Universal Shape properties of Mesoscopic Polymer stars and their Aggregates

O. Kalyuzhnyi\(^1\), J. M. Ilnytskyi\(^1\),

\(^1\) ICMP, NASU, Lviv, Ukraine,


Application of star polymer

- Viscosity modifiers
- Micelle formation for target drug delivery
- Building blocks of polymer hydrogels

Polymer shape characteristics

- The gyration tensor \( Q_i \) of the polymer chain:
  \[
  Q_i = \frac{1}{N} \sum_{n=1}^{N} \mathbf{r}_n^i - \mathbf{r}_N^i \mathbf{r}_n^i, \quad i = 1, \ldots, d.
  \]

  Here \( \mathbf{r}_n^i \) is the \( i \)-th Cartesian coordinate of \( n \)-th monomer. \( Q_i \) is the center of mass for the polymer chain.

- Radius of gyration: \( R_g = \sqrt{\langle Q_i^2 \rangle} \).

- Average center-end distance:
  \[
  \langle r_{CE}^2 \rangle = \frac{1}{N} \sum_{n=1}^{N} \mathbf{r}_n \mathbf{r}_n \tilde{x}_n^2.
  \]

- The stretch ratio:
  \[
  \tilde{a}(f) = \frac{R_g^2}{\langle r_{CE}^2 \rangle}.
  \]

- Shape factor:
  \[
  \tilde{g}(f) = \frac{R_g^2}{\langle r_{CE}^2 \rangle}.
  \]

- The asphericity of the polymer chain is defined as:
  \[
  A = \frac{d}{2} \frac{R_g^2}{\langle r_{CE}^2 \rangle}.
  \]

- The level of "spherization":
  \[
  \tilde{F}(f) = \frac{A(f)}{\tilde{d}(f)}.
  \]

Simulation approach

In our study we follow the mesoscopic method of dissipative particle dynamics (DPD) method. We consider the DPD approach as described in Ref. [3], the length is represented in units of the diameter of soft bead, and the energy scale is assumed to be \( \tau = k_B T = 1 \), where \( k_B \) is Boltzmann constant. The temperature, time is expressed in \( \tau = 1 \). The monomers are connected via harmonic springs, strains which results in the force:

\[
F_{ij}^{\text{spring}} = -k_{ij} \tilde{r}_{ij}.
\]

The non-bonded forces contain three contributions:

\[
F_{ij}^{\text{non-b}} = F_{ij}^{\text{r}} + F_{ij}^{\text{g}} + F_{ij}^{\text{h}}.
\]

The expressions for all these three contributions are given in Ref. [8]:

\[
F_{ij}^{\text{r}} = 4 \epsilon \left( \frac{\tilde{r}_{ij}}{\tilde{\rho}} - 1 \right) \tilde{\rho}, \quad \tilde{\rho} < 1,
\]

\[
F_{ij}^{\text{g}} = -\omega(\tilde{\rho}) \tilde{\rho} \left( \tilde{r}_{ij} + \tilde{r}_{ji}^{\text{rep}} \right),
\]

\[
F_{ij}^{\text{h}} = \omega(\tilde{\rho}) \tilde{\rho} \frac{\tilde{r}_{ij} \tilde{r}_{ji}^{\text{rep}}}{\tilde{r}_{ij}^{\text{rep}}},
\]

where \( \omega(\tilde{\rho}) \) is a repulsion coefficient, \( \tilde{\rho} \) is the amplitude for the conservative repulsive force. The dissipative force has an amplitude \( \gamma \) and decays with the distance according to the weight function \( w(\tilde{\rho}) \). The amplitude for the random force is \( \sigma \), and the respective weight function is \( w(\tilde{\rho}) \). A Gaussian random variable.

Results

- A Star polymer, the role of solvent quality: we consider the star shaped polymers with the number of arms \( f = 8 \). We have studied two types of arms: \( f_1 \) arms with constant solubility and \( f_2 \) arms with variable solubility [3].

Vesicle shape at \( N = 30 \):

<table>
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<th>B</th>
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<tbody>
<tr>
<td>0.0</td>
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<tr>
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<td>0.5</td>
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<tr>
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<td>0.7</td>
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<tr>
<td>0.8</td>
<td>0.9</td>
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<tr>
<td>1.0</td>
<td>1.1</td>
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</tbody>
</table>

Molecular architectures used in this study: (a) linear diblock copolymers, (b) miktoarm star-polymer, (c) diblock 1 star-copolymer and (d) diblock 2 star-copolymer. Where hydrophobic beads (type A) are shown in blue, hydrophilic (type B) in yellow, central bead is shown in red.

References