

Conformational Properties of Comb-shaped Polyelectrolytes with Negatively Charged Backbone and Neutral Side Chains Studied by a Generic Coarse-grained Bead-and-Spring Model

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Abstract A generic coarse-grained bead-and-spring model, mapped onto comb-shaped polycarboxylate-based (PCE) superplasticizers, is developed and studied by Langevin molecular dynamics simulations with implicit solvent and explicit counterions. The agreement on the radius of gyration of the PCEs with experiments shows that our model can be useful in studying the equilibrium sizes of PCEs in solution. The effects of ionic strength, side-chain number, and side-chain length on the conformational behavior of PCEs in solution are explored. Single-chain equilibrium properties, including the radius of gyration, end-to-end distance and persistence length of the polymer backbone, shape-asphericity parameter, and the mean span dimension, are determined. It is found that with the increase of ionic strength, the equilibrium sizes of the polymers decrease only slightly, and a linear dependence of the persistence length of backbone on the Debye screening length is found, in good agreement with the theory developed by Dobrynin. Increasing side-chain numbers and/or side-chain lengths increases not only the equilibrium sizes (radius of gyration and mean span) of the polymer as a whole, but also the persistence length of the backbone due to excluded volume interactions.

Keywords Comb-shaped polyelectrolyte; Molecular dynamics simulations; Coarse-grained model; Polymer conformations; Persistence length

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INTRODUCTION

Polyelectrolytes are polymers carrying either positively or negatively charged ionizable groups. The properties of such polymers in solutions and at charged surfaces depend on the fraction of dissociated ionic groups, solvent quality for polymer backbone, solution dielectric constant, polymer concentration, salt species and concentration, polymer-substrate interactions, etc.^[1,2] Generally speaking, electrostatic interactions between charges lead to a rich variety of interesting behaviors of polyelectrolytes different from those of uncharged neutral polymers. There exist different ways by which polyelectrolytes can be classified. On the basis of the magnitude of dissociation constant of the ionizable groups, they can be divided into weak and strong types. Based on the strength of electrostatic interactions relative to thermal energy, they can be divided into weakly and strongly charged polyelectrolytes. Depending on whether the polymer carries solely positive, negative, or both types of charges, polyelectrolytes can be classified into three categories: cationic,

anionic, polyanions, and polyampholytes. Furthermore, on the basis of the polymer architecture, they can be divided into linear and nonlinear (including branched and cyclic) types of polyelectrolytes. Properties of linear polyelectrolytes have been explored extensively in the literature.^[3–16] Branched polyelectrolytes, on the other hand, have received relatively little attention. This work deals with polyelectrolytes having the comb-shaped architecture, which can be further divided into different types depending on the location of the charged groups, whether along the polymer backbone, along the side chains, or only at the termini of the side chains.

Graft polyelectrolytes, especially comb-like polyelectrolytes, have received less attention, but such polymers are widely used as dispersants, stabilizers, biocompatible coatings, and biosensors due to their special physical properties.^[17–19] Many synthetic and biological polymers have comb-like architecture with ionizable groups located along side chains or at the termini of the side chains.^[20–23] In cement and concrete industry, comb-like polycarboxylate ether-based superplasticizers (PCEs) have been widely used as dispersants to regulate the flowability of cementitious materials.^[24,25] PCEs usually consist of ionizable backbone and grafted neutral side chains.^[26] The anionic groups mainly act as adsorption groups

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by electrostatic interaction with the charged groups on the surfaces of cement particles, while the side chains provide steric repulsion to prevent particles from coagulating.^[27,28] Conformational properties are generally believed to be important to the dispersion properties of PCE in cement suspensions.^[29,30] However, most researchers focus on the empirical structure-property relationships, namely the influences of various PCE chemical structures (especially monomer type and ratio) on the adsorption and dispersing properties.^[27,31–33] The microscopic conformation of PCE with different architectures is usually missing due to the difficulty of characterization by current experimental techniques.

Recently, computational simulations have become very powerful in studying the conformation of polyelectrolyte at the microscopic level. Typical methods include atomistic-level molecular dynamics (MD) simulations,^[34–42] Monte Carlo simulations,^[43–46] and coarse-grained MD simulations.^[8,47–56] The atomistic-level MD simulations are useful to study the local structure of polyelectrolytes, such as the interaction of the charged groups of polyelectrolytes with counterions or water and the arrangement of counterions or water around the polymer chains. However, due to the time-consuming and high-cost drawbacks of atomistic-level MD simulations, the polymer chain being simulated is much smaller than that of the realistic molecules and the simulation time is short. Therefore, the global conformational properties cannot be accurately investigated by those atomistic-level MD simulations. Coarse-grained MD simulations are more frequently used to study the conformation behavior of polyelectrolyte for the benefit of simulating larger systems for a longer time. The most commonly-used method is probably the MD simulation incorporated with Langevin thermostat, which is also called Langevin dynamics (LD) simulations. LD simulations allow the studies on polyelectrolyte brushes with different chain flexibilities,^[57,58] charge fractions and sequences,^[59–61] functional groups,^[62,63] and solvent qualities.^[64,65] For comb polyelectrolyte, Košovani^[54] studied the structural properties of comb-like polyelectrolytes with a neutral backbone and grafted polyelectrolyte side chains in selective solvent by coarse-grained MD simulations; they found that the intramolecular self-organized structures are formed at any concentration and comb-like polyelectrolytes qualitatively follow the same behavior of neutral comb-like copolymers in selective solvent but are controlled by the degree of dissociation of the grafts. Ghelichi^[49] used coarse-grained MD study to investigate the effects of different parameters (side chain length, side-chain number, backbone stiffness, and counterion valence) on the conformational properties of a single comb-like polyelectrolyte chain with a hydrophobic backbone and grafted side chains that terminate in anionic head-groups and concluded that coarse-grained model can capture the subtle conformational behavior of comb-polyelectrolyte and ionomer chains due to the qualitative agreement in the conformational trends with both experimental and similar theoretical studies. Turesson^[46,50] studied the adsorption conformation of comb-like polyelectrolyte onto like-charged surfaces by Monte Carlo simulations and found that the negatively charged polymer can be adsorbed on negatively surface through

an ion-pairing effect mediated by calcium cations.

Although many reports about the polyelectrolyte have been published, the study of comb-like polyelectrolyte is scarce. Especially, the conformation of PCE with charged backbone and grafted neutral side chains has rarely been reported. To our best knowledge, the development of a special coarse-grained model mapped on PCE and the comparison of simulation results with experiment have been seldom undertaken. Furthermore, the effects of divalent counterions, side-chain number, and side-chain length on the solution conformation of PCE are also seldom investigated. These parameters are important for PCE to adsorb on the surface of cement particle and give dispersion properties in cement suspensions, and are also significant for the design and synthesis of PCE with high performance.

In this study, we firstly build a coarse-grained model for three comb-like PCE samples, simulate the conformation of single PCE chain in implicit solvent and explicit counterions using Langevin dynamics simulations, and compare the size of the three PCE with experiments. Then, the effects of divalent counterions with different ionic strengths on the three PCE molecules are investigated. Furthermore, a series of PCE molecules with different side-chain numbers and side-chain lengths are designed and the conformation properties of these PCE molecules are analyzed. The parameters, including the radius of gyration (R_g), end-to-end distance (R_e) and persistence length of backbone (P_{bb}), asphericity parameters (A), and the mean span dimension, are calculated to analyze the changes in conformational properties.

MODEL AND SIMULATION METHOD

Model Systems in Connection with Experiment

Three PCE chains (named as PCEB, PCED, and PCEE) studied experimentally by Giraudeau *et al.*^[66] are comb-shaped copolymers of poly(methacrylic acid) (PMAA) backbone grafted with poly(ethylene oxide) (PEO) side chains by an ester bond. Firstly, we build a model of bead-spring comb-shaped polyelectrolyte chain in accordance with their original work. Fig. 1 shows schematically the three PCE samples studied in experiments.^[66] The results characterized by GPC (Table 1) include the number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of PCEs, the molecular weight of the side chains (M_{arm}), and the ratio of methacrylic acid to polyalkylene glycol methacrylate (known as the C/E ratio and denoted by β). We neglect the effects of polydispersity and assume our model polymer to be monodisperse. M_w is used to calculate the molecular weight of the backbone (M_{bb}) and the number of side chains (f), which is identical and equally spaced along the backbone.

$$f = M_w / (86(\beta + 1) + M_{arm}) \quad (1)$$

$$M_{bb} = M_w - fM_{arm} \quad (2)$$

$$N_{bb} = \beta + 1 = M_{bb} / (86f) \quad (3)$$

$$N_a = M_{arm} / 86 = (M_{arm} / 44) (44 / 86) = 0.52 N_a' \quad (4)$$

where the number 86 corresponds to the molecular weight of a repeat unit in PMAA. The molecular weight of a repeat unit in PEO is 44 g/mol. Thus, each backbone bead represents one

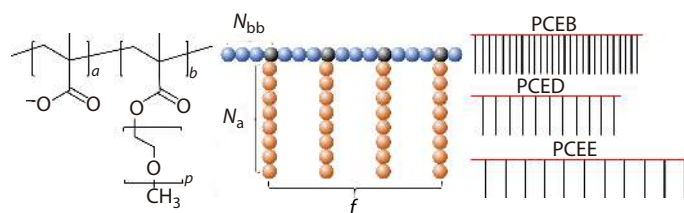


Fig. 1 Schematic illustrations of the PCE samples studied in experiment and the design of our coarse grained model.

Table 1 Experimental data of Giraudeau et al.^[66] on comb-shaped copolymers of PMAA backbone grafted with PEO side chains.

Polymer	M_n (g/mol)	M_w (g/mol)	PDI (M_w/M_n)	M_{arm} (g/mol)	Number of side chain (f)	C/E ratio (β)
PCEB	17900	35604	2.0	1012	27.5	2.3
PCED	9619	18619	1.9	1012	12.0	5.0
PCEE	10880	22346	2.0	1012	12.0	8.3

repeating unit (methacrylic acid) with diameter of σ and each side chain bead resembles two repeating unit (ethylene oxide) with diameter of 1.5σ . N_{bb} is the number of backbone beads per segments (containing 1 side chain), N_a is the number of beads in each arm (referred to as side chain or branches), and N_a' is the realistic number of ethylene oxide. The values of f and N_a should be integer in our model, so they are gained as the nearest integer value. Every backbone carries $-1e$ charge except the grafting beads and $+2e$ charge counterions are added to make charge neutral. To keep the comb shape of model and the integer number of counterions, the backbone contains $N_{bb}f + 2$ beads. Therefore, total $(N_{bb} - 1)f + 2$ beads on backbone are charged and total $((N_{bb} - 1)f + 2)/2$ counterions are added in the system. N_{bb} of the three PCE chains is designed as 3, 6, and 9 according to the C/E ratio, β . N_a is 12 for the three PCEs and f is set as 28, 12, and 12, respectively. The schematic illustration of three types of PCE is shown in Fig. 1. To study the effect of $+2$ ions on the conformation of PCE, different numbers of $+2e$ salt ions and $-1e$ ions are added to the system and the ionic strength is shown in Table 2. A cubic simulation box has the length $L = 40\sigma$ and the concentration of single PCE chain is about 5.56×10^{-4} mol/L.

Table 2 Details on the number of counterions and salts ions used in our simulations of the three PCE samples.

PCE	$N(\text{counterions}, +2e)$	$N(+2e)$	$N(-e)$	Ionic strength (mol/L)
PCEB	29	0	0	0.032
	29	8	16	0.046
	29	32	64	0.086
	29	64	128	0.139
	29	160	320	0.299
	29	800	1600	1.367
PCED	31	0	0	0.034
	31	8	16	0.048
	31	32	64	0.088
	31	64	128	0.141
	31	160	320	0.302
	31	800	1600	1.370
PCEE	49	0	0	0.055
	49	8	16	0.068
	49	32	64	0.108
	49	64	128	0.161
	49	160	320	0.322
	49	800	1600	1.390

PCE with Different Side-chain Numbers and Side-chain Lengths

A series of comb-shaped PCE molecules with the same contour length of backbone but different side-chain numbers and side-chain lengths are designed and the schematic illustration is shown in Fig. 2. Similar to the model mentioned in the above section, each backbone bead represents one repeating unit (methacrylic acid) with diameter of σ and each side chain bead resembles two repeating unit (ethylene oxide) with diameter of 1.5σ . There are 74 beads on the backbone for all PCE and the number of side chains is designed as 12, 24, 36, and 72. And the numbers of side chain bead are set as 6, 12, 24, and 48 for every kind of PCE with special number of side chains. Except the grafting beads, other beads on backbone are charged and carry $-1e$ charge. To compare with comb PCE, linear PMAA with no side-chain grafted is also calculated and all the 74 beads are charged. For all PCE molecules, corresponding numbers of counterions carrying $+2e$ charge are added to maintain the system electrically neutral. A cubic simulation box has the length $L = 60\sigma$ and the concentration of single PCE chain is about 1.65×10^{-4} mol/L.

Simulation Details

Molecular dynamics (MD) simulations with the Langevin thermostat are performed with LAMMPS code to investigate the conformational properties of comb-shaped PCE. The motion of beads is governed by:

$$m \frac{d^2 r_i}{dt^2} = -\nabla \sum_{j \neq i} U(r_{ij}) + F_i^D + F_i^R \quad (5)$$

$$F_i^D = -m\Gamma \frac{dr_i}{dt} \quad (6)$$

$$\langle F_i^R(t) \cdot F_i^R(t') \rangle = 6\Gamma k_B T m \delta_{ij} \delta(t - t') \quad (7)$$

$$\langle F_i^R(t) \rangle = 0 \quad (8)$$

where m is the mass of the i^{th} particle, r_i is the position vector, t is time, and $U(r)$ the interaction potential due to bonded and nonbonded interactions. F_i^R is the random force with zero average value. F_i^D is the friction force with solvent molecules, which are not simulated explicitly. The friction coefficient is $\Gamma = \tau_{LJ}^{-1}$, related to solvent viscosity and τ_{LJ} is the standard LJ time, $\tau_{LJ} = \sigma(m/\epsilon_L)^{1/2}$. The equations of motion for all beads in the

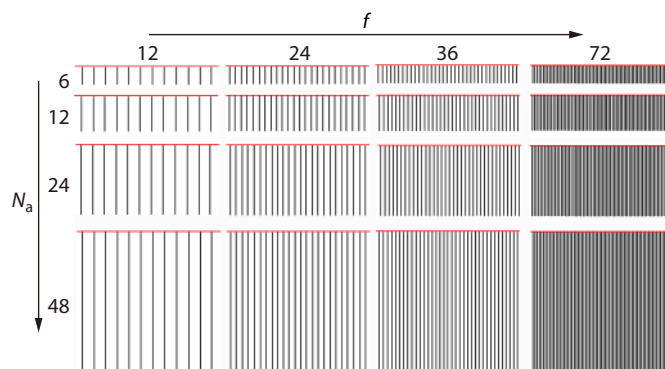


Fig. 2 Schematic illustration of designed PCE with the same contour length of backbone but different side-chain numbers (f) and side-chain lengths (N_a).

system are in the velocity Verlet algorithm with a time step of $\Delta t = 0.01\tau_{LJ}$. In our simulation, the temperature scale is defined as $k_B T = 1$ and energy is then measured in units of $\epsilon_{LJ} = 1k_B T$. The units of diameter and mass of all polymer beads are set to unity, i.e. $\sigma = 1$ and $m = 1$. Mapping the model onto the real system, we set $\sigma = 0.36$ nm and $m = 86$ g/mol. The set of counterions and salt ions is in accordance with polymer beads.

The interaction of adjacent beads in the backbone and side chain is modeled by harmonic potential with spring constant $k = 15\epsilon_{LJ}/\sigma^2$ and equilibrium bond length $l_0 = 0.97\sigma \approx 1\sigma$ for backbone while $k = 10\epsilon_{LJ}/\sigma^2$ and $l_0 = 1.504\sigma \approx 1.5\sigma$ for side chain.

$$U_{\text{bond}} = \frac{1}{2}k(l - l_0)^2 \quad (9)$$

The flexibility of the backbone and side chain is modeled with the cosine angle style,

$$U_{\text{bend}} = \kappa(1 + \cos\theta) \quad (10)$$

$$\kappa \approx k_B T l_p / l \quad (11)$$

where l_p and l are the persistence length and bond length, respectively. The persistence lengths of PMA and PEO are 0.64 and 0.38 nm gained from atomistic MD simulations.^[37,67] In reduced unit, the persistence lengths of PMA and PEO are 1.78σ and 1.06σ . Thus, κ equals $1.83k_B T$ for the beads of backbone and $0.71k_B T$ for the beads of side chain. Van der Waals interactions between all beads are modeled through the purely repulsive part of standard shifted Lennard-Jones (LJ) potential, namely WCA potential.

$$U_{\text{EV}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 + \frac{1}{4} \right] H(2^{1/6}\sigma - r) \quad (12)$$

The cutoff distance is set as $r = 2^{1/6}\sigma \approx 1.12\sigma$ for all pairwise interactions. The solvent is treated implicitly as a medium with the dielectric permittivity. Electrostatic interactions between charged beads are treated explicitly through Coulomb potential as the form,

$$U_{\text{coul}} = \frac{e^2}{4\pi\epsilon_0\epsilon_r r} = k_B T \frac{l_B}{r} \quad (13)$$

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (14)$$

where l_B is the Bjerrum length, e is the unit charge, and ϵ_0 and ϵ_r are the permittivity of vacuum and the relative dielectric constant of the solvent, respectively. The value of the Bjerrum length is $l_B = 0.7/0.36 \approx 2.0\sigma$, which corresponds to about 0.7 nm

of aqueous solution at room temperature. The dielectric constant of $\epsilon_r = 1/T_B = 0.36/0.7 = 0.514$. The cutoff is set as 10σ for short range electrostatic interactions. The particle-particle particle-mesh (PPPM) method implemented in LAMMPS with estimated accuracy of 10^{-4} is used for the calculation of long-range electrostatic interactions.

Simulations are carried out in NVT ensemble with periodic boundary conditions. A single polyelectrolyte chain placed in the middle of the simulation box is relaxed with 10^6 timesteps to reach equilibration, tracked through convergence in the total energy and the radius of gyration. Then the equilibration systems are further simulated for 10^7 timesteps to sample and data are saved every 10^4 timesteps, resulting in 1000 regularly time-spaced snapshots.

RESULTS AND DISCUSSION

Comparison with Experiments

In experimental studies, the radius of gyration (R_g) is measured by small-angle neutron scattering (SANS) within the deviation of ± 0.5 nm for three polymers (PCEB, PCED, and PCEE) and radius of hydrodynamic (R_H) is obtained by dynamics light scattering (DLS) with the standard deviation of ± 2 nm. Table 3 presents the size of three PCE molecules gained by the experiments, simulation, and theory. Generally, the R_g values of our simulations are close to the experimental data, especially for PCEB. In experimental studies, the R_g value of PCED is 4.9 ± 0.5 nm, which is larger than that of PCEE, 4.1 ± 0.5 nm. For PCED and PCEE, M_{arm} and the number of side chain are same but the C/E ratio of PCEE is greater. Under the same condition, the size of PCEE should be greater. The experimental uncertainties may induce the fluctuation of R_g value. In our simulation studies, the R_g value of PCEE is 4.93 ± 0.07 nm, which is larger than that of PCED, 4.15 ± 0.02 nm. In general, our model can be very useful in estimating the size of PCEs in solution, and the accuracy may be adequate for practical purposes.

Table 3 Sizes of three comb-shaped copolymers by experiments, simulation, and theory.

Polymer	R_g (SANS) (nm)	R_H (DLS) (nm)	R_g (simulation) (nm)	R_g (theory) (nm)
PCEB	5.1 ± 0.5	5.6 ± 2.0	5.11 ± 0.06	5.6
PCED	4.9 ± 0.5	4.6 ± 2.0	4.15 ± 0.02	3.6
PCEE	4.1 ± 0.5	4.8 ± 2.0	4.93 ± 0.07	4.2

The sizes of the three PCE are also analyzed through a Flory-type mean field theory developed by Gay and Raphaël and Flatt *et al.*^[30,68] Using a Flory-Huggins χ -parameter of 0.37 for PEO at 25 °C according to neutron scattering study^[69] and the same value for PCEs, the R_g results of the three PCEs according to the theoretical model by Flatt *et al.* are shown in Table 3, as obtained by the original authors.^[66] The predicted values of R_g are similar to the experimental results as well as our simulations results. However, one should keep in mind that the theoretical expression derived by Flatt *et al.* neglects an undetermined prefactor, which gives rise to ambiguity in its applications.

Effects of Ionic Strength

In our simulation, the three polymer samples (PCEB, PCED, and PCEE) are modeled as free-jointed-chain. The conformations of the three PCEs in implicit solvent and explicit salt ions with different ionic strengths are calculated. The radius of gyration (R_g), end-to-end distance (R_e) and persistence length (P_{bb}) of backbone, asphericity parameters (A), and span are used to analyze the change of conformation. In order to compare the conformational properties with comb-shaped PCE, only the backbone of PCEB (named as PMAA) is designed and calculated using the same simulation settings. C/E ratio of PCEB is 2 and thus the fraction of charged beads of PMAA is 2/3. R_g is defined as:

$$\langle R_g^2 \rangle^{1/2} = \left\langle \frac{1}{N} \sum_{i=1}^N (r_i - r_{com})^2 \right\rangle^{1/2} \quad (15)$$

where i is the bead index, r_i is the position vector of the i^{th} bead, r_{com} is the center-of-mass of the chain, and N is the number of beads. In our coarse-grained model, the masses of all beads are the same. Therefore, mass is ignored in the calculation of R_g . Generally, with the increase of ionic strength, the R_g values of four polymer chains are decreased but with no significant change. This is justified for the small size (3–5 nm) of these polymer chains and thus the change of R_g value in solution with different ionic strengths is slight. However, for linear polymer PMAA, the decrease of R_g is more remarkable than the comb PCE molecules. The electrostatic screening effect of counterions results in reduced electrostatic repulsion between charged backbone beads, which is more obvious for linear PMAA with no steric hindrance of grafting side chains. This can also explain the more remarkable decrease of R_g for PCEE than that of PCEB and PCED. Steric hindrance of PCEE with smaller side-chain number is less and the electrostatic screening effect is greater. When the ionic strength reaches 0.3 mol/L, R_g values of the four polymer chains are nearly changeless. It suggests that the electrostatic screening effect is saturated and the conformation of PCE is unaffected by greater ionic strength. R_e of the backbone also reaches the minimum at 0.3 mol/L ionic strength, except PCEB. For PCEB, a larger side-chain number results in greater steric hindrance and it is difficult to reach electrostatic screening saturation.

Asphericity parameter (A) describes the shape of polymer as rod or sphere and is calculated as follows:

$$Q_{\alpha\beta} = \frac{1}{2N^2} \sum_{i=1}^N \sum_{j=1}^N (r_{i,\alpha} - r_{j,\alpha})(r_{i,\beta} - r_{j,\beta}) \quad (16)$$

$$Tr = L_x^2 + L_y^2 + L_z^2 \quad (17)$$

$$M = L_x^2 L_y^2 + L_y^2 L_z^2 + L_x^2 L_z^2 \quad (18)$$

$$A = \frac{Tr^2 - 3M}{Tr^2} \quad (19)$$

where $\alpha, \beta = x, y, z$ denotes the Cartesian components in three dimension. L_x^2, L_y^2 , and L_z^2 are the three eigenvalues of R_g tensor, $Q_{\alpha\beta}$. Asphericity parameter, A , ranges from 0 for spherical symmetric object to 1 for extremely elongated or “cigar” shaped object. For three dimensional random walk chains, the value of A is 0.39 according to Diehl and Eisenriegler.^[70] For linear PMAA with 2/3 charged beads, A is 0.45–0.5, which indicates linear PMAA is curving at 0.03–1.4 mol/L ionic strength but is stretched than random walk chain. A of the three comb PCE polymer chains is 0.3–0.4 and A of PCED is the smallest. Compared with PCED, the stiffness of PCEB with larger side-chain number is greater and the length of backbone of PCEE is longer. Therefore, the shape of those two PCEs tends to be more rod-like than PCED. The mean span describes the occupied space of molecule in solution and is estimated as:^[71]

$$\langle \text{Span} \rangle = \left\langle \frac{1}{4\pi} \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} \left[\max_i (\vec{r}_i \cdot \hat{u}) - \min_i (\vec{r}_i \cdot \hat{u}) \right] \sin\theta d\theta d\phi \right\rangle \quad (20)$$

where $\hat{u} = (1, \theta, \phi)$ (θ = polar angle, ϕ = azimuth angle) is a unit vector (unit vector with radial distance, $r = 1$) and $\vec{r}_i$ is the position vector of the i^{th} bead. In solution with different ionic strengths, the mean spans of the four polymers are nearly unchanged, especially for the comb PCE. It can be concluded that the mean spans of the polymer chains are impervious at different ionic strengths.

The persistence length of backbone, P_{bb} , is calculated from the end-to-end distance, R_e , and contour length, L_{bb} , of a wormlike chain model, which is given by:^[72]

$$R_e^2 = 2 \times L_{bb} P_{bb} - 2 \times P_{bb}^2 \left(1 - e^{-\frac{L_{bb}}{P_{bb}}} \right) \quad (21)$$

where R_e is calculated from the simulation trajectory, L_{bb} is the contour length, which is equal to the diameter of each unit multiplied by the number of units. To compare our persistence length with the values derived from theoretical calculations, the persistence length and Debye screening length are firstly fitted according the equation of $P_{bb} = a + b\kappa^{-1}$ and $P_{bb} = a + b\kappa^{-2}$, respectively. Then we compare the fitted slope with the results presented by Dobrynin and Odijk-Skolnick-Fixman. According to Dobrynin,^[73] persistence length can be written as a sum of the bare persistence length P_{bb0} and the electrostatic persistence length, which is proportional to Debye screening length (κ^{-1}).

$$P_{bb} \approx P_{bb0} + 0.32Uf^2\kappa^{-1} \quad (22)$$

$$\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2N_A e^2 I}} = \frac{1}{\sqrt{8\pi l_B N_A I}} \quad (23)$$

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_r k_B T} \quad (24)$$

$$I = \frac{1}{2} \sum_i c_i z_i^2 \quad (25)$$

where P_{bb0} is the bare persistence length, $0.32Uf^2\kappa^{-1}$ is the

electrostatic persistence length, U is the ratio of the Bjerrum length l_b to the bond size b , $U = l_b/b$, f is the fraction of charged monomers of the backbone, e is the charge of an electron, ϵ_0 is the permittivity of vacuum, ϵ_r is the bulk permittivity of the medium, I is the ionic strength, and c_i is the concentration of species with valence z_i . The electrostatic persistence length in Eq. (22) shows a linear dependence on the Debye screening length instead of the quadratic dependence as it is in the Odijk-Skolnick-Fixman (OSF) expression,^[74] which is as follows:

Table 4 Comparison of the fitted slope using our simulated data by the equation of $P_{bb} = a + b\kappa^{-1}$ and $P_{bb} = a + b\kappa^{-2}$ with the coefficient of the second term on the right-hand of Eq. (22) developed by Dobrynin and Eq. (26) derived by the OSF theory.

Polymer	Slope ($P_{bb} = a + b\kappa^{-1}$)	$0.32Uf^2$	Slope ($P_{bb} = a + b\kappa^{-2}$)	$l_b f^2 / 4b^2$
PMAA	0.285	0.283	0.148	0.614
PCEB	0.315	0.283	0.148	0.614
PCED	0.235	0.437	0.123	0.948
PCEE	0.373	0.494	0.238	1.072

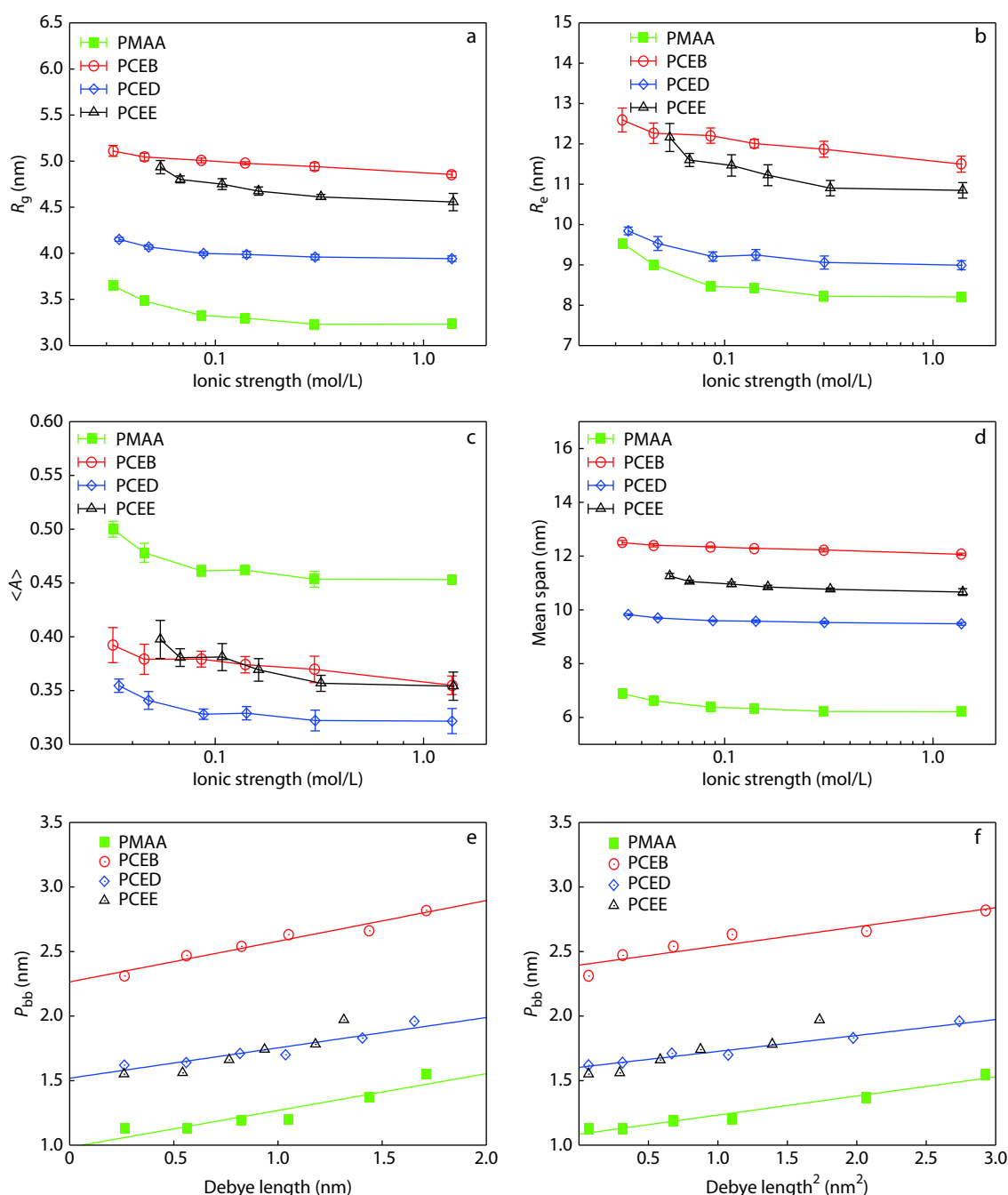


Fig. 3 (a) Radius of gyration, (b) root mean square end-to-end distance, (c) asphericity parameter, and (d) the mean span dimension plotted as a function of the ionic strength; Persistence length plotted as a function of (e) the Debye length and (f) the Debye length square.

$$P_{bb} \approx P_{bb0} + P_{bb}^{OSF} \approx P_{bb0} + \frac{l_B f^2}{4b^2} \kappa^{-2} \quad (26)$$

The fitted slope, b , with the coefficient $0.32Uf^2$ and $l_B f^2/4b^2$ are compared and the results are shown in Table 4. The fitted slope and the coefficient calculated by Dobrynin are well matched, especially for linear PMAA. Slight difference may be derived from the effect of side chains. Furthermore, the quadratic dependence of P_{bb} on the square of the Debye screening length, κ^{-2} , is also fitted and the results are given in Fig. 3 and Table 4. Linear relation between P_{bb} and κ^{-2} is also ob-

served. However, from the comparison of the R^2 -value of fitting and the coefficient of electrostatic part of the equation, we can find that the Dobrynin's equation is better and the linear dependence of persistence length of backbone on the Debye screening length is well described for the PCE studied in this work.

Effects of Side-chain Number and Side-chain Length

Conformational behavior of a branched polyelectrolyte chain depends on both steric effects of branching and the electrostatic interactions of charged units. Greater side-chain number

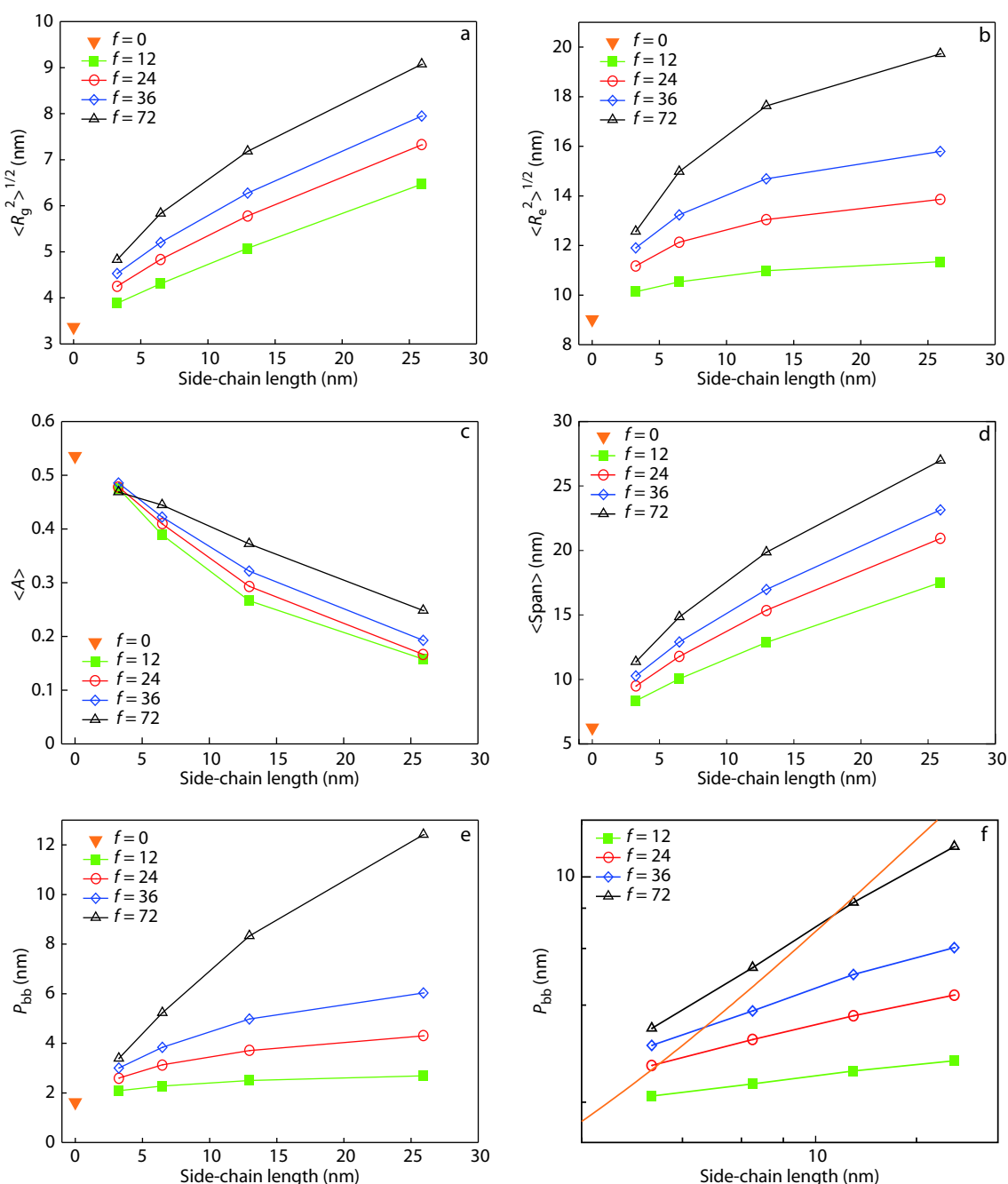


Fig. 4 (a) Radius of gyration, (b) root mean square end-to-end distance, (c) asphericity parameter, and (d) the mean span dimension plotted as a function of the side-chain length; Persistence length plotted as a function of the side-chain length on (e) a linear-linear scale and (f) a log-log scale (where the solid line without symbols has a slope of 1), respectively. f denotes side-chain number.

(f), larger side-chain length (N_a), and stronger electrostatic repulsion between the charged units of backbone can induce the extended conformation of PCE. For comb polyelectrolyte with the same contour length of backbone (L_{bb}), higher f results in fewer charged units and weaker electrostatic repulsion of backbone. To discriminate the two opposite effects, a series of PCE with the same L_{bb} but different f and N_a are designed. Except the grafting beads, other beads on the backbone carry $-1e$ charge. The conformational behavior of those PCEs in implicit solvent and explicit conterions is simulated.

The radius of gyration (R_g), end-to-end distance (R_e) and persistence length (P_{bb}) of backbone, asphericity parameters (A), and span are calculated to analyze the conformation of PCE with different f and N_a . The results are showed in Fig. 4. Increasing f and N_a increases R_g of PCE and this effect is more pronounced as f and N_a increase. The bending rigidity of backbone is significantly affected by higher f and larger N_a . This is further proved by the results of R_e and P_{bb} of backbone. Asphericity parameters, A , is about 0.55 for linear PMAA with all charged beads. The stretched PMAA results from the electrostatic repulsion between the charged units. A of comb PCE with the approximate L_{bb} (26.64 nm) and N_a (25.92 nm) is about 0.2, which suggests globular conformation. A is less influenced by f than N_a , especially at short side-chain length. At $N_a \ll L_{bb}$, the effect of f is weakened due to the diminished space of side-chain and reduced excluded-volume effect between side chains. With the increase of N_a , A is sensitive to the change of f due to stronger excluded-volume effect between side chains. The excluded-volume effect is also observed from the results of span and persistence length. The span of linear PMAA is the smallest and the span of the comb ones increases with the increase of f and N_a .

When 12 side chains are grafted on the backbone ($f = 12$), R_e increases from ~ 10 nm to ~ 11.5 nm with the increase of N_a . When $f = 72$, R_e increases from ~ 12 nm to ~ 20 nm with the increase of N_a . Additionally, R_e is about 9 nm when no side-chain ($f = 0$) is grafted and larger than 12 nm when 72 side chains ($f = 72$) are grafted. The stiffness of backbone is sharply increased due to the excluded-volume effect between the grafting side chains. This also indicates that the effect of branching, including f and N_a , is greater than that of electrostatic repulsion of backbone on the stiffness of backbone and the size of comb PCE in solution. The bending rigidity of backbone is also characterized by the persistence length, P_{bb} , which is calculated from R_e and L_{bb} by Eq. (21). According to reported data,^[75] P_{bb} is predicted to the scale as $P_{bb} \propto N_{sc}^\alpha$ (N_{sc} is the number of monomers on side-chain). The exponent for bottlebrushes in a θ solvent is predicted to be $2/3$ or 1.01 .^[76,77] We predict the scale of $P_{bb} \propto N_a^\alpha$ and the results are shown in Fig. 4. The exponents for all PCEs are less than 1. Higher f results in greater P_{bb} . At the lowest f ($f = 12$), P_{bb} increases from ~ 2.1 nm to ~ 2.7 nm with the increase of N_a (from 3.24 nm to 25.92 nm) and the exponent is the smallest, 0.12. At the highest f ($f = 72$), P_{bb} increases from ~ 3.4 nm to ~ 12.4 nm with the increase of N_a and the exponent is the largest, 0.63. Higher f and larger N_a yield greater backbone rigidity due to the steric repulsion between side chains. This is different from the comb polyelectrolyte with neutral backbone and grafting side chains terminated with negative bead

investigated by Ghelichi and Eikerling.^[49] They found that higher f and smaller N_a resulted in greater rigidity of the backbone due to both excluded-volume effect of side chains and end effect induced by the long-range coulomb forces. P_{bb} of linear PMAA with all the beads charged is also calculated and it equals 1.63 nm, which is smaller than that of comb PCE with grafting side chains but fewer charged beads on backbone. This indicates that the stiffness of backbone is significantly affected by branching rather than the electrostatic repulsion of charged beads on backbone. Representative snapshots of PCE conformations are shown in Fig. 5. Overall, the conformational behavior observed in Fig. 4 is in accordance with the trends in Fig. 5. The contour length of backbone is the same for all PCEs and greater side-chain number results in fewer charged units and weaker electrostatic repulsion of backbone. The stiffness of PCE with the same side-chain length increases with the increase of side-chain number, f . The dominant effect of branching, including side-chain number and side-chain length, is revealed and it is greater than that of electrostatic repulsion between charged beads of backbone on backbone stiffness. When $f = 72$, the conformation of PCE is stretched due to the strong excluded-volume effect between side chains. And the conformation is further extended with the increase of the side-chain length.

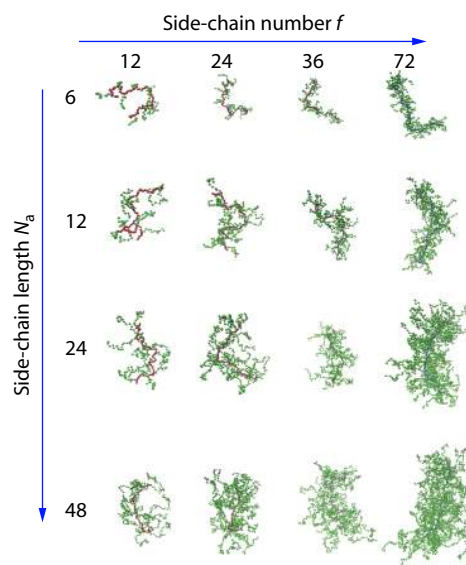


Fig. 5 Snapshots of PCE conformations with the same contour length of backbone but different side-chain numbers and side-chain lengths. (The red beads are the charged beads on backbone, the blue beads are the neutral linking beads on the backbone, and green chains are the side chains.)

CONCLUSIONS

A coarse-grained model for comb-like polycarboxylate ether-based superplasticizers is built and studied by Langevin MD simulation. The sizes of three PCE are compared with experiments, and the results indicate that our model is useful in estimating the conformation of PCEs in solution. The effect of ionic strength, side-chain number, and side-chain length on the conformational behavior of PCE in solution is further investigated by the

Langevin MD simulation. The parameters, including the radius of gyration, end-to-end distance and persistence length of backbone, asphericity parameters, and the mean span, are calculated to analyze the change of conformation.

It is found that with the increase of ionic strength, the R_g values of PCE are decreased but have no significant change due to the electrostatic screening effect of ions. When the ionic strength reaches 0.3 mol/L, the electrostatic screening effect is saturated and the conformation of PCE is unaffected by greater ionic strength. PCEs with greater stiffness and longer length of backbone tend to be rod-like and the mean spans of the three PCEs are impervious at different ionic strengths. The linear dependence of persistence length of backbone on the Debye screening length is better described according to Dobrynin than OSF.

It is also observed that the greater side-chain number and larger side-chain length increase the R_g value of PCE and this effect is pronounced as side-chain number and side-chain length increase due to the stronger excluded-volume effect. The excluded-volume effect is also observed from the results of asphericity parameters, span, and the persistence length. At side-chain length far smaller than the length of backbone, the effect of side chains number is weakened due to the diminished space of side chains and reduced excluded-volume effect between them. With the increase of side-chain length, asphericity parameter becomes more sensitive to the change of side-chain number due to stronger excluded-volume effect between side chains. The mean span of linear PMAA is the smallest, and it increases with the increase of side-chain number and side-chain length for comb samples. Furthermore, the effect of branching, including the side-chain number and side-chain length, is greater than that of electrostatic repulsion between charged beads of backbone on the stiffness of backbone and the size of comb PCE in solution.

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REFERENCES

- Voycheck, C. L.; Tan, J. S.; Hara, M. *Polyelectrolytes: science and technology*. Marcel Dekker, Inc., New York, **1993**, p. 250.
- Holm, C.; Joanny, J. F.; Kremer, K.; Netz, R. R.; Reineker, P.; Seidel, C.; Vilgis, T. A.; Winkler, R. G. Polyelectrolyte theory. in *Polyelectrolytes with defined molecular architecture II*. Berlin, Heidelberg, **2004**, p. 67.
- Chremos, A.; Douglas, J. F. Influence of higher valent ions on flexible polyelectrolyte stiffness and counter-ion distribution. *J. Chem. Phys.* **2016**, *144*, 164904–164913.
- Stevens, M. J.; McIntosh, D.; Saleh, O. Simulations of stretching a strong, flexible polyelectrolyte. *Macromolecules* **2012**, *45*, 5757–5765.
- Toan, N. M.; Thirumalai, D. On the origin of the unusual behavior in the stretching of single-stranded DNA. *J. Chem. Phys.* **2012**, *136*, 235103–235108.
- Elder, R. M.; Jayaraman, A. Coarse-grained simulation studies of effects of polycation architecture on structure of the polycation and polycation-polycation complexes. *Macromolecules* **2012**, *45*, 8083–8096.
- Bayramoglu, B.; Faller, R. Coarse-grained modeling of polystyrene in various environments by iterative Boltzmann inversion. *Macromolecules* **2012**, *45*, 9205–9249.
- Carrillo, J. M. Y.; Dobrynin, A. V. Polyelectrolytes in salt solutions: molecular dynamics simulations. *Macromolecules* **2011**, *44*, 5798–5816.
- Carrillo, J. M. Y.; Dobrynin, A. V. Detailed molecular dynamics simulations of a model NaPSS in water. *J. Phys. Chem. B* **2010**, *114*, 9391–9399.
- Saleh, O.; McIntosh, D.; Pincus, P.; Ribbeck, N. Nonlinear low-force elasticity of single-stranded DNA molecules. *Phys. Rev. Lett.* **2009**, *102*, 068301.
- Chang, R.; Yethiraj, A. Dilute solutions of strongly charged flexible polyelectrolytes in poor solvents: molecular dynamics simulations with explicit solvent. *Macromolecules* **2006**, *39*, 821–828.
- Liao, Q.; Dobrynin, A. V.; Rubinstein, M. Counterion-correlation-induced attraction and necklace formation in polyelectrolyte solutions: theory and simulations. *Macromolecules* **2006**, *39*, 1920–1938.
- Dobrynin, A. V.; Rubinstein, M. Theory of polyelectrolytes in solutions and at surfaces. *Prog. Polym. Sci.* **2005**, *30*, 1049–1118.
- Limbach, H. J.; Holm, C. Single-chain properties of polyelectrolytes in poor solvent. *J. Phys. Chem. B* **2003**, *107*, 8041–8055.
- Micka, U.; Holm, C.; Kremer, K. Strongly charged, flexible polyelectrolytes in poor solvents: molecular dynamics simulations. *Langmuir* **1999**, *15*, 4033–4044.
- Stevens, M. J.; Kremer, K. The nature of flexible linear polyelectrolytes in salt free solution: a molecular dynamics study. *J. Chem. Phys.* **1995**, *103*, 1669.
- Dobrynin, A. V. Theory and simulations of charged polymers: from solution properties to polymeric nanomaterials. *Curr. Opin. Colloid In.* **2008**, *13*, 376–388.
- Khokhlov, A. R.; Khalatur, P. G. Solution properties of charged hydrophobic/hydrophilic copolymers. *Curr. Opin. Colloid In.* **2005**, *10*, 22–29.
- Burak, Y.; Ariel, G.; Andelman, D. Onset of DNA aggregation in presence of monovalent and multivalent counterions. *Biophys. J.* **2003**, *85*, 2100–2110.
- Deming, T. J. Synthesis of side-chain modified polypeptides. *Chem. Rev.* **2015**, *116*, 786–808.
- Zhang, Y.; Lu, H.; Lin, Y.; Cheng, J. Water-soluble polypeptides with elongated, charged side chains adopt ultrastable helical conformations. *Macromolecules* **2011**, *44*, 6641–6644.
- Wang, Y.; Zheng, M.; Meng, F.; Zhang, J.; Peng, R.; Zhong, Z. Branched polyethylenimine derivatives with reductively cleavable periphery for safe and efficient *in vitro* gene transfer. *Biomacromolecules* **2011**, *12*, 1032–1040.
- Lu, H.; Wang, J.; Bai, Y.; Lang, J. W.; Liu, S.; Lin, Y.; Cheng, J. Ionic polypeptides with unusual helical stability. *Nat. Commun.* **2011**, *2*, 206.
- Alonso, M. M.; Palacios, M.; Puertas, F. Compatibility between polycarboxylate-based admixtures and blended-cement pastes. *Cem. Concr. Compos.* **2013**, *35*, 151–162.
- Malferrari, D.; Fermani, S.; Galletti, P.; Goisis, M.; Tagliavini, E.; Falini, G. Shaping calcite crystals by means of comb polyelectrolytes having neutral hydrophilic teeth. *Langmuir* **2013**, *29*, 1938–1947.
- Reese, J.; Plank, J. Adsorption of polyelectrolytes on calcium

- carbonate-which thermodynamic parameters are driving this process. *J. Am. Ceram. Soc.* **2011**, *94*, 3515–3522.
- 27 Yamada, K.; Takahashi, T.; Hanehara, S.; Matsuhisa, M. Effects of the chemical structure on the properties of polycarboxylate-type superplasticizer. *Cem. Concr. Res.* **2000**, *30*, 197–207.
 - 28 Ran, Q.; Qiao, M.; Liu, J. Influence of Ca^{2+} on the performance of poly(acrylic acid)-*g*-poly(ethylene glycol) comb-like copolymers in cement suspensions. *Iran Polym. J.* **2014**, *23*, 663–669.
 - 29 Shu, X.; Ran, Q.; Liu, J.; Zhao, H.; Zhang, Q.; Wang, X.; Yang, Y.; Liu, J. Tailoring the solution conformation of polycarboxylate superplasticizer toward the improvement of dispersing performance in cement paste. *Constr. Build. Mater.* **2016**, *116*, 289–298.
 - 30 Flatt, J. F.; Schober, I.; Raphael, E.; Plassard, C.; Lesniewska, E. Conformation of adsorbed comb copolymer dispersants. *Langmuir* **2008**, *25*, 845–855.
 - 31 Ran, Q.; Somasundaran, P.; Miao, C.; Liu, J.; Wu, S.; Shen, J. Effect of the length of the side chains of comb-like copolymer dispersants on dispersion and rheological properties of concentrated cement suspensions. *J. Colloid Interface Sci.* **2009**, *336*, 624–633.
 - 32 Winnefeld, F.; Becker, S.; Pakusch, J.; Götz, T. Effects of the molecular architecture of comb-shaped superplasticizers on their performance in cementitious systems. *Cem. Concr. Compos.* **2007**, *29*, 251–262.
 - 33 Kirby, G. H.; Lewis, J. A. Comb polymer architecture effects on the rheological property evolution of concentrated cement suspensions. *J. Am. Ceram. Soc.* **2004**, *87*, 1643–1652.
 - 34 Sappidi, P.; Muralidharan, S. S.; Natarajan, U. Conformations and hydration structure of hydrophobic polyelectrolyte atactic poly(ethacrylic acid) in dilute aqueous solution as a function of neutralization. *Mol. Simul.* **2014**, *40*, 295–305.
 - 35 Tong, K. F.; Song, X. F.; Sun, S. Y.; Xu, Y. X.; Yu, J. G. Molecular dynamics study of linear and comb-like polyelectrolytes in aqueous solution: effect of Ca^{2+} ions. *Mol. Phys.* **2014**, *112*, 2176–2183.
 - 36 Zidar, J.; Lim, G. S.; Cheong, D. W.; Klähn, M. Protein-like dynamics of polycarbonate polymers in water. *J. Phys. Chem. B* **2014**, *119*, 316–329.
 - 37 Sulatha, M. S.; Natarajan, U. Molecular dynamics simulations of PAA-PMA polyelectrolyte copolymers in dilute aqueous solution: chain conformations and hydration properties. *Ind. Eng. Chem. Res.* **2012**, *51*, 10833–10839.
 - 38 Sulatha, M. S.; Natarajan, U. Origin of the difference in structural behavior of poly(acrylic acid) and poly(methacrylic acid) in aqueous solution discerned by explicit-solvent explicit-ion MD simulations. *Ind. Eng. Chem. Res.* **2011**, *50*, 11785–11796.
 - 39 Maskey, S.; Pierce, F.; Perahia, D.; Grest, G. S. Conformational study of a single molecule of poly(*para* phenylene ethynylene)s in dilute solutions. *J. Chem. Phys.* **2011**, *134*, 244906–244914.
 - 40 Tribello, G. A.; Liew, C. C.; Parrinello, M. Binding of calcium and carbonate to polyacrylates. *J. Phys. Chem. B* **2009**, *113*, 7081–7085.
 - 41 Ju, S. P.; Lee, W. J.; Huang, C. I.; Cheng, W. Z.; Chung, Y. T. Structure and dynamics of water surrounding the poly(methacrylic acid): a molecular dynamics study. *J. Chem. Phys.* **2007**, *126*, 224901–224912.
 - 42 Molnar, F.; Rieger, J. “Like-charge attraction” between anionic polyelectrolytes: molecular dynamics simulations. *Langmuir* **2005**, *21*, 786–789.
 - 43 Hehmeyer, O. J.; Arya, G.; Panagiotopoulos, A. Z.; Szleifer, I. Monte Carlo simulation and molecular theory of tethered polyelectrolytes. *J. Chem. Phys.* **2007**, *126*, 244902.
 - 44 Luque-Caballero, G.; Martín-Molina, A.; Quesada-Pérez, M. Polyelectrolyte adsorption onto like-charged surfaces mediated by trivalent counterions: a Monte Carlo simulation study. *J. Chem. Phys.* **2014**, *140*, 174701.
 - 45 Yu, S.; Larson, R. G. Monte-Carlo simulations of PAMAM dendrimer-DNA interactions. *Soft Matter* **2014**, *10*, 5325–5336.
 - 46 Turesson, M.; Labbez, C.; Nonat, A. Calcium mediated polyelectrolyte adsorption on like-charged surfaces. *Langmuir* **2011**, *27*, 13572–13581.
 - 47 Chremos, A.; Douglas, J. F. Counter-ion distribution around flexible polyelectrolytes having different molecular architecture. *Soft Matter* **2016**, *12*, 2932–2941.
 - 48 Ghelichi, M.; Qazvini, N. T. Self-organization of hydrophobic-capped triblock copolymers with a polyelectrolyte midblock: a coarse-grained molecular dynamics simulation study. *Soft Matter* **2016**, *12*, 4611–4620.
 - 49 Ghelichi, M.; Eikerling, M. H. Conformational properties of comb-like polyelectrolytes: a coarse-grained MD study. *J. Phys. Chem. B* **2016**, *120*, 2859–2867.
 - 50 Turesson, M.; Nonat, A.; Labbez, C. Stability of negatively charged platelets in calcium-rich anionic copolymer solutions. *Langmuir* **2014**, *30*, 6713–6720.
 - 51 Liu, Z.; Shang, Y.; Feng, J.; Peng, C.; Liu, H.; Hu, Y. Effect of hydrophilicity or hydrophobicity of polyelectrolyte on the interaction between polyelectrolyte and surfactants: molecular dynamics simulations. *J. Phys. Chem. B* **2012**, *116*, 5516–5526.
 - 52 Spaeth, J. R.; Kevrekidis, I. G.; Panagiotopoulos, A. Z. A comparison of implicit and explicit-solvent simulations of self-assembly in block copolymer and solute systems. *J. Chem. Phys.* **2011**, *134*, 164902.
 - 53 Reddy, G.; Yethiraj, A. Solvent effects in polyelectrolyte adsorption: computer simulations with explicit and implicit solvent. *J. Chem. Phys.* **2010**, *132*, 074903.
 - 54 Košován, P.; Limpouchová, Z.; Procházka, K. Conformational behavior of comb-like polyelectrolytes in selective solvent: computer simulation study. *J. Phys. Chem. B* **2007**, *111*, 8605–8611.
 - 55 Hsiao, P. Y.; Luijten, E. Salt-induced collapse and reexpansion of highly charged flexible polyelectrolytes. *Phys. Rev. Lett.* **2006**, *97*, 148301–148305.
 - 56 Liao, Q.; Dobrynin, A. V.; Rubinstein, M. Molecular dynamics simulations of polyelectrolyte solutions: nonuniform stretching of chains and scaling behavior. *Macromolecules* **2003**, *36*, 3386–3398.
 - 57 Wynveen, A.; Likos, C. N. Interactions between planar polyelectrolyte brushes: effects of stiffness and salt. *Soft Matter* **2010**, *6*, 163–171.
 - 58 Baratto, M.; Fazli, H. Brushes of flexible, semiflexible, and rodlike diblock polyampholytes: molecular dynamics simulation and scaling analysis. *Phys. Rev. E* **2010**, *81*, 011801.
 - 59 Baratto, M.; Fazli, H. Molecular dynamics simulation of semiflexible polyampholyte brushes—the effect of charged monomers sequence. *Eur. Phys. J.* **2009**, *29*, 131–138.
 - 60 Csajka, F. S.; Netz, R. R.; Seidel, C.; Joanny, J. F. Collapse of polyelectrolyte brushes: scaling theory and simulations. *Eur. Phys. J.* **2001**, *4*, 505–513.
 - 61 Seidel, C. Strongly stretched polyelectrolyte brushes. *Macromolecules* **2003**, *36*, 2536–2543.
 - 62 Merlitz, H.; He, G. L.; Wu, C. X.; Sommer, J. U. Nanoscale brushes: how to build a smart surface coating. *Phys. Rev. Lett.* **2009**, *102*, 115702.
 - 63 Merlitz, H.; He, G. L.; Wu, C. X.; Sommer, J. U. Surface instabilities

- of monodisperse and densely grafted polymer brushes. *Macromolecules* **2008**, *41*, 5070–5072.
- 64 Carrillo, J. M. Y.; Dobrynin, A. V. Morphologies of planar polyelectrolyte brushes in a poor solvent: molecular dynamics simulations and scaling analysis. *Langmuir* **2009**, *25*, 13158–13168.
 - 65 Guptha, V. S.; Hsiao, P. Y. Polyelectrolyte brushes in monovalent and multivalent salt solutions. *Polymer* **2014**, *55*, 2900–2912.
 - 66 Giraudeau, C.; D'Espinose De Lacaillerie, J. B.; Souguir, Z.; Nonat, Z.; Flatt, R. J. Surface and intercalation chemistry of polycarboxylate copolymers in cementitious systems. *J. Am. Ceram. Soc.* **2009**, *92*, 2471–2488.
 - 67 Lee, H.; Venable, R. M.; MacKerell Jr, A. D.; Pastor, R. W. Molecular dynamics studies of polyethylene oxide and polyethylene glycol: hydrodynamic radius and shape anisotropy. *Biophys. J.* **2008**, *95*, 1590–1599.
 - 68 Gay, C.; Raphael, E. Comb-like polymers inside nanoscale pores. *Adv. Colloid Inter. Sci.* **2001**, *94*, 229–236.
 - 69 Pedersen, J. S.; Sommer, C. Temperature dependence of the virial coefficients and the chi parameter in semi-dilute solutions of PEG. In *Scattering methods and the properties of polymer materials*. Berlin, Heidelberg, **2005**, pp. 70–78.
 - 70 Diehl, H. W.; Eisenriegler, E. Universal shape ratios for open and closed random walks: exact results for all d. *J. Phys. A: Math. Gen.* **1989**, *22*, L87.
 - 71 Wang, Y.; Teraoka, I.; Hansen, F. Y.; Peters, G. H.; Hassager, O. Mean span dimensions of ideal polymer chains containing branches and rings. *Macromolecules* **2010**, *44*, 403–412.
 - 72 Hsu, H. P.; Paul, W.; Binder, K. Standard definitions of persistence length do not describe the local “intrinsic” stiffness of real polymer chains. *Macromolecules* **2010**, *43*, 3094–3102.
 - 73 Dobrynin, A. V. Electrostatic persistence length of semiflexible and flexible polyelectrolytes. *Macromolecules* **2005**, *38*, 9304–9314.
 - 74 Dorfman, K. D.; King, S. B.; Olson, D. W.; Thomas, J. D. P.; Tree, D. R. Beyond gel electrophoresis: microfluidic separations, fluorescence burst analysis and DNA stretching. *Chem. Rev.* **2012**, *113*, 2584–2667.
 - 75 Paturej, J.; Sheiko, S. S.; Panyukov, S.; Rubinstein, M. Molecular structure of bottlebrush polymers in melts. *Sci. Adv.* **2016**, *2*, 1601478–1601480.
 - 76 Birshtein, T. M.; Borisov, O. V.; Zhulina, Y. B.; Khokhlov, A. R.; Yurasova, T. A. Conformations of comb-like macromolecules. *Polym. Sci.* **1987**, *29*, 1293–1300.
 - 77 Feuz, L.; Leermakers, F. A. M.; Textor, M.; Borisov, O. Bending rigidity and induced persistence length of molecular bottle brushes: a self-consistent-field theory. *Macromolecules* **2005**, *38*, 8891–8901.