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Complexes between Poly(amido amine) Dendrimers and Poly(methacrlyic acid): Insight from Molecular Dynamics Simulations

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Summary: In this work we present results from fully atomistic molecular dynamics simulations of aqueous solutions of poly(amido amine) dendrimers and poly-(methacrylic) acid in the dilute regime and at low ionic strength and physiological pH conditions, in which the polymeric components are charged. We have studied stoichiometric (1:1) and non-stoichiometric (1:2) systems, comprised by dendrimers of two different generations and two different lengths of the linear polyelectrolyte. For all systems studied, a polymer-rich and a solvent-rich region is formed. The polymer-rich region consists of aggregated complexes between the polymeric components bearing similarities to percolated structures met in physical hydrogels. We examine morphological characteristics of the two components as well as the degree of ionic pairing between the different ionic moieties, providing information regarding the degree of physical adsorption of the linear chains on the dendrimer's surface and that of the respective counterions on the oppositely charged monomers.

Keywords: dendrimer; molecular dynamics; nanogels; poly(methacrylic acid); polyelectrolyte; simulation

Introduction

Complex systems based on polymer/colloid mixtures are among the most versatile materials for a large number of novel nanoscale applications.[1] In such systems comprised by dispersions of hard colloidal particles stabilized by polymeric components, aspects such as the responsiveness to external stimuli (i.e., by modification of the polymer conformation, or by rearrangement of local structures) can be crucial when it comes to the fabrication of "smart materials".[2] Especially in applications where rapid response of the systems in changes of the microenvironment is required (e.g., sensors and drug delivery applications[3,4]), soft particulates rather than hard colloidal particles appear as a more appropriate choice for complexation with linear polymers.[5] Dendritic polymers bearing nanosize dimensions and combining multifunctionality with monodisperse size can play this role, acting effectively as monomolecular micelles.[6] Their additional degrees of freedom with respect to hard colloids increases their ability to change their size, shape and charge under external stimuli such as pH, ionic strength and temperature.[7,8]

In recent years there are numerous examples in which a special category of cationic dendrimers, namely the poly(amido amine) (PAMAM) family, have been used as complexation agents for oppositely charged polyelectrolytes, such as nucleic acids,[9–11] proteins,[12] or synthetic polymers[13,14] in a wide range of applications. Some of the most characteristic examples of such dendrimer/linear-polymer systems with a continuously growing industrial and

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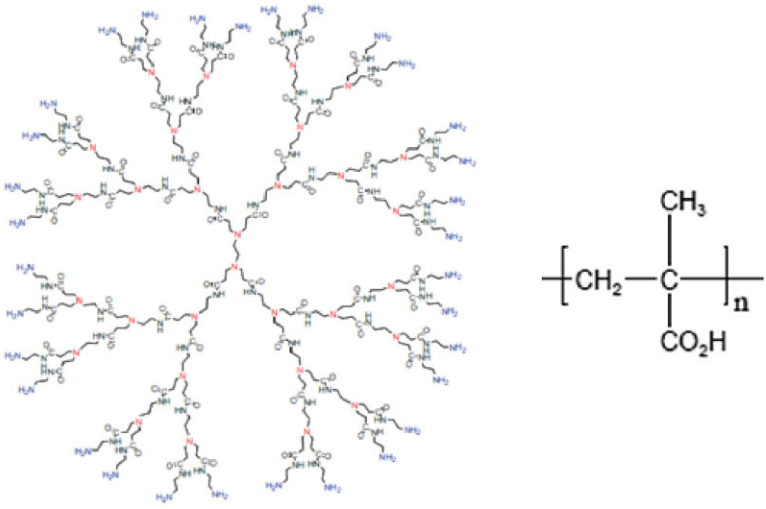
biomedical interest are those forming responsive hydrogels.[15,16] Particularly for biomedical applications, biocompatibility and biodegradability of such systems are also required.[17]

Fulfillment of the aforementioned prerequisites is challenging, as it entails the construction of water soluble dendrimer/linear-polymer systems with biocompatible/biodegradable components able to form stable complexes at physiological conditions while providing a mechanism that triggers structural rearrangements under environmental changes when needed (e.g., for drug release applications). Under these perspectives, we hereby study for the first time dendrimer/linear polyelectrolyte systems comprised of poly(amidoamine) (PAMAM) dendrimers and poly(methacrylic acid) (PMA) (see Scheme 1) in an aqueous environment at physiological pH (7.4) and low ionic strength by means of fully atomistic molecular dynamics (MD) simulations. Under such conditions, PAMAM dendrimers are peripherally charged due to the protonation of their primary amines[18] while PMA is also fully ionized[19,20] due to the dissociation of the hydrogens from the carboxylic groups (Scheme 1). At lower pH conditions tertiary amines of the PAMAM dendrimers start to ionize, resulting in a increase of the molecular size due to Coulombic repulsions, while PMA also undergoes an abrupt conformational transition towards a coiled form.[19] Therefore, PAMAM/PMA complexes are expected to be sensitive to changes in pH.

In the present work we have considered only the physiological pH case at $T = 300K$ and at a low ionic strength of 0.05M. We have opted in simulating syndiotactic PMA due to its lower hydrophobicity compared to its isotactic form[21] (atactic PMA is also predominantly syndiotactic[22]) and in order to compare some of our results to previous simulation works where syndiotactic PMA was also examined.[21,23,24]

Details of the Systems and Simulation Protocol

As has been noted in previous experimental[25,26] and simulation studies[27–29] the length of the linear polyanion chain can be a key parameter in controlling complex formation. To examine possible effects of



Scheme 1.
Structures of the non-ionized states of a 3rd generation diethylamine-core PAMAM dendrimer used in the present study (left) and the PMA monomer (right).

this molecular characteristic and to check the role of the size of the soft-colloidal particle (here the dendrimer) in the complex formation, we have simulated 4 systems comprised by second generation (G2) and third generation (G3) PAMAM dendrimers mixed with two PMA of different lengths, as described in Table 1.

In all systems the total number of PMA monomers matched the total number of the protonated amine groups of the dendrimers. The appropriate number of Cl^- and Na^+ counterions was added to each system to ensure overall system neutrality and mimic the low ionic strength conditions ($I = 0.05M$) adopted in relevant experiments.[19] A suitable number of water molecules were also explicitly included to allow for a hydration layer extending of at least 10Å from the solutes. To exclude the possibility of kinetically arrested states arising from jamming effects,[30] the concentration of the more massive components (i.e. dendrimers) did not exceed 10% of the corresponding overlap concentration, while the overall polymer volume fraction was kept below 0.15. All simulations were performed with the NAMD simulation package.[31] Interaction parameters for the polymer species were adopted from the AMBER forcefield[32] whereas solvent molecules were described by the TIP3P model.[33] Partial charges for the polymeric compounds were calculated applying the Gasteiger method,[34] while the TIP3P charges were assigned to water molecules. Previous computational studies have demonstrated that combination of the above parameters adequately describe PAMAM aqueous solutions,[35,36] while the AMBER forcefield was shown to provide a fair representation of aqueous PMA solutions as well.[37,38]

After the construction of the initial configurations, the systems were optimized and brought to the target temperature of 300K following a simulation protocol similar to that described in ref.[39]. In the next step, additional MD equilibration in isothermal/isobaric (NPT) ensemble was performed ($T = 300\,K$, $P = 1$ bar). To verify system equilibration, several thermodynamic (i.e., different energetic contributions) and conformational properties (radius of gyration of the polymeric species, radial density distribution of water molecules and counterions with respect to the dendrimer center of mass) were monitored. Production runs were then carried out for at least 30 ns for all systems with 1fs integration steps using the velocity Verlet algorithm under periodic boundary conditions.

Complex Formation and Conformational Features of the Components

Previous experimental[40,41] and computational studies[42] of the complexation of multi-dendrimer systems with oppositely charged linear polyelectrolytes in the presence of solvent molecules and counterions have shown that at low electrostatic screening conditions linear polyelectrolytes are preferentially physically adsorbed onto the dendrimers' surface. This behavior is mainly driven by the entropic gain due to the release of counterions that do not remain "bound" to the charged polymer moieties.[43–48]

Table 1.
description of the simulated systems.

System notation	No. of PAMAM molecules/charge per dendrimer	No. of PMA molecules/charge per chain	No. of monomers in PMA chains	No. of water molecules
G2_PMA16	10/+16	10/−16	16	18217
G2_PMA32	10/+32	5/−32	32	19569
G3_PMA32	10/+32	10/−32	32	49014
G3_PMA64	10/+32	5/−64	64	132558

Depending on the characteristic properties of the linear and multi-branched polymeric components (size, charge density, flexibility[26,49]) and on parameters such as ionic strength of the solution,[26,50] concentration of the solutes[51] and strength of the electrostatic[42] and hydrophobic[52] interactions, such systems may exhibit a rich phase Diagram.[53]. In our case, it appears that under conditions of low ionic strength, relatively low concentrations (i.e., below the semi-dilute regime), and at molar ratios (dendrimer/linear polyanion) 1:1 and 2:1 the equilibrium state corresponds to the formation of a solvent-rich and a polymer-rich phase, as depicted in Figure 1.

In all systems the PMA chains appear to be physically adsorbed on the dendrimers' surface resulting in the formation of interconnected aggregates which resemble gel-like percolated structures.[54]

To quantify the effects of complexation on the morphological characteristics of the two polymeric components we examined some pertinent structural/conformational properties of the two molecular entities and compared them (where possible) to previous studies referring to their uncomplexed states under similar conditions. Focusing on the PMA behavior, Figure 2 compares our values of the radius of gyration R_g and the end-to-end vector R_{ee} to those estimated in past computational efforts where oligomeric poly(acrylic acid) (PAA) and PMA models were studied under conditions similar to those employed

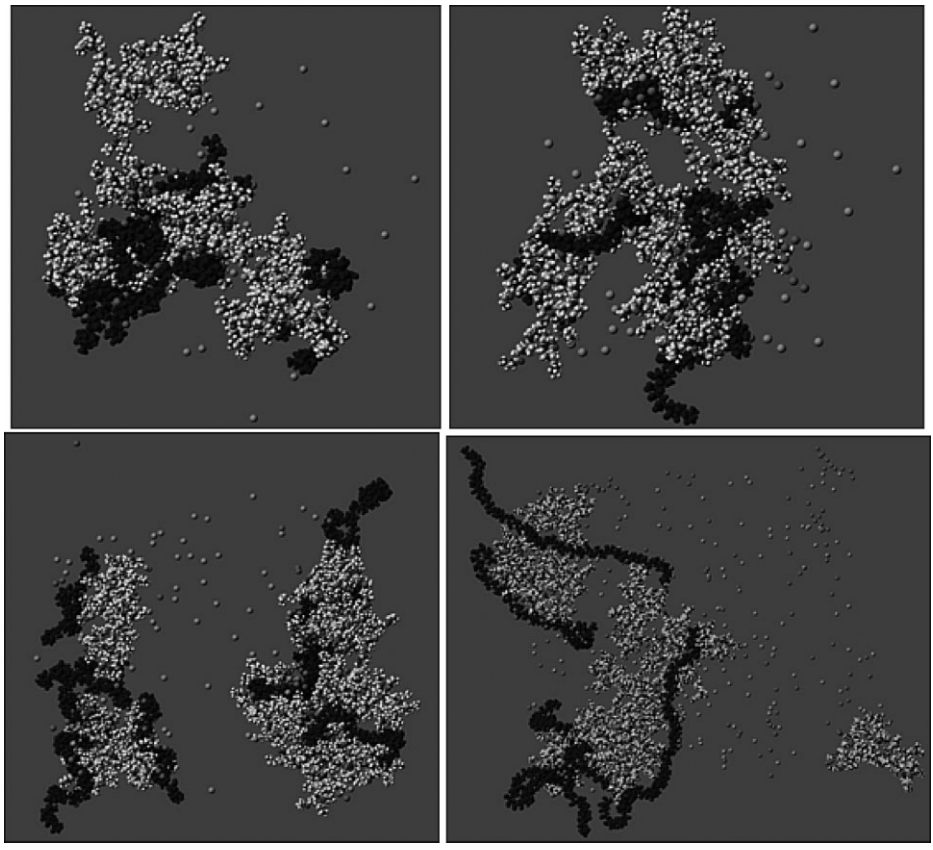


Figure 1.
Snapshots of the simulated systems. G2_PMA16 (upper left), G2_PMA32 (upper right), G3PMA_32 (lower left), G3PMA_64 (lower right). PMA chains are shown in black, Cl^- and Na^+ counterions as light and dark spheres respectively. Water molecules are omitted for clarity. Note that the G3 models are shown in smaller scale.

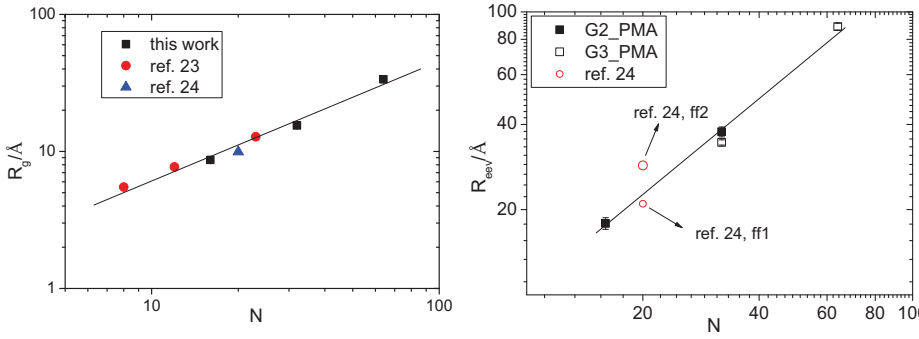


Figure 2.
(Left) Average radius of gyration (R_g) as a function of the number (N) of PMA and PAA monomers (see text) from current work, ref.[23] and ref.[24]. (Right) End-to-end distance (R_{ee}) as a function of the number of PMA monomers from present work and ref.[24]. Arrows indicate values obtained by two different forcefields in ref.[24]. The lines are guides to the eye.

here. In ref.[24] the authors studied a 20 monomer PMA and PAA chain using two different forcefields and at different degrees of ionization. They found that, in the fully ionized state, the R_g values of the two polymers were practically identical, irrespectively of the forcefield used. Based on this finding we have included in the left panel of Figure 2 also the values of the radius of gyration for PAA oligomers at fully ionized state.[23]

Apparently, all points follow the same power law. Similarly, for the end-to-end distance in Figure 2 (right panel) we also included the values for the PMA 20mer predicted from simulations performed with two different sets of interaction parameters.[24] As in the case of R_g, the end-to-end distances of the PMA models in ref.[24] appear to be compatible with the power law behavior defined by the values obtained in our simulations. In other words, complexation of the PMA chains with the PAMAM dendrimers does not appear to induce any appreciable change in the average size of the linear polyelectrolytes, at least for the chain length values considered here. For the dendritic components the estimated average radii of gyration values are 10.84 ± 0.07 Å and 10.87 ± 0.07 Å in the G2_PMA16 and the G2_PMA32 models respectively, while G3 dendrimers assumes R_g values of 16.00 ± 0.06 Å in the G3_PMA32 and 15.95 ± 0.13 Å in the G3_PMA64 model. These values are in close agreement with measurements obtained by small angle neutron and x-ray scattering experiments on peripherally charged PAMAM dendrimers of analogous sizes.[55] Namely, at a degree of ionization at which the number of protonated amines equals that of the dendrimer primary amines, the radius of gyration for the G3 dendrimer amounts to $R_g(G3) \cong 16.7$Å while the corresponding value for G2 extrapolated from the molecular-weight dependence of R_g found in this study is $R_g(G2) \cong 11.0$ Å. For both dendrimer sizes the experimental values are in close agreement with those calculated from our simulations. Therefore, the apparent dimensional invariance upon complexation for the charged PMA chains discussed above applies to the dendritic molecules in the complexes as well.

However, this invariance of the average molecular dimensions does not necessarily imply that other morphological characteristics (such as shape) remain unchanged upon complexation.[55] Such changes are actually expected for the linear polyelectrolytes.[29,56,57] Although analogous detailed information is not available for the dendritic components yet, recent studies[41,42,51] have demonstrated that upon complexation with oppositely charged

linear chains, film-like flattened structures can be formed, implying that changes in dendrimer shape can also be anticipated. To check whether this is the case for the present PAMAM/PMA complexes, we have calculated the asphericity parameter δ for our G2 and G3 dendrimers. δ is a parameter currently adopted to quantify the deviation from the spherical shape of molecular objects;[58] according to its definition, a linear array of atoms is characterized by $\delta = 1$, a planar one has $\delta = 0.25$, while molecular shapes characterized by high three-dimensional similarity have $\delta = 0$. Figure 3 shows the variation of δ for the dendritic components along the entire MD trajectories. We see that no noticeable differences can be observed between the G2_PMA16 and G2_PMA32 systems. The average asphericity value of $\delta \cong 0.19$ is appreciably higher compared to that calculated for their non-protonated analogues[59] (i.e. $\delta = 0.13$), whilst no literature data are available for charged PAMAM dendrimers of the 2nd generation.

On the other hand, G3 assumes a distinctly different behavior in the two complexes. For the G3_PMA32 model, the asphericity parameter is significantly lower compared to that of the G2 systems. The asphericity of dendrimers is known to decrease as the generation grows,[59] but the observed value is much larger compared to those previously calculated for neutral[59] (i.e., $\delta = 0.04$) and peripherally charged PAMAM dendrimers[14] (i.e., $\delta = 0.02$) in aqueous solutions, respectively. For the G3_PMA64 the average asphericity parameter amounts to $\delta \cong 0.23$, a value even higher than that describing the G2 systems. Therefore, for all models complexation appears to increase the asymmetry in the dendrimer shape, while the difference in the length of the linear component seems to drastically affect the morphological characteristics of the dendrimer as the dendrimer generation grows.

Ionic Pairing between Oppositely Charged Moieties

As quoted in past studies,[44,60] a key factor which promotes complexation in systems such as those considered here is an overall entropic gain due to the release of counterions upon binding, which outmatches the entropic loss from the physical adsorption of the linear chains on the dendrimers' surface. Therefore, the behavior of the two kinds of counterions plays a decisive role in the equilibrium thermodynamic state of

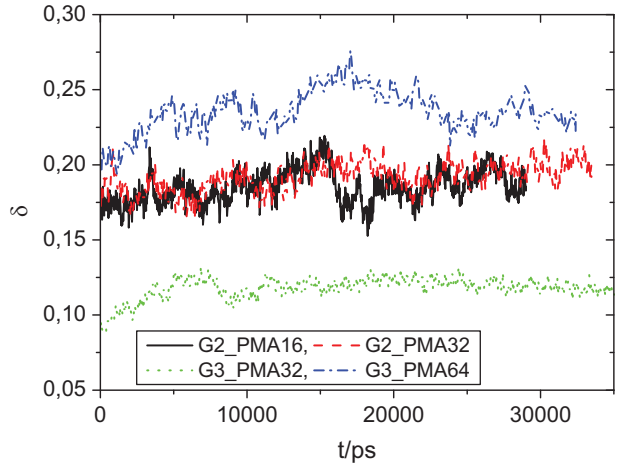


Figure 3.
Asphericity parameter δ for the dendrimer molecules in the examined systems.

such systems. To elaborate more on the counterions' behavior we have calculated the degree of ionic pairing between oppositely charged ionic moieties (i.e., charged monomers and counterions). Namely, we examined pairs formed by the hydrogens of the dendrimers' protonated amines and the Cl^- counterions, by the negatively charged oxygen of the COO^- group of PMA and the Na^+ counterions, and by the aforementioned charged atoms of the dendrimers and PMA. Two ionic moieties are considered as an ionic pair if their distance is shorter than the first minimum of the corresponding pair correlation function.[43] The degree of pairing is calculated by the ratio of the number of the detected pairs over the number of the relevant charged monomers. Figure 4 shows the degree of ionic paring between oppositely charged moieties in the examined systems.

The picture emerging from Figure 4 as far as the electrostatic pairing is concerned, is particularly informative. In all systems a very low degree of ionic paring is observed between the dendritic protonated amines and the respective counterions, implying that the dendrimers' counterions are much less spatially restricted compared to their positively charged counterparts. In the G2 models, the degree of ionic pairing between the oppositely charged polymeric monomers is higher compared to that between PMA and its counterions, while in the G3 systems this relation is reversed. This notion suggests that an increase in the dendrimer's surface charge density (G3 dendrimer possesses a higher surface charge density than G2) reflects in a decrease in dendrimer/PMA contacts. Regarding the role of the PMA length, the two dendrimer generations exhibit a somewhat different behavior. In the G2-based complexes the degree of ionic pairing is higher in the short length PMA systems, while in the case of G3 there is a preferential ionic pairing between the longer PMA chains with their counterions.

Conclusion

In this work we have performed an *in silico* study of complexation of PAMAM/PMA systems (1:1 and 1:2 molar ratios) in dilute aqueous solutions at physiological pH and at low ionic strength. According to our simulations, under these conditions, a polymer-rich and a solvent-rich phase are predicted. In the polymer-rich region aggregates of dendrimer/linear complexes are formed, resembling percolating structures commonly met in physical nanogels. The average dimensions of the polymeric components are not affected appreciably by complexation, but the dendrtitic molecules assume much more asymmetric shapes compared to those in the corresponding uncomplexed systems.

The polyanion linear chains are preferentially adsorbed onto the dendrimers' surface, whereas the degree of ionic pairing

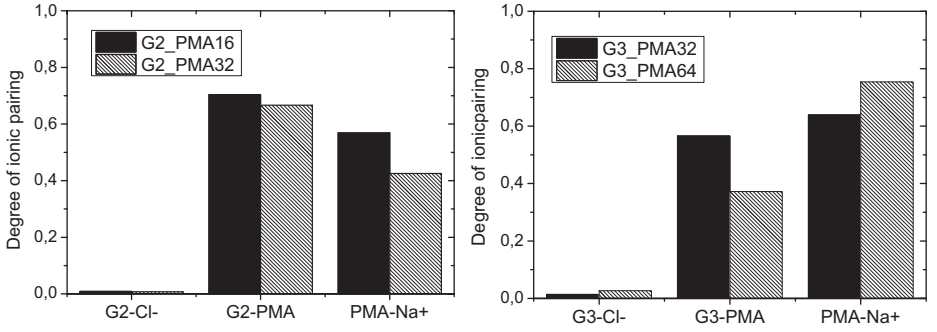


Figure 4.
Degree of electrostatic pairing between oppositely charged moieties (monomers or counterions).

between dendrimers' protonated amines and the negative counterions is very low. Depending on the size of the dendrimer and the PMA chains, different characteristics of the electrostatic pairing are observed. Taking into account that the intensity and the nature of electrostatic interactions between the various components contribute significantly to the final equilibrium morphologies of such systems, the differences observed between the studied models can be particularly useful in the design of responsive hydrogels formed by PAMAM and PMA mixtures.

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[1] A. M. Lowman, T. D. Dziubla, P. Bures, N. A. Peppas, *Adv. Chem. Eng.* **2004**, *29*, 75.
[2] L. Zha, B. Banik, F. Alexis, *Soft Matter* **2011**, *7*, 5908.
[3] S. Argentiere, L. Blasi, G. Morello, G. Gigli, *J. Phys. Chem. C* **2011**, *115*, 16347.
[4] G. Pasparakis, M. Vamvakaki, *Polym. Chem.* **2011**, *2*, 1234.
[5] N. Sahiner, W. T. Godbey, G. L. McPherson, V. T. John, *Colloid Polym. Sci.* **2006**, *284*, 1121.
[6] I. J. Majoros, T. P. Thomas, C. B. Mehta, J. R. Baker, *J. Med. Chem.* **2005**, *48*, 5892.
[7] S. Xu, Kr auml, M. mer, R. Haag, *J. Drug Target.* **2006**, *14*, 367.
[8] C. Alexander, K. M. Shakesheff, *Adv. Mater.* **2006**, *18*, 3321.
[9] P. Posocco, E. Laurini, V. Dal Col, D. Marson, K. Karatasos, M. Fermeglia, S. Pricl, *Curr. Med. Chem.* **2012**, *19*, 5062.
[10] K. Karatasos, P. Posocco, E. Laurini, S. Pricl, *Macromol. Biosci.* **2012**, *12*, 225.
[11] G. M. Pavan, P. Posocco, A. Tagliabue, M. Maly, A. Malek, A. Danani, E. Ragg, C. V. Catapano, S. Pricl, *Chem. Eur. J.* **2010**, *16*, 7781.
[12] D. Shukla, C. P. Schneider, B. L. Trout, *J. Phys. Chem. Lett.* **2011**, *2*, 1782.
[13] K. Tsutsumiuchi, K. Aoi, M. Okada, *Polym. J.* **2000**, *32*, 107.
[14] I. Tanis, K. Karatasos, *Phys. Chem. Chem. Phys.* **2009**, *11*, 10017.
[15] V. A. Kabanov, A. B. Zezin, V. B. Rogacheva, T. V. Panova, E. V. Bykova, J. G. H. Joosten, J. Brackman, *Faraday Discuss.* **2005**, *128*, 341.
[16] J. T. Zhang, S. W. Huang, R. X. Zhuo, *Macromol. Biosci.* **2004**, *4*, 575.
[17] R. S. Navath, A. R. Menjoge, H. Dai, R. Romero, S. Kannan, R. M. Kannan, *Mol. Pharm.* **2011**, *8*, 1209.
[18] D. Cakara, J. Kleimann, M. Borkovec, *Macromolecules* **2003**, *36*, 4201.
[19] L. Ruiz-Perez, A. Pryke, M. Sommer, G. Battaglia, I. Soutar, L. Swanson, M. Geoghegan, *Macromolecules* **2008**, *41*, 2203.
[20] A. Pohlmeier, S. Haber-Pohlmeier, *J. Colloid Interface Sci.* **2004**, *273*, 369.
[21] B. Jerman, C. Podlipnik, K. Kogej, *Acta Chim. Slov.* **2007**, *54*, 509.
[22] V. Crescenzi, *Adv. Polymer Sci.* **1968**, *5/3*, 358.
[23] D. Reith, B. Muller, F. Muller-Plathe, S. Wiegand, *J. Chem. Phys.* **2002**, *116*, 9100.
[24] M. S. Sulatha, U. Natarajan, *Ind. Eng. Chem. Res.* **2011**, *50*, 11785.
[25] E. Tsuchida, K. Abe, *Adv Polym Sci* **1982**, *45*, 1.
[26] M. Peláez-Fernández, A. Moncho-Jordá, J. Callejas-Fernández, *Epl* **2010**, *90*, 46005.
[27] S. V. Lyulin, K. Karatasos, A. Darinskii, S. Larin, A. V. Lyulin, *Soft Matter* **2008**, *4*, 453.
[28] S. V. Larin, A. A. Darinskii, A. V. Lyulin, S. V. Lyulin, *J. Phys. Chem. B* **2010**, *114*, 2910.
[29] G. Dalakoglou, K. Karatasos, S. Lyulin, S. Larin, A. Darinskii, A. Lyulin, *Polymers* **2012**, *4*, 240.
[30] J. C. Conrad, H. M. Wyss, V. Trappe, S. Manley, K. Miyazaki, L. J. Kaufman, A. B. Schofield, D. R. Reichman, D. A. Weitz, *J. Rheol.* **2010**, *54*, 421.
[31] J. C. Phillips, R. Braun, W. Wang, J. Gumbart, E. Tajkhorshid, E. Villa, C. Chipot, R. D. Skeel, L. Kalé, K. Schulten, *J. Comput. Chem.* **2005**, *26*, 1781.
[32] W. D. Cornell, P. Cieplak, C. I. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, P. A. Kollman, *J. Am. Chem. Soc.* **1995**, *117*, 5179.
[33] W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, M. L. Klein, *J. Chem. Phys.* **1983**, *79*, 926.
[34] J. Gasteiger, M. Marsili, *Tetrahedron* **1980**, *36*, 3219.
[35] I. Tanis, K. Karatasos, *J. Phys. Chem. B* **2009**, *113*, 10984.
[36] H. Lee, J. R. Baker, R. G. Larson, *J. Phys. Chem. B* **2006**, *110*, 4014.
[37] A. Soldera, N. Metatla, *Internet Electron. J. Mol. Des.* **2005**, *4*, 721.
[38] B. Sibeko, Y. E. Choonara, L. C. du Toit, G. Modi, D. Naidoo, R. A. Khan, P. Kumar, V. M. K. Ndesendo, S. E. Iyuke, V. Pillay, *J. Drug Deliv.* **2012**, *2012*, 579629.
[39] K. Karatasos, *J. Phys. Chem. B.* **2013**, DOI: 10.1021/jp312125c
[40] D. Leisner, T. Imae, *J. Phys. Chem. B* **2003**, *107*, 13158.

[41] M. Ujihara, T. Imae, *Polym. Int.* **2010**, *59*, 137.
[42] E. Eleftheriou, K. Karatasos, *J. Chem. Phys.* **2012**, *137*, 144905.
[43] K. Karatasos, M. Krystallis, *J. Chem. Phys.* **2009**, *130*, 114903.
[44] K. Krohne, S. Duschner, D. Storkle, M. Schmidt, M. Maskos, *Macromolecules* **2010**, *43*, 8645.
[45] B. Jerman, M. Breznik, K. Kogej, S. Paoletti, *J. Phys. Chem. B* **2007**, *111*, 8435.
[46] W. D. Tian, Y. D. Ma, *Chem. Soc. Rev.* **2013**.
[47] W. D. Tian, Y. Q. Ma, *J Phys. Chem. B* **2009**, *113*, 13161.
[48] W. D. Tian, Y. Q. Ma, *Soft Matter* **2010**, *6*, 1308.
[49] S. Huissmann, A. Wynveen, C. N. Likos, R. Blaak, *J. Phys-Condens. Mat.* **2010**, *22*, 232101.
[50] C. L. de Vasconcelos, P. M. Bezerril, D. E. S. dos Santos, T. N. C. Dantas, M. R. Pereira, J. L. C. Fonseca, *Biomacromolecules* **2006**, *7*, 1245.
[51] A. J. Khopade, F. Caruso, *Langmuir* **2002**, *18*, 7669.
[52] N. S. Karybiants, O. E. Philippova, S. G. Starodoubtsev, A. R. Khokhlov, *Macromol. Chem. Phys.* **1996**, *197*, 2373.
[53] P. G. Ferreira, M. Dymitrowska, L. Belloni, *J. Chem. Phys.* **2000**, *113*, 9849.
[54] D. Bernin, G.-J. Goudappel, M. van Ruijven, A. Altskar, A. Strom, M. Rudemo, A.-M. Hermansson, M. Nyden, *Soft Matter* **2011**, *7*.
[55] Y. Liu, C. Y. Chen, H. L. Chen, K. Hong, C. Y. Shew, X. Li, L. Liu, Y. B. Melnichenko, G. S. Smith, K. W. Herwig, L. Porcar, W. R. Chen, *J. Phys. Chem. Lett.* **2010**, *1*, 2020.
[56] G. K. Dalakoglou, K. Karatasos, S. V. Lyulin, A. V. Lyulin, *J. Chem. Phys.* **2007**, *127*, 214903.
[57] W. D. Tian, Y. Q. Na, *Macromolecules* **2010**, *43*, 1575.
[58] J. Rudnick, G. Gaspari, *J. Phys. A: Math. Gen.* **1986**, *19*, L191.
[59] P. K. Maiti, T. Cagin, B. Wang, W. A. Goddard, III, *Macromolecules* **2004**, *37*, 6236.
[60] E. Tsuchida, Abe, K., *Adv. Polym. Sci.* **1982**, *45*, 1.

