The two-body, three-body and four-body interactions for all types of atoms were identified and the corresponding parameters for these interactions were taken from the OPLS-L,[S3,S4] OLPS-AA[S5] and in one particular case also from PLAFF3 force field. The parameters are listed in Tabs. S2-S6.

The simulations were designed as follows: firstly, the chains were simulated in vacuum, which mimics a bad solvent environment and leads to the collapsing of the chains. The fully collapsed configurations were used to prepare the systems in solution and the partially collapsed chains to build the systems in melt. The details of the preparation of each system are summarized below:

1. **Vacuum**: A fully extended polymer chain was placed in a simulation box. Because of its maximum extension, the chain was centred first in a simulation box large enough to encompass the entire molecule without solvent molecules. Stochastic dynamics was applied together with a larger cutting radius r_c of 2 nm, in line with the simulation protocol published in ref.[S6] After a certain time which depends on the chain length, the chain acquires a collapsed state and its radius of gyration stabilizes. The simulation was stopped shortly after obtaining this collapsed state.

2. **Solution**: The final configuration from the vacuum simulation was used as an initial input for the simulation in solution. The collapsed molecule was placed in the center of a simulation box (see Fig. S1(a)), which was large enough to accommodate the desired

number of solvent molecules. The SPC[S7] model of water was employed for the solvent molecules in agreement with ref.[S8] The number of water molecules in each system was adjusted to obtain a weight fraction of PCL in water of 6% (see Tab. S1). Two consecutive simulations were performed, the first with a time step of 0.5 fs and the length of 1 ns to stabilize the randomly prepared system and the second with the time step of 1 fs and the length of 100 ns. The velocity-rescale thermostat and Berendsen barostat were used to keep the temperature at 300K and the pressure at 1 atm in both simulations.

Table S1: Details about the systems in solution. M_w refers to the molecular weight of the chain, N_c denotes the number of chains in the system, N is the number of monomers per chain and N_s is the number of water molecules in the system.

Label	N	M_w [g/mol]	N_c	N_s
PCL10	10	1143.5	1	1041
PCL30	30	3426.3	1	3118
PCL50	50	5709.2	1	5195
PCL100	100	11416.4	1	10389
PCL125	125	14270.0	1	12986

Comparison with literature

In Fig. S1(b) the radius of gyration of PCL systems in water is plotted as a function of the number of monomers together with the data reported in literature. More specifically, the data are compared to the results reported in ref.[S8] and in ref.[S9] The PCL chains of $N = 10$ and $N = 30$ in Di Pasquale et al. were modelled by OPLS-AA force field, which is intended to describe well small molecules. Drenscko and Loverde based their model on CHARMM force field, namely on CHARMM27 for PCL and CHARMM TIP3P for water. Our results agree very well with the published data within the obtained accuracy. In addition, the R_g obtained for our systems scales as $Rg \sim N^{0.28}$, as expected for collapsed configurations in a bad solvent, for which the theoretical exponent is close to 1/3.

Owing to the good agreement with the published data, we conclude that the L-OPLS force field, combined with some parameters from the OPLS-AA force field, satisfactorily reproduces the expected behaviour of PCL in water.

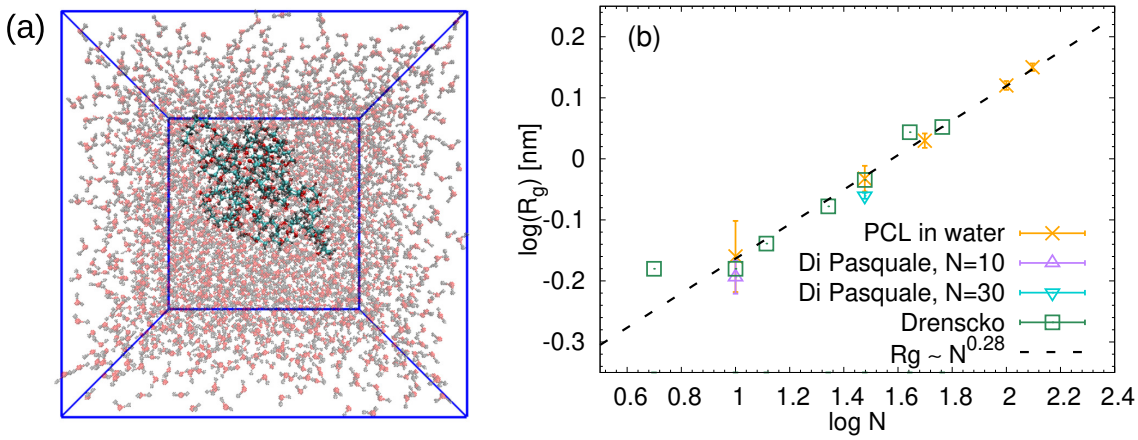

Figure S1: (a) Snapshot of the PCL chain of 30 monomers dissolved in water. (b) The radius of gyration R_g as a function of the number of monomers per chain, N. The data labelled in legend as "Di Pasquale" are from ref.[S8] and "Drenscko" from ref.[S9]

Table S2: Atom types according to L-OPLS,[S3] OPLS-AA[S5] and SPC force field.[S7]

Atom types			
Name of the atom	**Label**	**Description**	**Type**
Alkane -CH2-	CT	sp3 carbon with 2 hydrogens	opls_136
Carboxyl C=O	C_2	CO in carboxylic acid	opls_267
Ester C=O	C_2	carbon in carboxyl group in ester	opls_4651
Carboxyl C=O	O_2	oxygen in carboxylic acid	opls_269
Ester C=O	O_2	oxygen in ester group	opls_4662
Ester -O-	OS	oxygen in alkoxide	opls_4671
Alkane H-C	HC	hydrogen connected to carbon	opls_140
Alcohol O-H	OH	oxygen in hydroxyl group	opls_154
Alcohol O-H	OH	oxygen in carboxyl acid	opls_268
Alcohol H-O	HO	hydrogen in hydroxyl group	opls_155
Alcohol H-O	HO	hydrogen in carboxyl acid	opls_270
Alkane -CH2-OH	CT	sp2 carbon connected to hydroxyl group	opls_157
Alkane -CH2-OH	HC	hydrogen connected to sp2 carbon in alcohol	opls_176
Alkane -CH2-CO	CT	sp2 carbon connected to ester group	opls_490
Alkane -CH2-CO	HC	hydrogen connected to sp2 carbon in ester	opls_469
water O=H	OW	water SPC	opls_116
water H=O	HW	water SPC	opls_117

Table S3: Nonbonded interactions.[S3,S5]

Nonbonded interactions: $V_{LJ}(\mathbf{r}_{ij}) = 4\epsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)$					
Atom type	**weight** [g/mol]	**charge** [e]	σ [nm]	ϵ [KJ/mol]	**Note**
HC	1.0080	0.060	2.50000E-01	1.25520E-01	L-OPLS
CT	12.0110	-0.120	3.50000E-01	2.76144E-01	L-OPLS
OH	15.9990	-0.683	3.12000E-01	7.11280E-01	L-OPS
CT	12.0110	0.145	3.50000E-01	2.76144E-01	OPLS
HC	1.0080	0.040	2.50000E-01	1.25520E-01	OPLS
C_2	12.0110	0.520	3.75000E-01	4.39320E-01	OPLS
HO	1.0080	0.418	0.00000E+00	0.00000E+00	L-OPLS
HO	1.0080	0.450	0.00000E+00	0.00000E+00	OPLS
O_2	15.9994	-0.440	2.96000E-01	8.78640E-01	OPLS
OH	15.9994	-0.530	3.00000E-01	7.11280E-01	OPLS
CT	12.0110	0.190	3.50000E-01	2.76144E-01	OPLS, L-OPLS
HC	1.0080	0.030	2.42000E-01	6.27600E-02	OPLS, L-OPLS
OS	15.9994	-0.450	2.55000E-01	7.11280E-01	L-OPLS
O_2	15.9994	-0.550	3.10800E-01	7.02912E-01	L-OPLS
C_2	12.0110	0.750	3.18750E-01	4.39320E-01	L-OPLS
HC	1.0080	0.060	2.50000E-01	1.25520E-01	L-OPLS
OW	15.99940	-0.820	3.16557e-01	6.50194e-01	OPLS
HW	1.00800	0.410	0.00000e+00	0.00000e+00	OPLS

Table S4: Parameters of bond stretching.[S5]

Bond stretching: $V_b\ (r_{ij}) = \frac{1}{2}k^b_{ij}(r_{ij} - b_{ij})^2$			
Bond	**Equilibrium bond length** [nm]	k^b_{ij} [KJ/mol nm^2]	**Note**
OH HO	0.0945	462750.4	OPLS
C_2 OH	0.1364	376560.0	OPLS
CT C_2	0.1522	265265.6	OPLS
O_2 C_2	0.1229	476976.0	OPLS
CT CT	0.1529	224262.4	OPLS
HC CT	0.1090	284512.0	OPLS
OH CT	0.1410	267776.0	OPLS
CT OS	0.14100	267776.0	OPLS
OS C_2	0.13217	179075.2	OPLS

Table S5: Parameters of the angle potential.[S5]

Angle potential: $V_a(\theta_{ijk}) = \frac{1}{2}k^{\theta}_{ijk}(\theta_{ijk} - {\theta_{ijk}}^0)^2$			
Angle	θ_{ijk} [°]	k^{θ}_{ij} [KJ/mol rad^2]	**Note**
OH C_2 C_2	113.000	292.880	OPLS
OH C_2 CT	108.000	585.760	OPLS
OH C_2 O_2	121.000	669.440	OPLS
C_2 CT CT	111.100	527.184	OPLS
C_2 CT HC	109.500	292.880	OPLS
CT CT CT	112.700	488.273	OPLS
CT CT HC	110.700	313.800	OPLS
CT CT OH	109.500	418.400	OPLS
CT OH HO	108.500	460.240	OPLS
HC CT HC	107.800	276.144	OPLS
OH CT HC	109.500	292.880	OPLS
CT C_2 O_2	120.400	669.440	OPLS
CT OS C_2	116.900	694.544	OPLS
HC CT OS	109.500	292.880	OPLS
CT CT OS	109.500	418.400	OPLS
OS C_2 O_2	123.400	694.544	OPLS
OS C_2 CT	111.400	677.808	OPLS

Table S6: Parameters of the proper dihedral potential.[S3,S4,S10]

Proper dihedral potential: $V_{rb}(\phi_{ijkl}) = \sum_{p=0}^{5} C_p(\cos(\psi))^p$							
Dihedral	C_0 [KJ/mol]	C_1 [KJ/mol]	C_2 [KJ/mol]	C_3 [KJ/mol]	C_4 [KJ/mol]	C_5 [KJ/mol]	**Note**
CT C_2 OH HO	26.150	-3.138	-23.012	0.000	0.000	0.000	OPLS
CT CT C_2 O_2	3.05944	-3.63216	-5.17499	5.61279	0.000	0.000	L-OPLS
CT CT C_2 OH	5.318	0.732	-2.284	-3.766	0.000	0.000	OPLS
CT CT CT C_2	6.01526	8.73040	2.62473	-5.20449	0.000	0.000	L-OPLS
CT CT CT CT	0.518787	-0.230192	0.896807	-1.49134	0.000	0.000	L-OPLS
CT CT CT HC	0.628	1.883	0.000	-2.510	0.000	0.000	OPLS
HC CT C_2 O_2	0.17512	0.71721	-0.00911	-0.93557	0.000	0.000	L-OPLS
HC CT C_2 OH	0.000	0.000	0.000	-0.000	0.000	0.000	OPLS
HC CT CT C_2	-0.73096	-1.84830	-0.07261	2.47030	0.000	0.000	L-OPLS
HC CT CT CT	0.628	1.883	0.000	-2.510	0.000	0.000	OPLS
HC CT CT HC	0.628	1.883	0.000	-2.510	0.000	0.000	OPLS
HO OH CT CT	-0.79464	3.75594	0.06712	-3.12293	0.000	0.000	L-OPLS
HO OH CT HC	0.76205	2.37159	0.06090	-3.18897	0.000	0.000	L-OPLS
O_2 C_2 OH HO	23.012	0.000	-23.012	0.000	0.000	0.000	OPLS
OH CT CT CT	2.97554	1.25728	1.11423	-5.33767	0.000	0.000	L-OPLS
OH CT CT HC	0.979	2.937	0.000	-3.916	0.000	0.000	OPLS
CT CT C_2 OS	-1.88531	-4.94762	2.62297	4.12830	0.000	0.000	L-OPLS
CT OS C_2 O_2	22.82916	0.000	-24.00662	0.000	0.000	0.000	L-OPLS
HC CT C_2 OS	0.17512	0.71721	-0.00911	-0.93557	0.000	0.000	L-OPLS
CT CT OS C_2	-7.05897	7.54603	5.22349	-5.22077	0.000	0.000	L-OPLS
CT CT CT OS	2.67162	1.59535	4.28477	-8.42744	0.000	0.000	L-OPLS
HC CT OS C_2	0.41421	1.24265	0.000	-1.65686	0.000	0.000	PLA[S10]
HC CT CT OS	0.91475	2.67338	-0.09883	-3.59612	0.000	0.000	L-OPLS
CT OS C_2 CT	32.59672	-6.52543	-24.00659	0.000	0.000	0.000	L-OPLS

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