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Molecular Dynamics Simulations of Strain-Induced Phase Transition of Poly(ethylene oxide) in Water

Sergii Donets[†] and Jens-Uwe Sommer^{*,†,‡}

[†]*Institute Theory of Polymers, Leibniz-Institute of Polymer Research, 01069 Dresden,
Germany*

[‡]*Technische Universität Dresden, Institute for Theoretical Physics, 01069 Dresden,
Germany*

E-mail: sommer@ipfdd.de

Phone: +49 (0)351 4658 750. Fax: +49 (0)351 4658 752

Abstract

We study dilute aqueous solutions of PEO oligomers which are subject to an elongating force dipole acting on both chain ends using atomistic molecular dynamics. By increasing the force liquid-liquid demixing can be observed at room temperature far below the lower critical solution temperature. For forces above 35 pN fibrillar nanostructures are spontaneously formed related with a decrease in hydrogen bonding between PEO and water. Most notable is a rapid decrease of bifurcated hydrogen bonds during stretching which can also be observed for isolated single chains. The phase-segregated structures display signs of chain ordering, but a clear signature of crystalline order is not obtained during the simulation time, indicating a liquid-liquid phase transition induced by chain stretching. Our results indicate that the solvent quality of the aqueous solution of PEO depends on the conformational state of the

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3 chains, which is most likely related with the specific hydrogen-bond induced solvation
4 of PEO in water. The strain-induced demixing of PEO opens the possibility to ob-
5 tain polymer fibers with low energy costs since crystallization starts via strain-induced
6 demixing in the extended state only.
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10 11 12 13 **Introduction** 14 15

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17 Fibers made of extended and crystallized polymer chains can have extraordinary strength
18 such as a yield stress in the order of 10 GPa.¹ However, to obtain such materials in practice
19 the stretching of chains has to be achieved against the interactions of the crystal-forming
20 polymer which requires high processing energies and still leads to imperfect molecular ar-
21 rangements. Metastable polymer solutions, which can undergo a disorder-to-order transition
22 in response to stress are therefore of great interest for developing new low energy solidification
23 techniques. The solidification with minimal energy input will drastically reduce the costs for
24 producing polymeric materials.² Natural silk is an example of an efficient system that pro-
25 duces high performance and biodegradable materials with superb mechanical properties.^{3,4}
26 The material being mechanically drawn from the silk gland into the external air undergoes a
27 liquid-to-solid phase transition.⁴ The structural variation of these semi-crystalline polymers
28 is, however, very wide. For instance, the crystallites may consist of β -sheets, α -helical coiled-
29 coils, collagen helices etc.⁴ In addition, the ordered crystalline and disordered amorphous
30 domains possess high and low hydrogen bonding densities, respectively.⁴ This biological com-
31 plexity hampers a physical understanding of the process of fiber formation. On the other
32 hand, an aqueous solution of poly(ethylene oxide) (PEO) is a potential candidate also capa-
33 ble to undergo a phase transition as a result of loss of the hydrated structure. Thus, PEO
34 can serve as suitable model system to study strain-induced phase transition which may guide
35 the understanding of complex biological composites such as spider silk.
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54 PEO is one of the best studied and widely used polymer in biomedical and technological
55 applications.⁵ PEO is an amphiphilic, low toxic and water-soluble homopolymer with a gen-
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3 eral formula $\text{CH}_3 - [\text{O} - \text{CH}_2 - \text{CH}_2]_n - \text{O} - \text{CH}_3$.⁶ In addition to the solubility in water, PEO
4 is also soluble in organic solvents due to its unique chemical structure with both hydrophilic
5 and hydrophobic character. Its excellent solubility in water at ambient conditions can be
6 explained by the match in the oxygen - oxygen interdistance in the PEO and in the structure
7 of pure water.⁷ In contrast, decreased water solubility of its homologues, i.e poly(methylene
8 oxide) (PMO) and poly(propylene oxide) (PPO), can be explained by the poor match in
9 oxygen - oxygen interdistances.⁷ However, the solubility of PEO decreases upon heating
10 and its aqueous solutions undergo phase separation at a lower critical solution temperature
11 (LCST).⁸ The intriguing properties of PEO in water were already considered in previous
12 simulation studies using different force fields and degree of coarse-graining.⁹⁻¹³ Recently,
13 Dahal and Dormidontova^{14,15} have studied the hydration, static and dynamic properties of
14 PEO chains both in aqueous solutions and grafted to the surface using atomistic molecular
15 dynamics simulations.

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A tensile stress introduced into the amorphous material can enhance the phase separation, if the binding or coordination of water with respect to the monomers is reduced by stretching. Holland *et al.*² have found indication for transient crystallization of PEO in dilute solutions under flow. In a very recent work by Semenov *et al.*¹⁶ the formation of stable jets from dilute PEO solutions has been explained by an increase of the intermolecular interactions between the chains due to extension-induced orientation of macromolecules. In a combined experimental and computational study, Netz *et al.*¹⁷ have shown that stretching of single PEO chains in water is related with a release of hydrogen-bonded water which can compensate the entropic forces at high strains.

In this work we will give evidence that stretching of PEO chains in water leads indeed to liquid-liquid phase separation far below the LCST. This is demonstrated by applying a force dipole to both ends of the chains which are otherwise freely movable in the solution. We argue that this observation is related to a change in the state of hydrogen bonding due to a change in the population of conformational states involving two successive oxygens

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3 from gauche to trans. This is in contrast to the usual paradigm of polymer physics that
4 the polymer-solvent interaction parameter, often referred to as the χ -parameter,¹⁸ does not
5 depend on the conformational state of the chains. As a consequence stretching of PEO chains
6 in aqueous solutions involves forces typical for flexible polymers and only in the extended
7 state crystallization can set in within the segregated polymer phase.
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All simulations in this work were performed by using the molecular dynamics package LAMMPS¹⁹ with a velocity-Verlet integrator and an integration time step of 2 fs. MD simulations were conducted either in the isothermal-isobaric (NPT) ensemble or in the isothermal-isochoric (NVT) ensemble. The temperature and pressure were kept constant using Nose-Hoover thermostat and barostat with relaxation times of 0.2 ps and 2.0 ps, respectively. The Lennard-Jones interactions were switched to zero between 8 Å and 12 Å. The real space electrostatic interactions were cutoff at 12 Å, while the long-range electrostatic interactions were evaluated using particle-particle particle-mesh method. Bonds and angles in water as well as bonds involving hydrogen and any other atom were kept rigid using the SHAKE algorithm with the relative tolerance of 10^{-4} . The revised version of the CHARMM ether force field (c35r) was used for PEO.²⁰ Water was represented using TIP3P model. The simulated system consists of 100 PEO chains (each with total 46 ether units) and 133341 water molecules in a periodic box with following dimensions: $x = y = 150$ Å and $z = 210$ Å. The concentration is well below overlap of the PEO chain under the given solvent condition. Therefore, entanglement constraints should not play an important role. For the calculation of hydrogen bonds we used geometrical criteria following the classical work of Luzar and Chandler: $d(\text{D-A}) \leq 3.5$ Å and $\angle(\text{D-H-A}) \leq 30^\circ$.²¹ The conclusions about our findings of the conformation-dependent hydrogen bonding remains unchanged if different cut-off criteria are used such as proposed in Ref.¹⁷ The MD results were mainly

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3 analyzed using VMD software.²²
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5 Comparison of the computed force-extension curve with that measured using atomic force
6 microscopy (AFM)¹⁷ for a single molecule, see Fig. S1 (a), shows a quantitative agreement
7 with experiment and confirms that the properties of PEO in water are well described by
8 classical MD simulations. Simulations were carried out at temperature of $T = 298$ K far
9 below the LCST of these oligomers which is located approximately at $T_{LCST} = 423$ K in our
10 model system.
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19 Results and Discussion

20 Force-induced phase-separation

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23 Classical MD simulations were performed to study the tensile deformation and stress-
24 induced phase transition behavior of PEO in solution at atomic level. To this end, 100 PEO
25 molecules were solvated by water in a rectangular box with following dimensions: $x = y =$
26 150 Å and $z = 210$ Å. The larger size in z-direction is to ensure that the fully stretched
27 oligomer chain will not interact with itself through the periodic boundary conditions. The
28 oligomer considered was PEO46. The system first was equilibrated at room temperature
29 and then a constant mechanical force dipole was applied to two end points on the PEO
30 molecules. The sum of the forces acting on both chain ends is exactly zero, therefore center
31 of mass motion is unrestricted by the applied forces. This implies that the ends are not
32 fixed in space and the chains can rearrange in different phases in response to the external
33 field. In this way the distances between two end points were continuously elongating until
34 a plateau for the averaged end-to-end distance for a given value of externally applied force
35 was reached.
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51 First of all, it is worth to note that at temperature of 298 K and without external
52 forces the oligomer chains are fully dissolved in water with homogeneous distribution in the
53 simulation box. Only upon heating at around $T = 373$ K the PEO-water solution starts to
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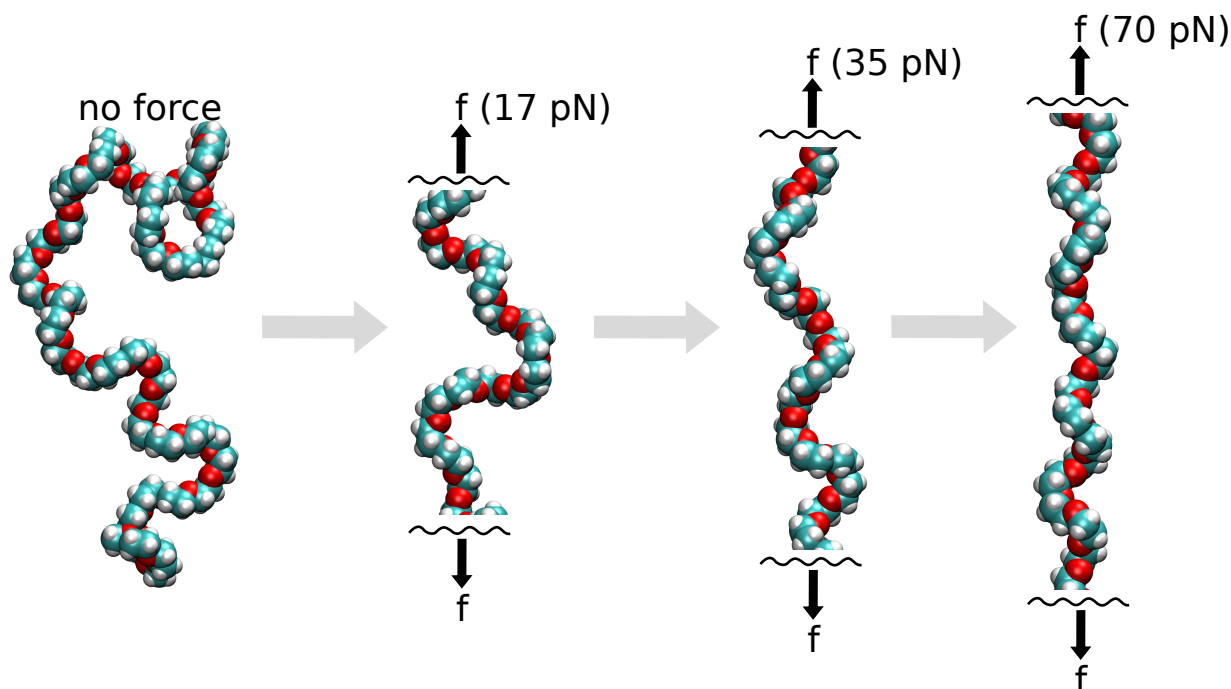


Figure 1: Snapshots of an individual PEO chain picked from the simulation box under various values of the external force. Black arrows show the directions of the applied forces. Except for the force-free chain (left) only a short sequence is displayed to illustrate the change in conformation.

phase-separate. It is known that PEO exhibits lower critical solution temperature (LCST) behavior for high enough molecular weight. The LCST of PEO with a molecular weight greater than 10^4 Da approaches an asymptote at temperature of ~ 373 K.⁸ On the other hand, according to the theoretical predictions based on the Flory-Huggins theory, which are supported by experimental measurements, the phase separation of PEO with a molecular weight of $\sim 2 \cdot 10^3$ Da (which was considered in this study) should occur at slightly elevated temperatures in the range of 410 – 440 K.⁸ In our own simulations using atomistic model the increase in the temperature from $T = 373$ K up to $T = 423$ K results in the formation of spherical aggregates of PEO molecules. The decreased solubility of PEO in water upon heating can be explained by the fact that at higher temperatures the hydrogen bond network between the ether oxygens of PEO and surrounding water molecules breaks due to thermal fluctuations, allowing the PEO-water system to demix with the formation of a two-phase region.

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3 During stretching the PEO conformations are altered significantly by the applied forces,
4 as shown in Fig. 1. As we show later in more detail, deformation of the chains in response to
5 external mechanical forces leads to the formation of highly oriented fibrillar nanostructures.
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7 However, the stress-induced phase separation can only be observed if the load is above some
8 threshold value.
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13 As expected, the deformation of individual chains grows monotonously with the applied
14 force. In Fig. S1 (a) we compare the force-extension curve of the chains after relaxation
15 with the corresponding results for single chains. Inspection of the local structure of bonds
16 clearly proves that valence angles are not changed even up to a very high force of 350 pN
17 and the deformation is the result of changing the distribution of torsion angles related with
18 a decrease of conformational entropy.
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25 Local conformations can be classified based on the dihedral angles involving carbon and
26 oxygen atoms along the backbone of the PEO chains. In Fig. 2 (a,c) we show probability
27 densities for the O-C-C-O dihedral angles. We define populations of trans (gauche) con-
28 formers as the ratio between the area for the trans (gauche) conformation and the total area
29 under the curve. The corresponding results are displayed in Fig. 2 (b,d). It is worth to note
30 that without external forces the O-C-C-O torsion angles have a preference for the gauche
31 conformation, which is known as the gauche effect.²³ This is displayed by the black curve
32 in Fig. 2 (a). The transformation of gauche conformers into the trans conformers requires
33 a relaxation time which also depends on the applied force. For instance, at time of 2.0 ns
34 and force of 350 pN most of gauche conformers are transformed into trans conformers with
35 population of about 98 %, see Fig. 2 (a,b). For smaller magnitudes of force, the population
36 of trans conformers can further increase as time goes on, see Fig. 2 (c). This indicates a
37 cooperative process between several chains which takes place at lower forces. In Fig. 2 (d)
38 we display the two populations at the maximum relaxation time which we have applied to
39 the systems. An abrupt change in the populations from gauche to trans occurs in the range
40 from 70 - 140 pN, as indicated by the arrows.
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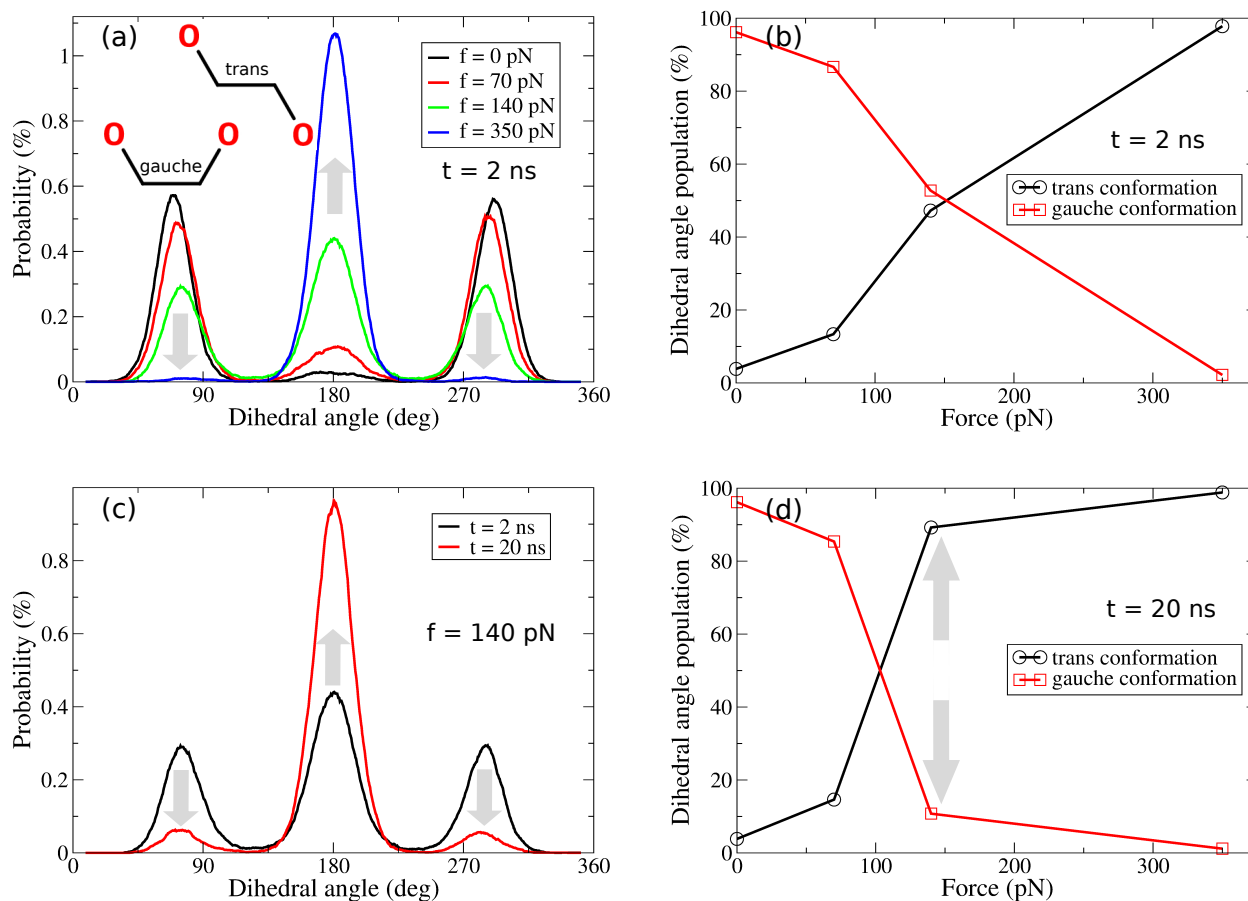


Figure 2: Normalized probability distributions of O-C-C-O digedral angles for different applied forces (a,c) and corresponding populations of conformers of PEO oligomers (b,d). The temperature is $T = 298$ K.

Without an external force the PEO chains are in good solvent conditions and do not aggregate. To study the impact of stretching the chains on the solubility, the two-dimensional intermolecular pair correlation functions (PCF) between the PEO monomers were calculated. The PCF is defined as:

$$g(r) = \lim_{dr \rightarrow 0} \frac{p(r)}{2\pi N(N/A)rdr} \quad (1)$$

where r is the distance between the pair of monomers, $p(r)$ denotes the average number of monomer pairs found at a distance r and $r + dr$, while N and A are the number of reference particles and the total area of the layer perpendicular to the direction of the applied force, respectively. A two-dimensional PCF takes into account only the correlations within the layers perpendicular to the force and, as a result, this eliminates the correlations

arising from the alignment of PEO chains along the force. These results are displayed in Fig. 3. The correlation intensities strongly depend on both the magnitude of the force

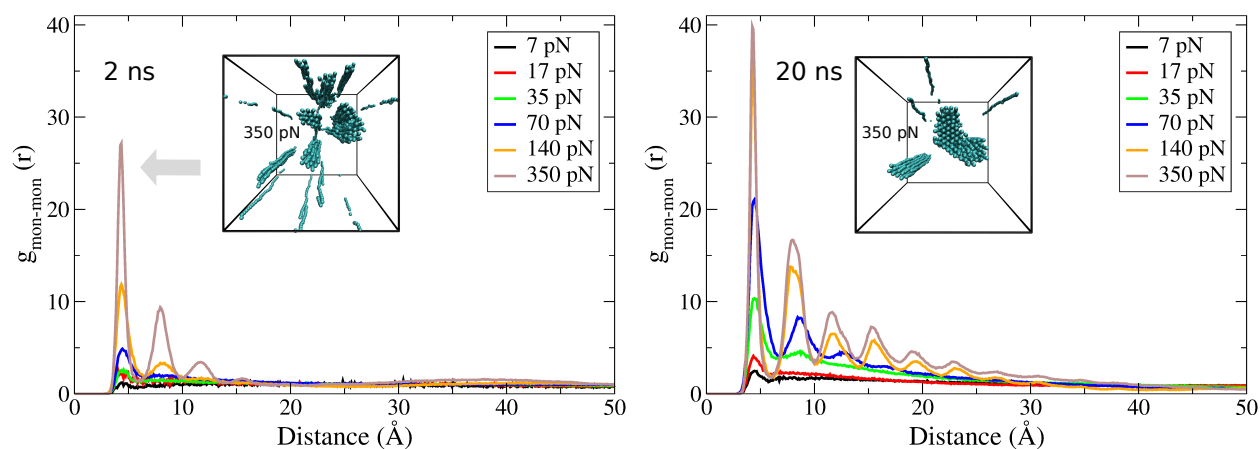


Figure 3: Two-dimensional intermolecular pair correlation function (PCF) between the monomers of PEO oligomers at times of 2 ns and 20 ns, respectively. The insets illustrate the PEO molecules in monomer representation (water molecules are omitted for clarity). The temperature is $T = 298$ K.

and elapsed simulation time (compare left versus right plots). Initially at time of 2.0 ns there is a big difference in correlation intensities for different forces, especially for the one of 350 pN. Nevertheless, the correlations are building-up with time and become relevant even for smaller forces, such as 35 pN and 70 pN, as it is illustrated by the green and blue curves in Fig. 3, respectively. As the order parameter indicating the phase separation one can use the appearance of higher order peaks in the PCF. Given the relaxation time of 20 ns in our simulations, deformation-induced phase separation of PEO can be thus observed above a threshold value of the force of about 35 pN. The appearance of fibrillar clusters can be detected by an oscillating pair correlation function in Fig. 3 (right) which, however, decreases rapidly with the distance. A more detailed analysis of the scattering data, not shown here, indicates the absence of crystalline order yet. Thus, the resulting clusters should be considered as a simple demixed phase of stretched oligomers. However, it is expected that the once demixed bundles occur they are able to crystallize given a sufficiently long time for nucleation and possibly further reorganization.

To understand the origin of deformation-induced phase separation, we relate the local

conformational changes (as shown in Fig. 2) with the change in the number of hydrogen bonds. In Fig. 4 we display our calculations of the number of intramolecular bifurcated and single hydrogen bonds, respectively. As it was mentioned above, at high enough strains the

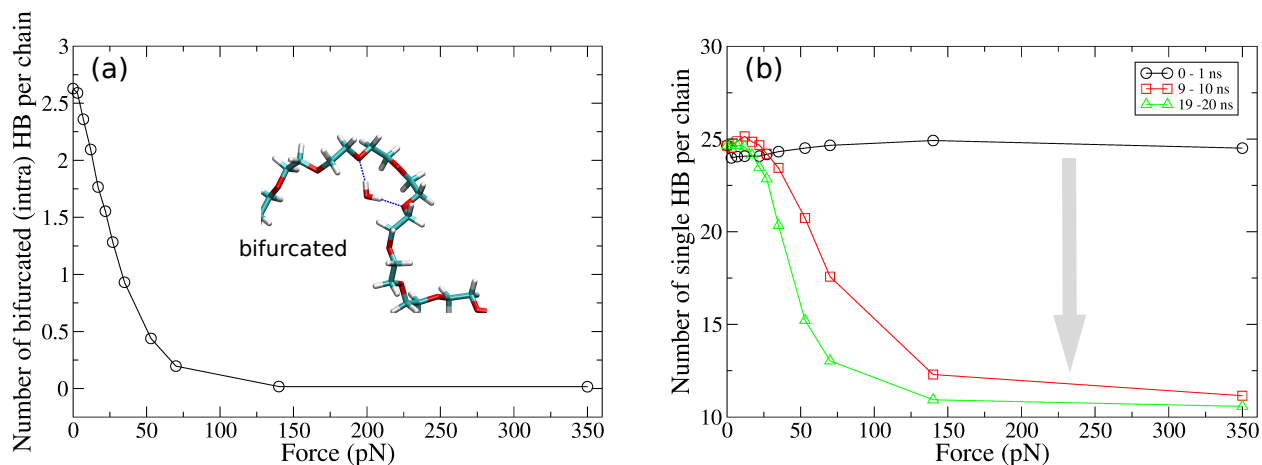


Figure 4: (a) Number of intramolecular bifurcated (obtained by averaging over last 10 ns of the simulation) as well as (b) single hydrogen bonds per oligomer chain as a function of force. The temperature is $T = 298$ K.

helical structures (enhancement of the gauche O-C-C-O and trans C-O-C-C populations) of PEO chains undergo a strong deformation, which ultimately leads to a drastic reduction in the number of intramolecular bifurcated hydrogen bonds, involving two ether oxygens within the oligomer chain and one water molecule, as shown in Fig. 4 (a). This result corresponds to that of Ref.¹⁷ These bifurcated hydrogen bonds almost completely destroyed already for the force of 70 pN. This can be explained by the steric hindrance due to the fact that hydrogen atoms of methylene bridges in trans conformation occupy certain amount of space between two adjacent oxygens, which prevents the formation of bifurcated hydrogen bonds. The number of single hydrogen bonds is displayed in Fig. 4 (b), which are also much reduced if the force reaches values of the order of 70 pN. This finding may appear somewhat counterintuitive, since the stretching of oligomers results in more extended PEO conformations in which all ether oxygens become exposed to the surrounding water molecules. However, the simulation results indicate a more than twofold reduction in the number of single hydrogen bonds from ~ 25 down to ~ 11 per one oligomer molecule for large enough

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3 forces, as illustrated by the arrow in Fig. 4 (b). A possible explanation is that the tensile
4 deformation of PEO oligomers leads to an increase in their hydrophobicity due to favorable
5 van der Waals interactions. As a consequence the PEO chains start to segregate, eventually
6 resulting in the formation of the fibrillar nanoclusters. This reduces the surface between
7 PEO and water and, hence, less ether oxygens can be exposed to water molecules.
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13 This conclusion is supported by the trends in interaction energies (which include the van
14 der Waals and Coulomb energies) between PEO and PEO, and between PEO and water, as
15 illustrated in Fig. S4. In this regard, it is worth to note that for a single oligomer chain
16 we do not observe a reduction in the number of single hydrogen bonds, see Fig. S3 (a).
17 In addition, we may assume that large aggregates will grow on the expense of smaller ones
18 with increasing time, a process known as Ostwald ripening, with the formation of one large
19 aggregate to minimize the total surface area, since the PEO oligomers are energetically more
20 stable in the interior of the aggregate.
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31 Discussion and Conclusion

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34 Our results clearly indicate that the stretching of oligomer chains initiates interchain
35 aggregation, which ultimately leads to the phase separation of the PEO solution with the
36 formation of highly oriented fibrillar nanostructures. This agrees with experimental results
37 regarding the fiber formation, induced by shearing of PEO-water solution using SIPLI and
38 SAXS/WAXD techniques.² In this respect also the work by Semenov *et al.*¹⁶ should be
39 noted where the authors explain their findings of the formation of stable jets from dilute
40 PEO solutions by enhanced intermolecular interactions of elongated macromolecules. We
41 found that the strain-induced phase transition of PEO oligomers is associated with the
42 reduction in the number of intramolecular bifurcated as well as single hydrogen bonds. The
43 intramolecular bifurcated hydrogen bonds are presumably responsible for the stabilization
44 of the local helical structures.²⁴ Accordingly, at high enough magnitudes of the force the
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3 helical structure elements unfold and most of gauche conformers transform into the trans
4 conformers.
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7 The strain-induced demixing transition occurs due to the favorable interaction energies
8 between the PEO chains, i.e. primarily due to van der Waals interactions. In addition, the
9 electrostatic interactions between PEO and water molecules become unfavorable as force
10 increases, which further encourages the oligomer clustering, resulting in the loss of the hy-
11 drated structure. We note that the fibrillar structures we have obtained in our simulations
12 are not crystalline but correspond to a concentrated polymer phase consisting of (partially)
13 stretched chains segregated from water.
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21 Summing up, a tensile stress introduced into the PEO-water solution reduces the solu-
22 bility of the former and, if there are other oligomer chains present in the simulation box,
23 leads to a phase separation of PEO from water. In terms of polymer physics this corre-
24 sponds to an increase of the χ -parameter due to elongation of the chains, or, in other words
25 a conformation-dependent χ -parameter between PEO and water. Thus, we expect a change
26 in the whole phase diagram of PEO in water which contains besides the temperature and
27 concentration also the force as a coordinate. As a consequence one can expect a shift in
28 the LCST-line in the concentration-temperature space induced by the external force. The
29 demixed state is a possible precursor to crystallization of the extended chains and thus pro-
30 vides the possibility to obtain a low-energy cost stretching-crystallization pathway in the
31 PEO solutions.
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4 stimulating discussions.
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9 Supporting Information Available

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12 Supporting information contains the results about force-extension curves of multiple PEO
13 chains after relaxation and for single chains, as well as the results about the number of
14 hydrogen bonds as a function of force for a single oligomer chain. In addition, intermolecular
15 interaction energies (which include van der Waals and Coulomb energies) between PEO and
16 PEO, and between PEO and water are also provided. This material is available free of
17 charge via the Internet at <http://pubs.acs.org/>.
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26 References

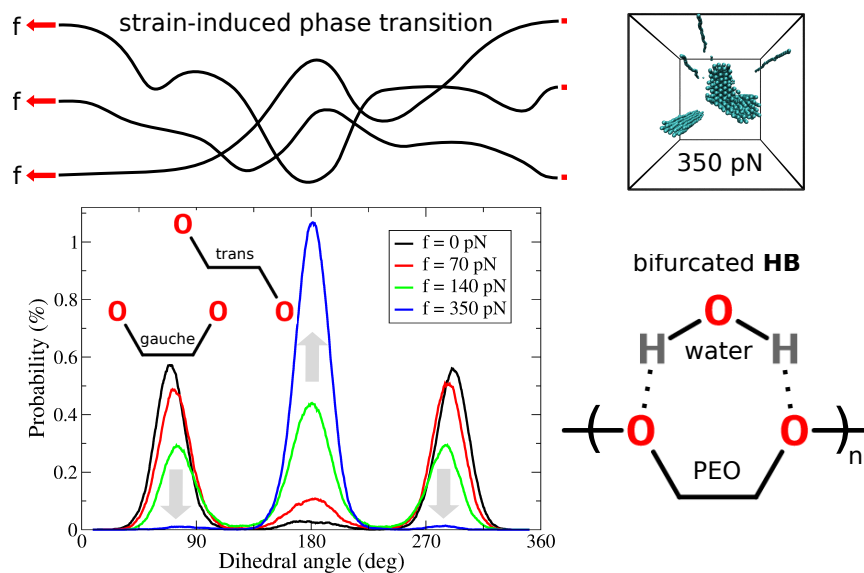
- 27
28
29
30 (1) OConnor, T. C.; Robbins, M. O. Chain Ends and the Ultimate Strength of Polyethylene
31 Fibers. *ACS Macro Letters* **2016**, *5*, 263–267.
32
33
34 (2) Holland, C.; Vollrath, F.; Ryan, A. J.; Mykhaylyk, O. O. Silk and Synthetic Polymers:
35 Reconciling 100 Degrees of Separation. *Adv. Mat.* **2012**, *24*, 105–109.
36
37
38 (3) Holland, C.; Terry, A.; Porter, D.; Vollrath, F. Natural and Unnatural Silks. *Polymer*
39 **2007**, *48*, 3388 – 3392.
40
41
42 (4) Walker, A. A.; Holland, C.; Sutherland, T. D. More Than One Way to Spin a Crystallite:
43 Multiple Trajectories Through Liquid Crystallinity to Solid Silk. *Proc. R. Soc. B* **2015**,
44 *282*, 1–9.
45
46
47 (5) Wang, S.; Larson, R. G. A Coarse-Grained Implicit Solvent Model for Poly(ethylene
48 oxide), CnEm Surfactants, and Hydrophobically End-Capped Poly(ethylene oxide) and
49
50
51
52
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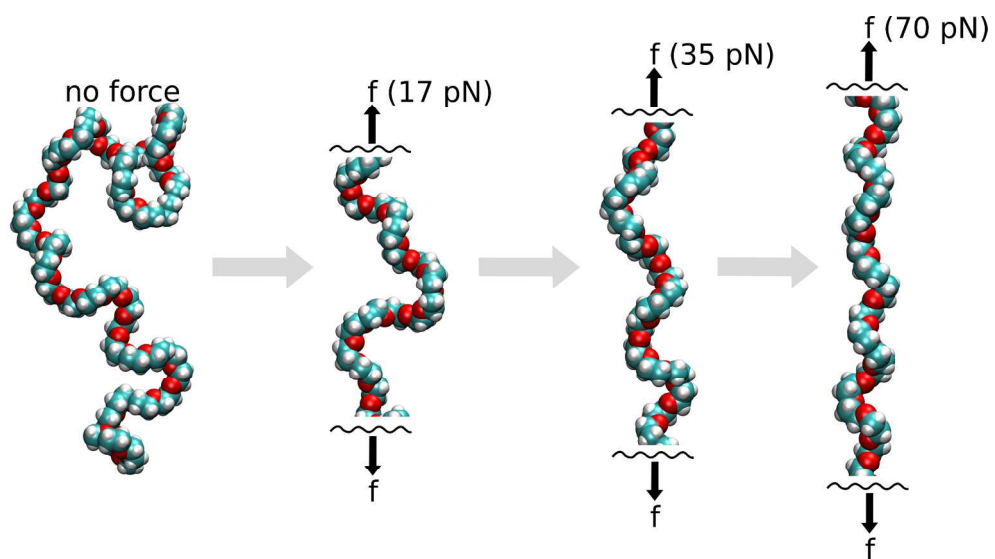
- 1
2
3 Its Application to Micelle Self-Assembly and Phase Behavior. *Macromolecules* **2015**,
4 *48*, 7709–7718.
5
6
7
8 (6) Hezaveh, S.; Samanta, S.; Milano, G.; Roccatano, D. Molecular Dynamics Simulation
9 Study of Solvent Effects on Conformation and Dynamics of Polyethylene Oxide and
10 Polypropylene Oxide Chains in Water and in Common Organic Solvents. *J. Chem.*
11 *Phys.* **2012**, *136*, 124901.
12
13
14
15
16
17 (7) Hammouda, B.; Ho, D. L.; Kline, S. Insight into Clustering in Poly(ethylene oxide)
18 Solutions. *Macromolecules* **2004**, *37*, 6932–6937.
19
20
21
22 (8) Ashbaugh, H. S.; Paulaitis, M. E. Monomer Hydrophobicity as a Mechanism for the
23 LCST Behavior of Poly(ethylene oxide) in Water. *Ind. Eng. Chem. Res.* **2006**, *45*,
24 5531–5537.
25
26
27
28
29 (9) Bedrov, D.; Pekny, M.; Smith, G. D. Quantum-Chemistry-Based Force Field for 1,2-
30 Dimethoxyethane and Poly(ethylene oxide) in Aqueous Solution. *J. Phys. Chem. B*
31 **1998**, *102*, 996–1001.
32
33
34
35 (10) Dormidontova, E. E. Role of Competitive PEOWater and WaterWater Hydrogen Bond-
36 ing in Aqueous Solution PEO Behavior. *Macromolecules* **2002**, *35*, 987–1001.
37
38
39
40 (11) Dormidontova, E. E. Influence of End Groups on Phase Behavior and Properties of
41 PEO in Aqueous Solutions. *Macromolecules* **2004**, *37*, 7747–7761.
42
43
44
45 (12) Lee, H.; de Vries, A. H.; Marrink, S.-J.; Pastor, R. W. A Coarse-Grained Model for
46 Polyethylene Oxide and Polyethylene Glycol: Conformation and Hydrodynamics. *J.*
47 *Phys. Chem. B* **2009**, *113*, 13186–13194, PMID: 19754083.
48
49
50
51 (13) Starovoytov, O. N.; Borodin, O.; Bedrov, D.; Smith, G. D. Development of a Polarizable
52 Force Field for Molecular Dynamics Simulations of Poly (Ethylene Oxide) in Aqueous
53 Solution. *J. Chem. Theory Comput.* **2011**, *7*, 1902–1915, PMID: 26596451.
54
55
56
57
58
59
60

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2
3
4 (14) Dahal, U. R.; Dormidontova, E. E. The Dynamics of Solvation Dictates the Conforma-
5 tion of Polyethylene Oxide in Aqueous, Isobutyric Acid and Binary Solutions. *Phys.*
6 *Chem. Chem. Phys.* **2017**, *19*, 9823–9832.
7
8
9
10 (15) Dahal, U. R.; Wang, Z.; Dormidontova, E. E. Hydration and Mobility of Poly(ethylene
11 oxide) Brushes. *Macromolecules* **2017**, *50*, 6722–6732.
12
13
14 (16) Malkin, A. Y.; Semakov, A. V.; Skvortsov, I. Y.; Zatonskikh, P.; Kulichikhin, V. G.;
15 Subbotin, A. V.; Semenov, A. N. Spinnability of Dilute Polymer Solutions. *Macro-*
16 *molecules* **2017**, *50*, 8231–8244.
17
18
19 (17) Liese, S.; Gensler, M.; Krysiak, S.; Schwarzl, R.; Achazi, A.; Paulus, B.; Hugel, T.;
20 Rabe, J. P.; Netz, R. R. Hydration Effects Turn a Highly Stretched Polymer from an
21 Entropic into an Energetic Spring. *ACS Nano* **2017**, *11*, 702–712, PMID: 27977927.
22
23
24 (18) Gennes, P. G. d. *Scaling Concepts in Polymer Physics*; Cornell University Press, 1979.
25
26
27 (19) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput.*
28 *Phys.* **1995**, *117*, 1–19, (<http://lammmps.sandia.gov>).
29
30
31 (20) Lee, H.; Venable, R. M.; MacKerell, A. D.; Pastor, R. W. Molecular Dynamics Stud-
32 ies of Polyethylene Oxide and Polyethylene Glycol: Hydrodynamic Radius and Shape
33 Anisotropy. *Biophys. J.* **2008**, *95*, 1590–1599.
34
35
36 (21) Luzar, A.; Chandler, D. Effect of Environment on Hydrogen Bond Dynamics in Liquid
37 Water. *Phys. Rev. Lett.* **1996**, *76*, 928–931.
38
39
40 (22) Humphrey, W.; Dalke, A.; Schulten, K. VMD – Visual Molecular Dynamics. *J. Mol.*
41 *Graph.* **1996**, *14*, 33–38, (<http://www.ks.uiuc.edu/Research/vmd/>).
42
43
44 (23) Wang, Y.-L.; Lawrence, R. S.; Lu, Z.-Y.; Laaksonen, A. Molecular Dynamics Study
45 of Aqueous Solution of Polyethylene Oxide: Critical Test of Force Field Models. *Soft*
46 *Materials* **2013**, *11*, 371–383.
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- (24) Heymann, B.; Grubmüller, H. Elastic Properties of Poly(ethylene-glycol) Studied by Molecular Dynamics Stretching Simulations. *Chem. Phys. Lett.* **1999**, *307*, 425 – 432.

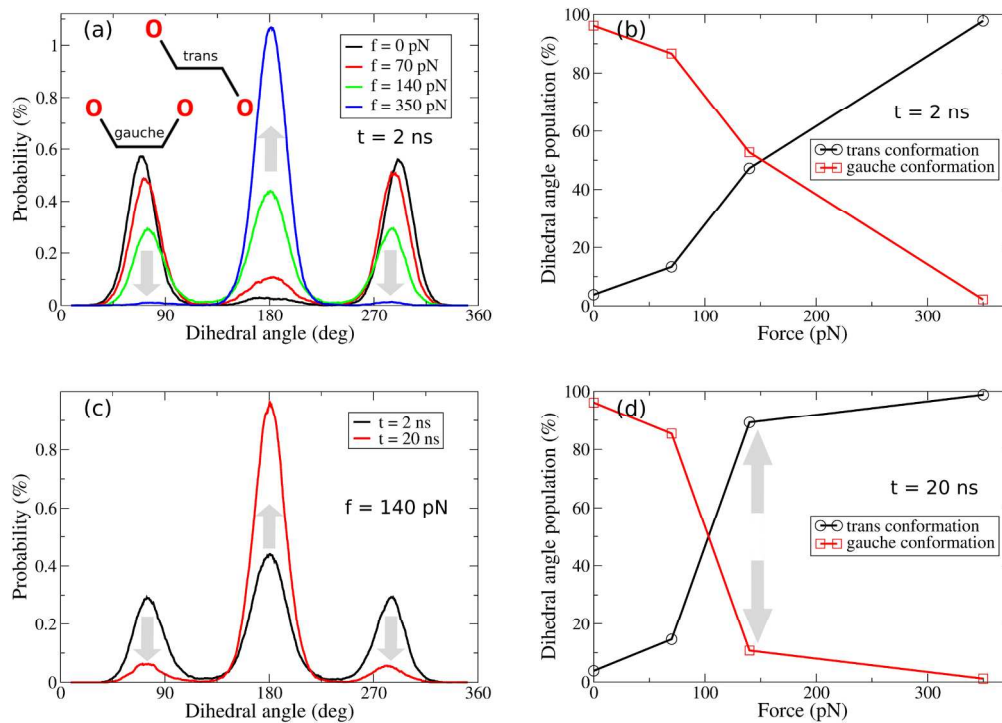
TOC graphic





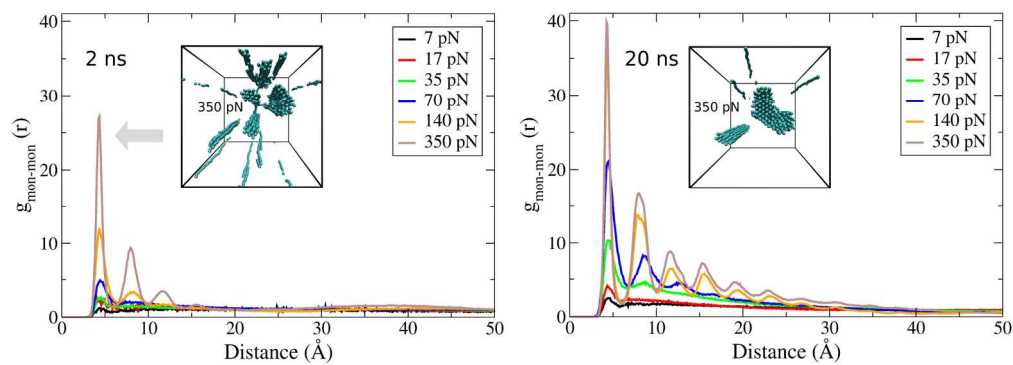
Snapshots of an individual PEO chain picked from the simulation box under various values of the external force. Black arrows show the directions of the applied forces. Except for the force-free chain (left) only a short sequence is displayed to illustrate the change in conformation.

177x96mm (300 x 300 DPI)



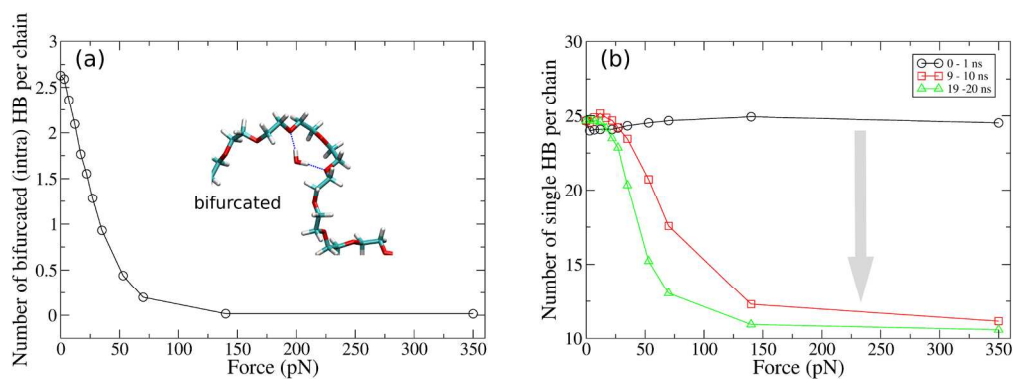
Normalized probability distributions of O-C-C-O digedral angles for different applied forces (a,c) and corresponding populations of conformers of PEO oligomers (b,d). The temperature is $T = 298$ K.

177x127mm (300 x 300 DPI)



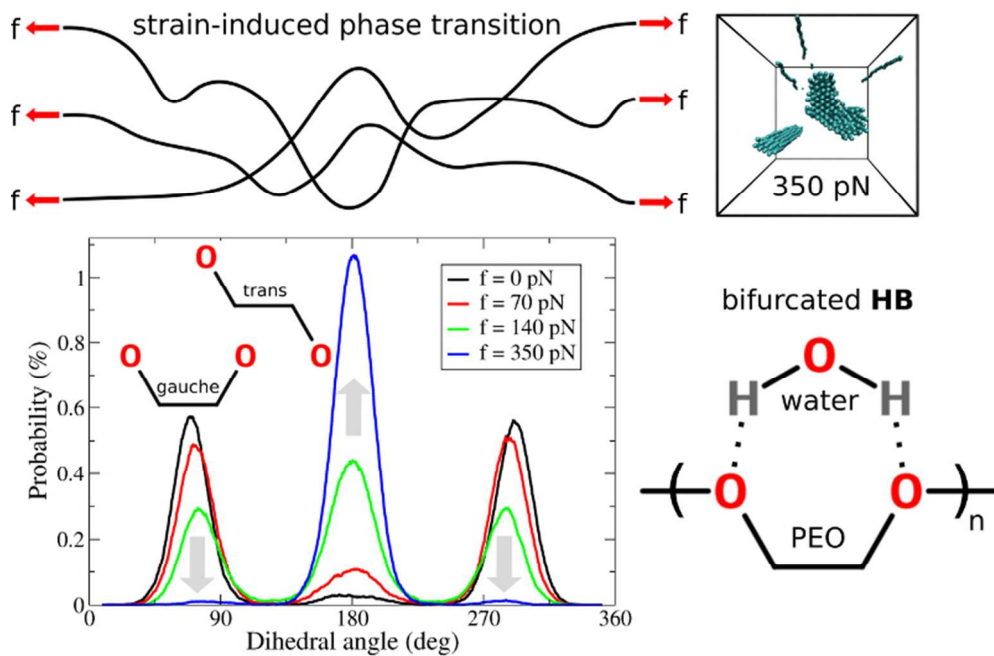
Two-dimensional intermolecular pair correlation function (PCF) between the monomers of PEO oligomers at times of 2 ns and 20 ns, respectively. The insets illustrate the PEO molecules in monomer representation (water molecules are omitted for clarity). The temperature is $T = 298$ K.

177×62mm (300 × 300 DPI)



(a) Number of intramolecular bifurcated (obtained by averaging over last 10 ns of the simulation) as well as
(b) single hydrogen bonds per oligomer chain as a function of force. The temperature is $T = 298$ K.

177x65mm (300 x 300 DPI)



68x44mm (300 x 300 DPI)