Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary information

Analog Modeling of Worm-Like Chain Molecules Using Macroscopic Beads-on-a-String

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Material and Methods

Macroscopic Experiments

Materials. Nylon-6,6 beads with a diameter of 6 mm, PMMA beads with a diameter of 3 mm, and Nylon-6,6 long rods with a diameter of 6 mm were purchased from McMaster Carr Supply Company. The rods were cut to 14 mm-long cylinders. A poly(isocyanurate) board was purchased from Home Depot. Silver-coated, 2 × 2-mm crimp beads were purchased from Beadalon. Nylon-6,6 threads with a diameter of 75-µm and 150 µm were purchased from thethreadexchange.com. Holes with a diameter of 1.3 mm were drilled through the beads and the cylinders. Fadeless® paper was purchased from Pacon Corp.

Staining the Nylon Beads. Nylon beads and cylinders were immersed in an aqueous solution of Disperse Blue 14 and placed on a hot plate at a temperature of 100 °C for 30 min. Dyed beads were washed with water and ethanol and dried with a N_2 stream.

Construction and Agitation of a Large Flat Surface. A poly(isocyanurate)board was suspended from the ceiling by four hooks (one in each corner of the surface) which connected the surface to four chains. The chains were joined together and connected with a hook to a turnbuckle that was, in turn, connected to a Bungee cord hanging from the ceiling (Fig. S1). We attached a pendulum to the bottom of the surface; to form the pendulum, we connected a ring to the bottom of the surface, from which we hung a 1-kg disc-shaped weight (McMaster Carr Supply Company). The overall weight of the pendulum was 1.5 kg. To agitate the surface, we connected an orbital motor to the edge of the surface via a polyurethane tie-down cord (length = 35 cm; McMaster Carr Supply Company). The orbital motor (shaking displacement ~ 10 mm) was set to work at 120 to 160 rpm. We also placed a linear motor (LinMot) below the surface to strike the pendulum. The linear motor had an amplitude of 2 cm and a frequency of 4 Hz.

To create a humidity-controlled environment, we covered the entire apparatus with vinyl curtains and attached them to the surface with Velcro to make a sealed enclosure. To increase the humidity, we connected a humidifier (Vicks Ultrasonic Humidifier; P&G) with a tube to the enclosed apparatus. We maintained relative humidity (RH) higher than 60% as we have previously proven that contact electrification is negligible at this RH for our particular system (see supporting information of M. Reches, P. W. Snyder and G. M. Whitesides, *Proc. Nat. Acad. Sci.*, 2009, **106**, 17644-17649).

Construction of a Randomized Motion Generator. To construct a randomized motion generator, we suspended the surface supporting the beads from the ceiling of the room, and applied two mechanical inputs to the system: (i) a periodic propulsion delivered by an orbital motor attached to the surface by a flexible polyurethane cord, and (ii) an aperiodic propulsion delivered by a computer-controlled linear actuator striking a pendulum suspended from the underside of the surface (Fig. S1).

Delimitation of the Area of Agitation. The area of agitation of the chains was defined by an aluminum rim (diameter of the zone = 1 m). The chain reached the border of the area by random displacement after times longer than the time of data acquisition. We covered the surface of the board with paper to control the movement of the chains; paper roughness and softness indeed made the beads of the chain roll and not slide consistently.

Preparation of the Sequences of the Beads. To control the persistence length of the chain, we placed small, spherical (diameter = 3 mm) PMMA beads between the larger Nylon beads, and fixed the separation between the large beads by inserting small, silver-coated beads before and after the PMMA spacer beads (Fig. 1a). The silver beads were crimped to define the length and tension of the spacer region. We used small beads on string, rather than simple lengths of string, to define the length and stiffness of the linker regions reproducibly. In addition, these small beads acted as a physical barrier that prevented the string from crossing over itself during agitation. The Nylon string was loaded through the eye of a needle. Using the needle, various sequences were constructed by threading the beads onto the string. We threaded the beads in the following order: large bead, crimp bead, small beads, crimp bead, large bead, etc. The beads were fastened in position by crimping the 2 × 2-mm, silver-coated beads. The string was maintained in a horizontal position throughout the sequence-making process to ensure that it would not be deformed (stretched) under the gravitational force acting on the beads. The length of the string was the sum of the diameters of the beads comprising the sequence.

We chose six systems of different contour lengths L, with 4, 7, 11, 14, 17, and 21 beads per string corresponding to L = 5.8, 11.6, 19.4, 25.2, 31.0 and 38.8 cm. The longest chain we studied was 38.8 cm cm long (21 beads). Longer chains reached the physical limit of our apparatus, and collapsed on the side of the dish during the time of agitation. To change the rigidity of the chain, we changed the diameter of the thread, from a 75 μm to 150 μm. We also exchanged beads by cylinders on a 75 μm-diameter thread. In that case, we used nylon cylinders with a diameter of 6 mm and a length of 14 mm. We chose six systems of different contour lengths L, with 3, 5, 8, 10, 12, and 15 cylinders per string corresponding to L = 5.4, 10.7, 18.4, 23.9, 29.2, and 37.5 cm.

Image Analysis. To increase the visual contrast between the beads of the chain and the beads at the ends of the chain, we stained the beads at both termini with a neutral organic dye. We observed the evolution in time of the end-to-end distance by collecting one digital image of the system every 30 s under continuous agitation. The mean-square end-to-end distance was calculated from data of 200-400 pictures. The longer the chain was, the greater the number of pictures was necessary, as the number of possible conformations increased.

The length of the chain was measured from the centers of each bead at the termini, with a home-made program developed in MatLab. We imported raw images into Matlab and then analyzed each frame separately. First, we converted the image to black and white and inverted the image, such that the blue colored end beads appeared white and the rest of the image appeared black. We then segmented the image and identified the location of the center of mass of each bead using the "regionprops" function built into Matlab; we then calculated the end-to-end distance between the coordinates of these two centers of mass for each frame in the image sequence. A calibration curve was beforehand established to relate the distance in pixels in the image to the physical distance in cm in the experimental setup.

Monte-Carlo Simulation

Description of the System. We simulated three types of beads: 1. Large beads (size = 0.25), 2. Small beads (size = 0.125), 3. Small restricted beads (size = 0.1). The string is a fixed length unidimensional object. The fixed beads are centered at defined positions along the string. Inside a bead, the string is fixed straight from its entry point to its exit point. At the entry and exit points, the string is allowed to bend at any angle between -90 degrees and 90 degrees. Bends greater than that would cause the string to overlap the beads. Non fixed beads can also shift in one dimension into adjacent empty space along the string. Beads are not allowed to overlap in space. The rigidity of the chain is controlled by the ratio of the total length of the string to the length that is covered by beads. (A string of flexibility 1.0 is exactly rigid. 1.01 has 1% additional length, 1.20 has 20% additional length.) Distances in the simulation are of arbitrary dimension on a linear scale. Each large bead is surrounded by restricted beads and between each set are three small beads. We performed simulations for the different chains with the same number of beads as the physical experiments.

Update of the Simulation in Time. Initially, the beads on a string were positioned as a straight line, with all entry and exit angles equal to 0 and all beads positioned in the centers of their spaces. At each simulation iteration (time point), a randomly selected subset of beads no more than ¼ of the total number of beads attempted to make random coordinated movements, where each bead slid along the string into adjacent exposed space or introduced a small change to the bend angle ($< \pi/10$ rad) at the string's entry or exit point. All the beads on the string would then adjust their absolute positions according to all of the proposed motions, defining the new positions of the beads at the next time point. If any beads overlapped in space, the proposed move was disallowed and the system started the next attempt from the previous allowed position. A subset of beads was fixed in position along the string, so they were unable to move laterally. The simulation output was the set of bead positions as a function of simulation step.

Effect of Temperature. The effect of temperature on the simulated system was studied by the addition of an inertial term to act as an energetic penalty to bead movement. The energy required to move a bead was proportional to the bead volume and the distance the bead moved. The proportionality factor was determined such that moving 10 beads a distance of 1 bead radius each would result in a constant energetic penalty, which was varied over two orders of magnitude in the simulations (from 0.01 to 5). The thermal energy of the system, $kT=1$, set the energetic scale of the system. In simulations with the inertial term, the Metropolis Monte Carlo condition determined whether each simulation move would be allowed to proceed forward.

Figure S1. Scheme of the experimental apparatus: a poly(isocyanurate) board covered with paper is surrounded by a circular aluminum frame to define the area of agitation.

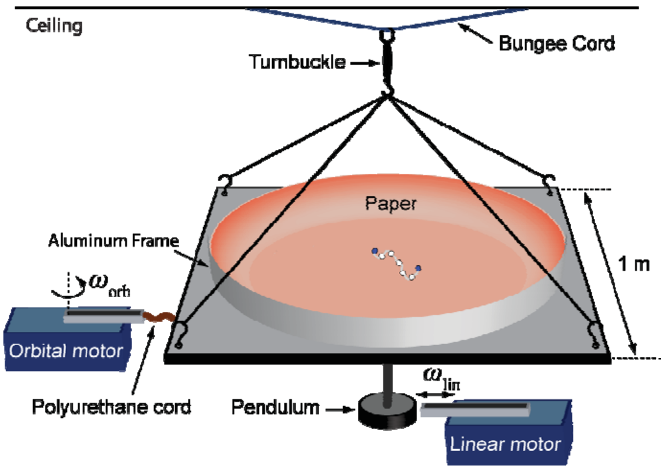
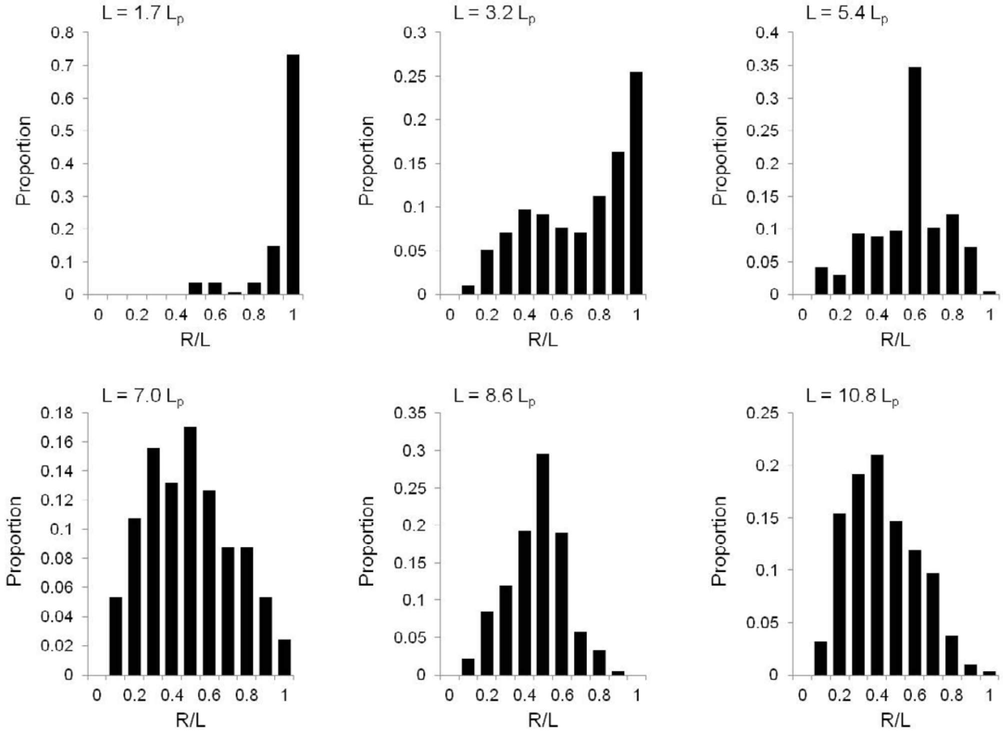


Figure S2. Distributions of the end-to-end distance *R* divided by the contour length *L* for different lengths *L* of the macroscopic chains and: a), b) $1.7 < L/L_p < 11.1$; c), d) $0.6 < L/L_p < 5.0$; e), f) $0.4 < L/L_p < 3.1$.

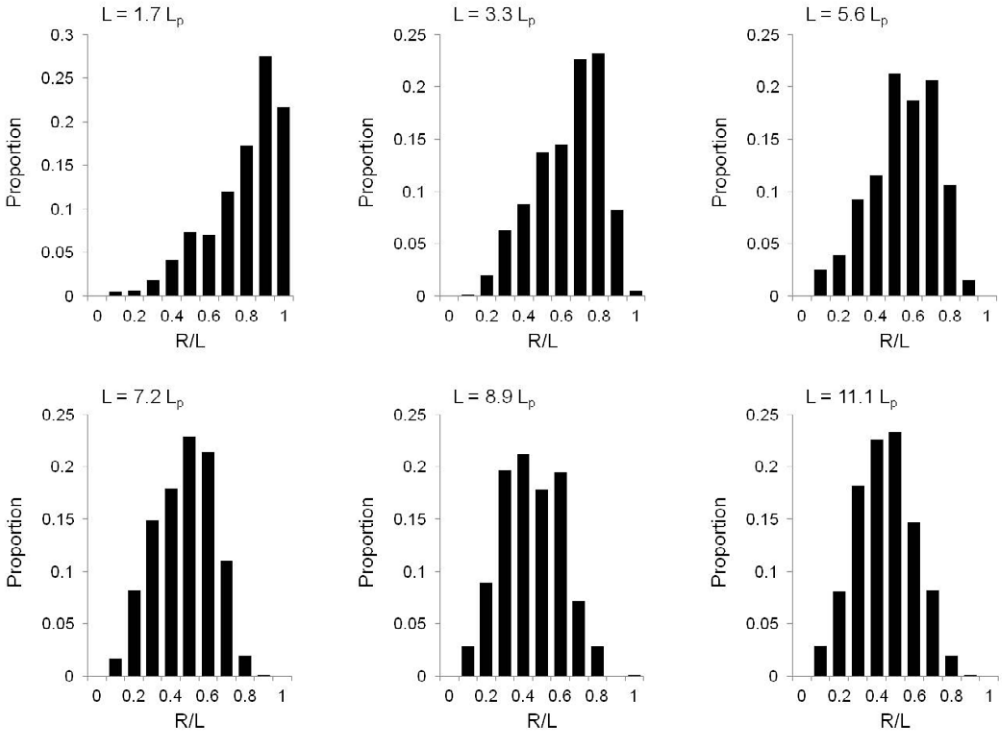
a) c) e) correspond to the macroscopic MacAg model: a) spheres on a 75 µm-diameter thread, c) spheres on a 150 µm-diameter thread, and e) cylinders on a 75 µm-diameter thread.

b) d) f) correspond to the MC simulations: b) flexibility 1.1, d) flexibility 1.02, f) flexibility 1.01.

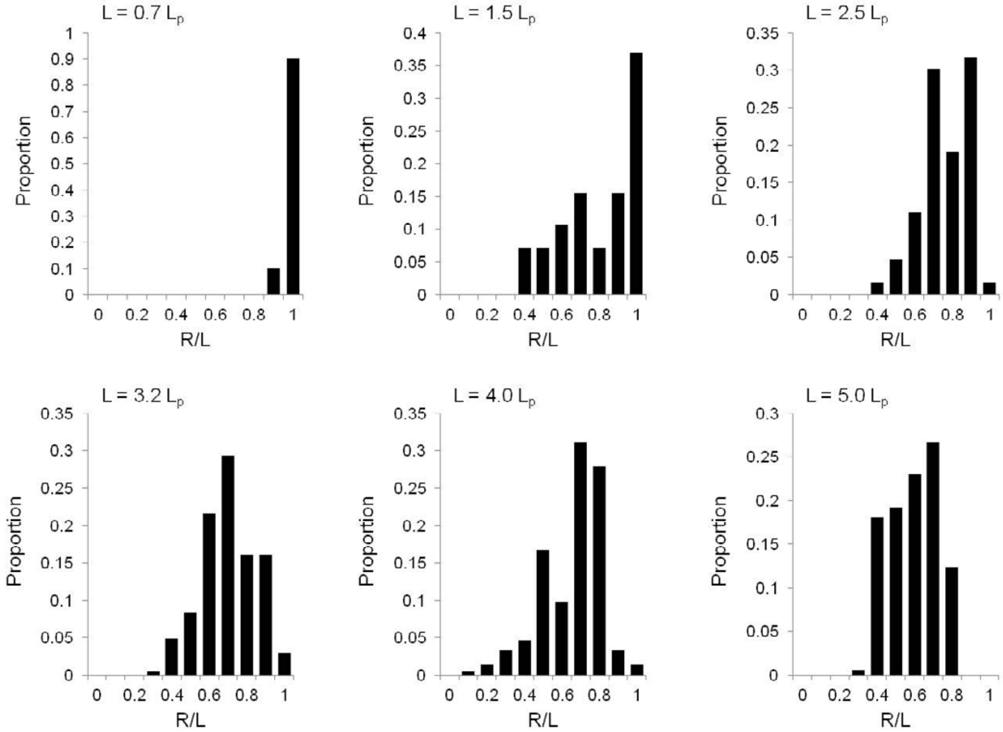
a)


L = 1.7 Lp
L = 3.2 Lp
L = 5.4 Lp
L = 7.0 Lp
L = 8.6 Lp
L = 10.8 Lp
Proportion
R/L

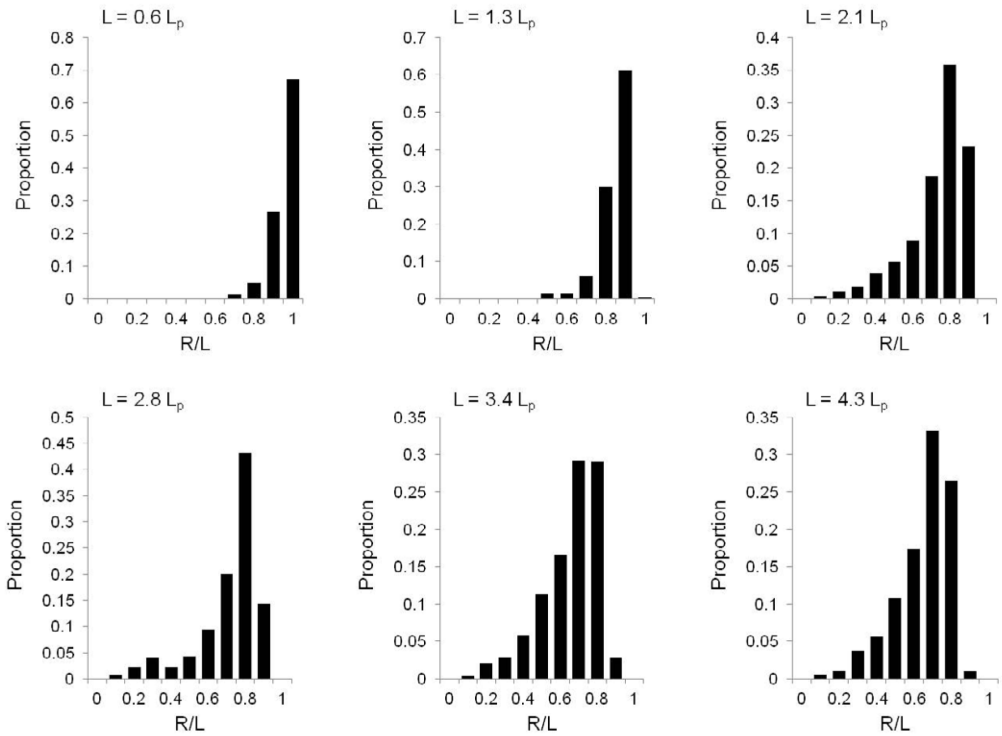
b)


L = 1.7 Lp
L = 3.3 Lp
L = 5.6 Lp
L = 7.2 Lp
L = 8.9 Lp
L = 11.1 Lp
Proportion
R/L

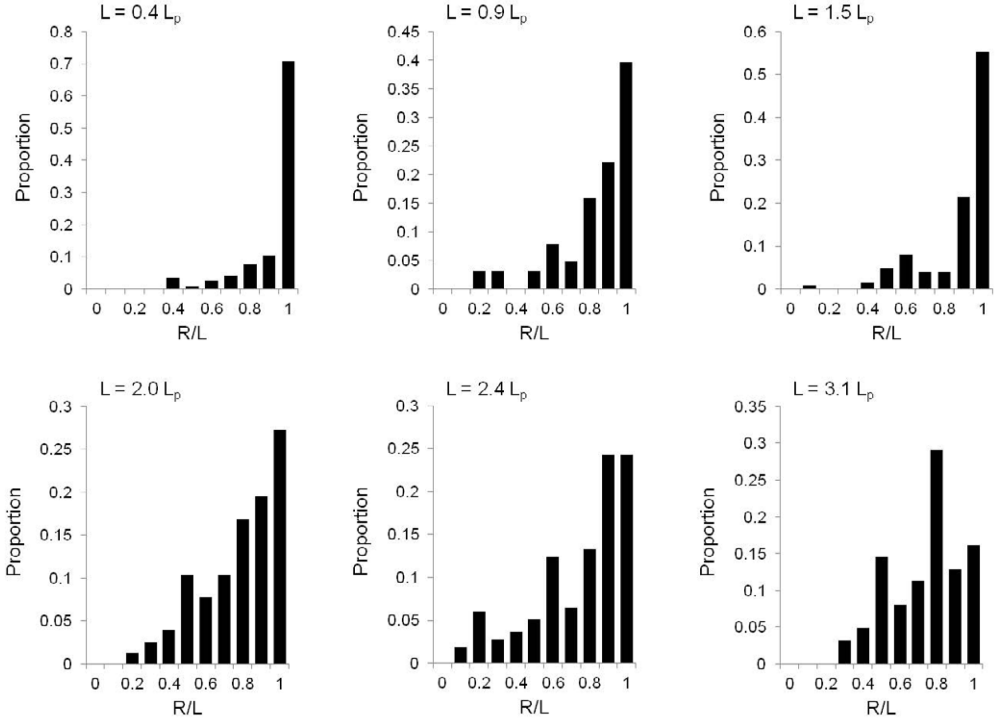
c)


L = 0.7 L$_p$
L = 1.5 L$_p$
L = 2.5 L$_p$
L = 3.2 L$_p$
L = 4.0 L$_p$
L = 5.0 L$_p$
Proportion
R/L

d)


L = 0.6 L$_p$
L = 1.3 L$_p$
L = 2.1 L$_p$
L = 2.8 L$_p$
L = 3.4 L$_p$
L = 4.3 L$_p$
Proportion
R/L

e)


L = 0.4 L_p
L = 0.9 L_p
L = 1.5 L_p
L = 2.0 L_p
L = 2.4 L_p
L = 3.1 L_p
Proportion
R/L

f)

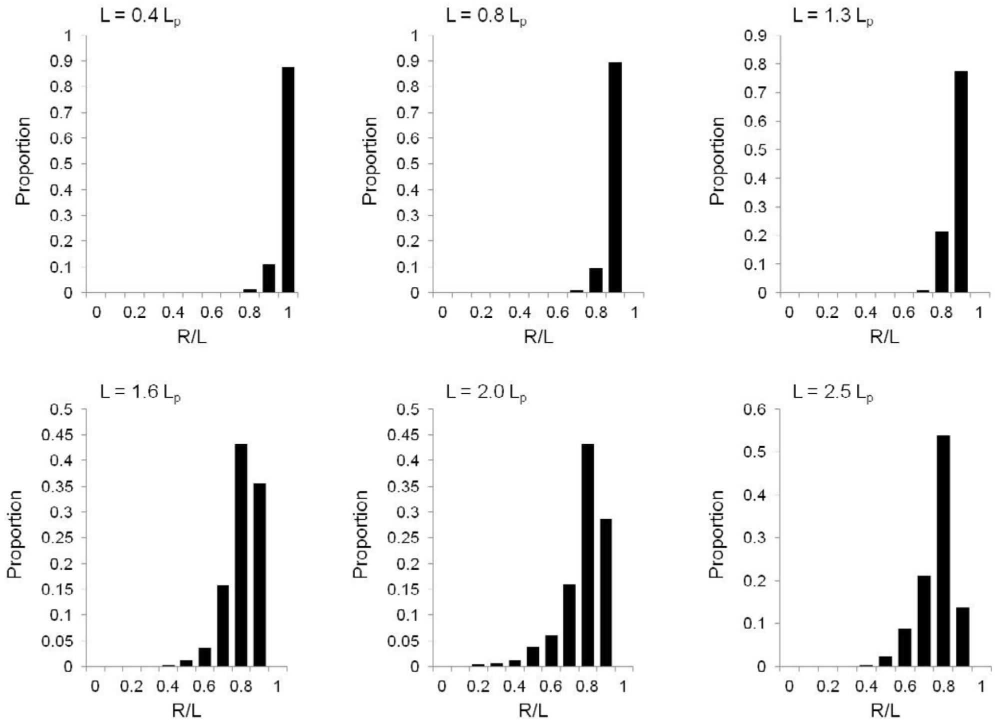

L = 0.4 L_p
L = 0.8 L_p
L = 1.3 L_p
L = 1.6 L_p
L = 2.0 L_p
L = 2.5 L_p
Proportion
R/L

Figure S3. Mean-square end-to-end distance as a function of the length of the chain obtained by Monte-Carlo simulation in presence of an inertial energy equal to 0.01 and 5 arbitrary units and for thermal energy of the system, kT, equal to 3 arbitrary unit, and their corresponding L_p calculated using the Worm-Like Chain model. The flexibility was constant at 1.05. See the Material and Methods sections for the definition of inertial and thermal energies. Error bars are 95% confidence intervals.