

Electrostatically-driven Ordering in Model Dendrimer Polyelectrolytes: Effects of Concentration

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Summary: In this study we extend our previous work in the self-organization of dendrimer polyelectrolytes (Macromolecules, 2008, 41, 225) by examining the effects of dendrimer concentration and/or total volume fraction in the ordering process and the resulting structure, in the arrangement of counterions and dendrimer beads and in the diffusive motion of dendrimers at different strengths of Coulombic interactions. It is found that as long as the total volume fraction remains low (i.e. no jamming phenomena intervene) the symmetry of the resulted cubic phases is unaltered. At a higher volume fraction and at the strong electrostatic regime a kinetic arrest of the dendrimer molecules much in analogy to a colloidal glass-like transition is observed, inhibiting thus the ordering process. Changes in the strength of electrostatic interactions and dendrimer concentration induces a systematic variation of the counterion - counterion and the counterion - charged-dendrimer-bead spatial arrangement. These findings are in qualitative agreement with previous studies in systems with very different structural details of the considered solutes, indicating a more general behaviour in charged macroion/counterion solutions.

Keywords: dendrimer; molecular dynamics; polyelectrolyte; simulation; self-organization

Introduction

Self-organization of charged macroions in solution is a phenomenon frequently encountered not only in synthetic (micelles, colloids etc)^[1–3] but also in biological systems (e.g. DNA, globular proteins).^[4,5] Control of the self-association properties of such systems through manipulation of their structural details and their thermodynamic environment as well as by means of external stimuli, is an important issue pertinent to a wide range of potential applications.^[6–8] Dendritic polymers, already possessing nanoscale spatial dimensions combined with attributes like multifunctionality and versatility in modifying their specific structural details (flexibility of the monomers, branching and core functionality, spacer

bond length, identity of the surface groups) constitute a particularly promising class of materials for applications based on our capability to control the formed structures.^[9–11] As has been experimentally verified, attributes like surface charge density, concentration and ionic strength of the solutions are among those parameters that directly affect their self-assembly behavior.^[3,12,13] Along these lines, our previous work^[14] in the self-organization of charged dendrimers under the influence of varying electrostatic interactions utilizing molecular dynamic simulations, have elucidated several details on the mechanisms involved in this process. The increased spatial correlations between the counterions which led to their condensation on the dendrimers' surface triggering also overcharging phenomena, the counterion-mediated development of a short-range attraction followed by a longer range repulsion between dendrimer molecules, the depletion of the solvent molecules from

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Table 1.

Details on the composition of the simulated systems. C represents the dendrimer concentration and C^* the corresponding dendrimer overlap limit.

System Code	G3_1	G3_2	G4_1	G4_2	G4_3
Generation	3	3	4	4	4
C/C^* of dendrimer	0.10	0.07	0.09	0.06	0.17
Number of counterions	720	720	1440	1440	1440
Number of solvent beads	1086	1629	2300	6534	2300
Total vol. frac.	0.44	0.33	0.36	0.36	0.70

within the dendrimer interior and the effect of varying molecular weight/surface charge density in the resulted ordered structures, were among those characteristics found to play a principal role in the dendrimer self-organization. In the present manuscript we describe effects associated with variation of the dendrimer concentration/total volume fraction (remaining though in the dilute regime) in the ordering phenomena for systems comprised by terminally charged dendrimers of two different sizes in solutions of explicit counterions and solvent beads.

Model Description

Models of peripherally dendrimers in an atomistic (united atom) representation with the explicit inclusion of neutralizing counterions and solvent beads were simulated by means of molecular dynamic simulations (NVT ensemble). AB_2 type dendritic molecules starting from a trifunctional core and emanating radially outwards with two spacer bonds between branching points were constructed.^[15] Systems of generations 3 and 4 (abbreviated to G3 and G4 respectively henceforth) were considered in this work. Each system was comprised by 30 dendrimer molecules with their terminal bead charged, the appropriate number of counterions in order to preserve overall neutrality, and a number of neutral solvent beads in order to accomplish the desired total volume fractions. Two models of G3 and three models of G4 dendrimers were simulated, spanning different total volume fractions and/or varying box sizes at constant total volume fraction as listed in

Table 1 (the systems studied in our previous work^[14] are included as well). It must be noted that at all cases the dendrimer concentration remains below the corresponding overlap limit.

Variation of the strength of electrostatic interactions was performed by altering the Bjerrum length (l_B)^[14] in a wide range covering from very weak to very strong electrostatic interaction regimes.

The simulation protocol adopted (generation of initial structures, simulation force field, other simulation parameters, i.e., time step, potential cutoffs, procedure for equilibration and generation of production runs, etc.) for all the examined systems, follows that described in our previous work,^[14] referred to as R1 hereafter.

Effects on Dendrimer Arrangement/ordered Structure

As was noted in R1, the dependence of the radius of gyration (R_g) of dendrimers of both sizes, exhibited a maximum as a function of Bjerrum length due to the competition between the repulsive forces acting on the like-charged dendrimer beads and their attractive interactions with the oppositely charged counterions.^[16,17] Figure 1 shows the same dependence for all the G4 systems (the behaviour of the G3 models is similar).

Apparently, existence of the peak structure is independent of the dendrimer concentration/total volume fraction while the relative change of R_g with respect to the value at very low l_B (approximately 6% higher) remains practically unaffected. In addition, the Bjerrum length at which the

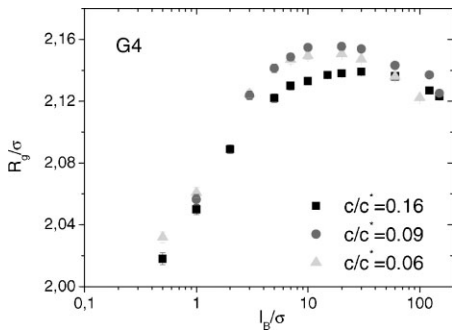


Figure 1.

Dependence of the radius of gyration of the dendrimers as a function of Bjerrum length for the G4 models.

size of the dendrimers is maximized seems to be insensitive to the dendrimer concentration. These features attest to the localized nature of the interactions responsible for this behavior. The location of the peak at a larger l_B value compared to previous simulation results^[16] should be attributed to the detailed nature of the forcefield adopted in our simulations, where all common internal degrees of freedom of the dendrimers have been taken into account (i.e. bond stretching, angle bending, torsion rotation) rendering these models more resistant to deformation.

To monitor the relative arrangement of dendrimer molecules we can follow the location of the main peak of the static

structure factor arising from the center of mass of the molecules (see section IV in R1). As depicted in Figure 2, the magnitude of the scattering vector q^* corresponding to the first-neighbor maxima, increases (i.e. the average distance between first neighbors decreases) upon increase of the dendrimer concentration.

The difference observed in the q^* values in regime I, diminishes for systems at the two lower concentrations as the strength of electrostatic interactions increases (regimes II and III), indicating that the average distance between dendrimer centers effectively becomes independent of dendrimer concentration in this limit. This occurrence implies a similarity between the resulted ordered structures. Only the G4_3 system possessing the higher concentration/total volume fraction seems to deviate from this behavior.

To check whether the above observation influences in any way the symmetry of the resulted structures, we compare in Figure 3 the static structure factors arising from the centers of mass for systems at different concentrations for dendrimer models of both sizes. A direct visual inspection of the spectra describing the G3 systems shows that the symmetry of the ordered structure (body centered cubic) remains unaffected by the change in dendrimer concentration/total volume fraction for the examined

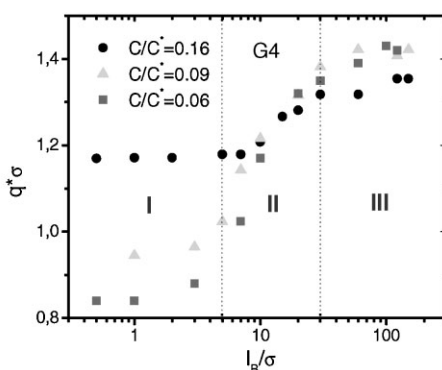
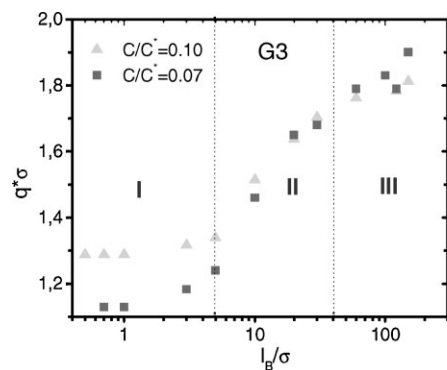


Figure 2.

Dependence of the magnitude of the scattering vector corresponding to the main peak of the static structure factor arising from the center of mass of the dendrimer molecules, for G3 (left side) and G4 (right side) systems. σ represents the unit of length of the simulation. Ranges of Bjerrum length denoted by I, II, III correspond to low, intermediate and strong electrostatic regimes respectively.

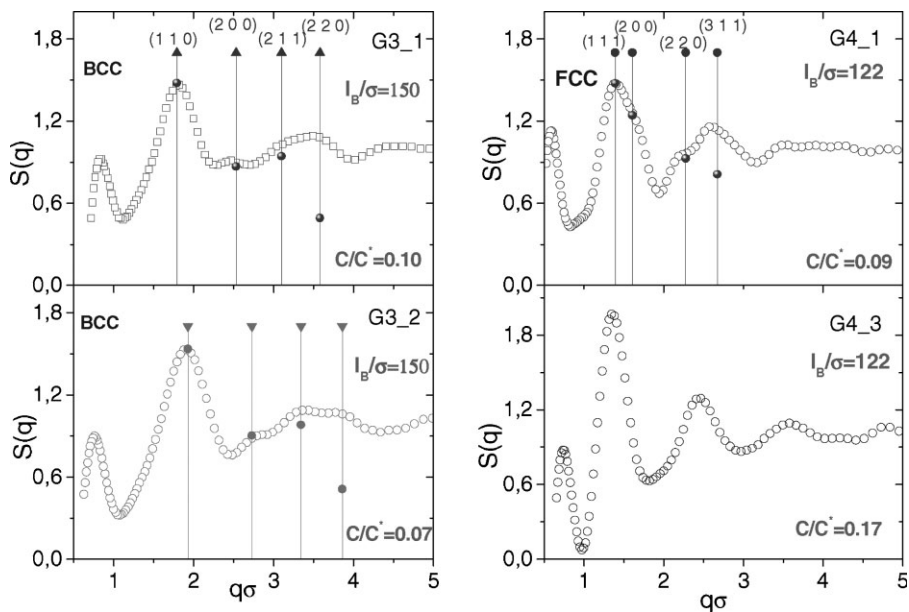


Figure 3.

Static structure factors arising from the centers of mass at the strong electrostatic regime for the examined models. Vertical lines denote the locations corresponding to the high-intensity diffraction peaks corresponding to the symmetry of a body centered cubic (left side, G3_1 lower and G3_2 upper panel) and a face-centered cubic (right side, G4_1 upper panel) lattice. Miller indices of the corresponding scattering planes are shown on top of each line (upper panels). Solid symbols represent the expected relative amplitudes of each peak with respect to that of the larger maximum.

cases. However, this is not the case when comparing the G4 models corresponding to the lower and the higher concentrations/total volume fractions. While at the G4_1 an ordered structure bearing the symmetry of a face centered cubic phase is observed, a similar structure cannot be discerned in the G4_3 system. This finding should be correlated to the distinct behavior noted in Figure 2 for the G4_3 model regarding the values of the scattering vector corresponding to the average distance between dendrimers, and will be discussed later on in conjunction with the total volume fraction of that system.

Effects on Spatial Correlations of Charges

As was described in R1, the development of the effective potential between dendrimer

molecules which drives the system to the ordered state, is mediated by the enhanced correlations between counterions and counterion - charged dendrimer beads as the strength of electrostatic interactions increases. In this regime, a counterion “ordering” close to the dendritic structure takes place, which combined with a mechanism for counterion “sharing” between neighboring molecules may lead to dendrimer overcharging phenomena.^[14] To examine the effects of dendrimer concentration in the counterion spatial correlations we have compared the radial distribution functions arising from counterion-counterion pairs. Figure 4 shows this comparison for the G4 models (the presented behavior is representative for the G3 systems as well).

At the weak electrostatic regime (top-most panel) no particular ordering apart from the liquid-like arrangement of the

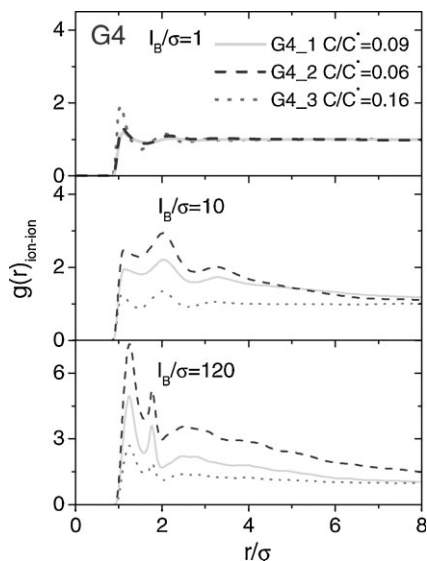


Figure 4.

Counterion-counterion pair correlations functions for the G4 systems at different strengths of electrostatic interactions.

counterions is observed. The amplitude of the first-coordination shell is larger at the higher volume fraction system, G4_3, as anticipated. At the stronger electrostatic regimes however, (middle and lowermost panel) two characteristic peaks appear indicating the spatial correlation between counterions. One at relative separations corresponding approximately to one diameter due to the strong repulsive forces close to this distance, and a second associated with a distance near or moderately below two ion diameters denoting their preferred separation when localized close to the charged dendrimers. For all different concentrations, increase of Bjerrum length induces a better ordering of the counterions (the peaks increase in amplitude and grow sharper) due to the combined effect of their localization close to the dendrimer surface upon increase of the attractive electrostatic forces and their effort to arrange their relative distance in order to minimize the repulsive interactions between each other.^[14] The effect of increasing the dendrimer concentration (note that systems G4_1 and G4_2 are at

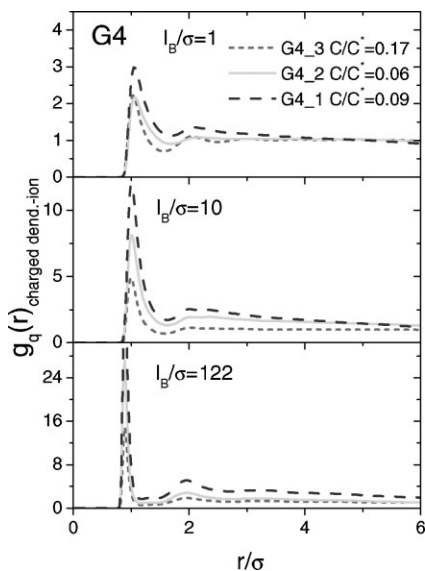


Figure 5.

Pair distributions function between the terminal (charged) dendrimer beads and the counterions for the G4 systems.

the same total volume fraction) is a smearing out of the peaks (lowering of their amplitudes), indicating a lower degree of localization of the counterions with respect to each other. The same effect has been observed in computer simulation studies examining the counterion-counterion correlations around a cylindrical polyion^[18] indicating that this behavior appears to be independent of the structural details of the considered polyion. A similar behaviour is noted in the relative spatial arrangement between the counterions and the charged dendrimer beads as depicted in Figure 5. As in the case between counterion-counterion pairs, the degree of spatial correlations is enhanced upon elevation of Bjerrum length but decreases upon increase of the dendrimer concentration.

To assess a possible role of solvent on the observed ion correlations it is helpful to examine the corresponding behaviour of the ion-solvent pairs. Figure 6 presents the radial distribution functions of the counterion-solvent bead pairs for models of the largest examined dendrimer size (the same features characterize the G3 models

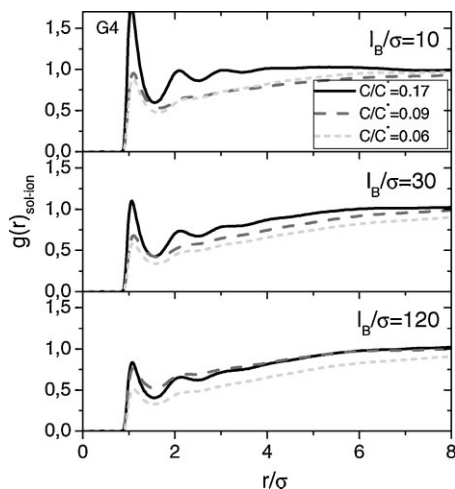


Figure 6. Pair distribution functions between counterion and solvent beads for the G4 systems.

as well). For all the examined concentrations, the probability of finding ion-solvent pairs at short distances decreases upon increasing the strength of electrostatic interactions. At constant Bjerrum length, the amplitude of the peak corresponding to the first coordination shell diminishes upon decrease of the dendrimer concentration. This lowering of the degree of the counterion-solvent clustering upon increase of l_B and decrease of dendrimer concentration, indicates a strong link to the corresponding probabilities between the charged-bead pairs as described in Figure 5.

Effects of Concentration on Dendrimer Diffusion

As has theoretically been predicted in charged colloidal systems,^[19] upon increase of the strength of electrostatic interactions a glass-like transition can be detected. The volume fraction at which vitrification of the colloidal particles is observed, depends on the intensity of Coulombic interactions (i.e. on Bjerrum length). Much in analogy to such systems, since dendrimers can actually be considered as soft colloids,^[20] a similar behavior in solutions of charged

dendrimers can be expected. To check the validity of this argument we have calculated the mean squared displacement (MSD) arising from the centers of mass of the dendrimer molecules, as shown in Figure 7 for the G4 systems (the behavior of the G3 models is in close analogy). In all the examined systems development of a plateau-like region is observed at values of l_B residing well within regime III as defined in Figure 2. Emergence of this plateau region is characteristic for caged-dynamics in colloidal systems^[21] prior to the diffusive behaviour associated with glass transition.

For the low concentrations/total volume fraction systems G4_1 (Figure 7b) and G4_2 (Figure 7a) the transition from a diffusive to a subdiffusive behaviour (at times longer than the initial subdiffusive motion) takes place very close to the transient region between regimes II and III (Figure 2) with respect to l_B . On the other hand, a subdiffusive motion is observed through the entire range of l_B s for the G4_3 system which corresponds to the higher total volume fraction.

In the context of the description of charged colloidal systems and the vitrification/gelation behaviour of colloids mentioned earlier, one can interpret this finding as a kinetic arrest of the dendrimer molecules at such high total volume fraction. Such an intervention of jamming phenomena would inhibit the self-assembly of dendrimers towards the formation of an ordered structure, in line with the absence of a cubic phase in system G4_3 (Figure 3). For the lower total volume fraction systems, the effect of the increase of dendrimer concentration appears to be related to a more gradual transition from the diffusive to the subdiffusive regime as the concentration increases (compare the behaviour of the MSDs in Figures 7a and 7b).

Conclusions

In this work we have examined the effects of concentration and/or total volume fraction in systems of terminally charged

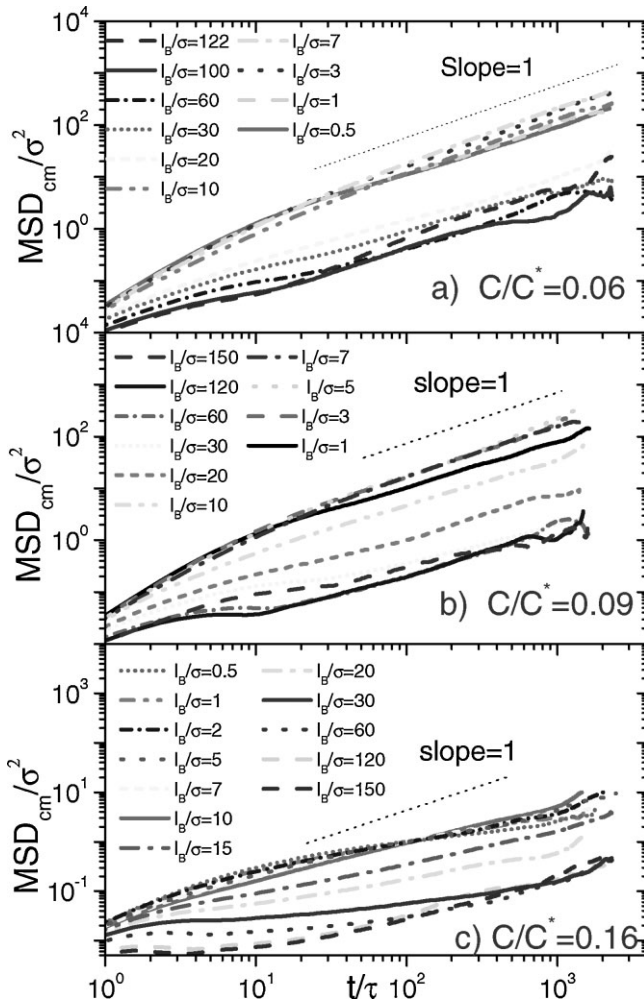


Figure 7.

Mean squared displacement of the centers of mass for the G4 systems at the examined Bjerrum lengths a) G4_2, b) G4_1, c) G4_3. Dotted lines denote a slope of 1.

dendrimers with explicit counterions and solvent beads. It was found that at low concentrations (in the dilute limit) and total volume fractions where jamming phenomena are absent, the main structural characteristics of individual dendrimers as well as of the symmetry of the structure formed at high intensities of electrostatic interactions, remain practically unaffected. Although the relative distances between charged beads are rather insensitive to changes in concentration and in the strength of electrostatic interactions (Figure 2, regimes II and III), a systematic

dependence of the degree of counterion clustering around charged dendrimers (i.e. change in the relative amplitudes of the pair correlation peaks) on these parameters was observed. In view of the advantages related to dendrimer molecules (multifunctionality, potential for hosting guest molecules, low viscosity compared to similar molecular weight linear polymers), control of the strength of ion-ion correlations (e.g. by changing the concentration of the dendrimers or the ionic strength of the solution) could be of potential use in applications involving catalytic action.^[22,23] The direct

relation between the ion-ion and the solvent-ion spatial arrangements observed in the examined systems, may provide further insight in mechanisms like the solvent-mediated charge-charge interactions which can be important in order to understand the electrolytic behaviour of more complex systems.^[24]

At all the systems examined, increase of the strength of electrostatic interactions imparts a gradual slow down of the dendrimer motion driving the systems to a virtual freezing-in of their centers of mass motion at large I_B s, in analogy to similar phenomena met in charged colloidal systems. At large total volume fractions (system G4_3), characteristics of a sub-diffusive behaviour is observed even at low strengths of electrostatic interaction, leading to a kinetic arrest which inhibits the ordering process (at least at the timescales examined).

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