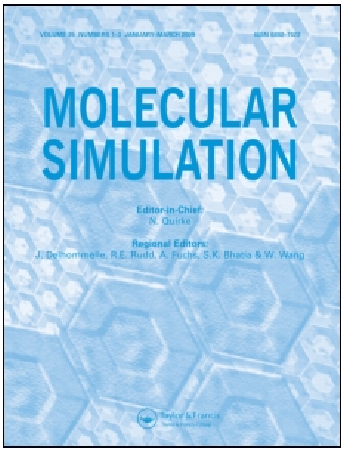

Molecular Simulation
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713644482

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To cite this Article Yarovsky, Irene and Evans, Evan(2002) 'Atomistic simulation of the sol formation during synthesis of organic/inorganic hybrid materials', Molecular Simulation, 28: 10, 993 — 1004
To link to this Article: DOI: 10.1080/08927020400002629
URL: http://dx.doi.org/10.1080/08927020400002629

Molecular Simulation, 2002 Vol. 28 (10–11), pp. 993–1004

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ATOMISTIC SIMULATION OF THE SOL FORMATION DURING SYNTHESIS OF ORGANIC/INORGANIC HYBRID MATERIALS

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(Received February 2001; In final form November 2001)

Atomistic modelling was employed to investigate interactions between the precursors used in preparation of organic/inorganic polymer hybrids. Three molecular systems composed of different kinds of organofunctionalised silanes and an organic polymer in aqueous solution have been simulated, representing various model stages of the hydrolysis reaction during the sol/gel processing. The equilibrium configurations obtained by Molecular Dynamics were analysed in order to elucidate the extent of the hydrogen bonding network and clustering of components within the systems. Diffusion coefficients were obtained to estimate the mobility of the components and the stability of the molecular associations. It has been concluded that the molecular mechanism of the initial stages of the sol/gel process used for preparation of the organic/inorganic hybrids involves clustering of the organofunctionalysed inorganic components as a first step and then progressive hydrolysis as consequent steps. The organic polymer component plays a role of the cluster "wrap" and thus prevents the particles from unlimited growth and precipitation from the solution.

Keywords: Hydrolysis; Molecular dynamics; Organic/inorganic polymer hybrids; Sol/gel process; Hydrogen bonding; Hydrophobic effect

INTRODUCTION

Organic/Inorganic Polymer Hybrids (OIPHs) have recently attracted a lot of attention from both academia and industry due to their unique properties and a possibility to manipulate those properties via knowledge based materials design

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ISSN 0892-7022 © 2002 Taylor & Francis Ltd
DOI: 10.1080/0892702021000002629

[1,2]. Coatings formulation is one of the most important applications of this class of materials since they can offer increased hardness due to their inorganic components and, at the same time, retained or improved flexibility due to their polymeric component [3]. Several hypotheses have been suggested on the molecular mechanisms of formation of the hybrid materials based primarily on experimental measurements during various stages of the sol-gel process, the most important method for preparation of inorganic amorphous solids [1,2]. However, precise formation mechanisms at various conditions that would allow materials with desired properties to be designed need further investigation.

Molecular dynamics simulations have been demonstrated to provide structural and dynamic information on aqueous systems, including polymer hydrogels, that is unavailable by any other method [4–9]. The purpose of this study was to use molecular modelling to better understand the molecular interactions at the initial stages of the sol-gel process used for preparation of select organic inorganic hybrid materials, namely the formation of a sol. This involved construction of molecular models of aqueous solutions of different kinds of organofunctionalised silanes and organic polymer representing various *model* stages of the hydrolysis reaction. Information about the materials composition at the various reaction stages was obtained by NMR spectroscopy [10]. Structural and dynamic developments of the model molecular systems representing stages of the hydrolysis reaction have been observed and interpreted in terms of fundamental intermolecular interactions and their effects on molecular mechanisms of the initial phase of the sol/gel process.

COMPOSITION OF MOLECULAR MODELS

Formulations of water based OIPH solutions for this modelling study included 3-Glycidyloxypropyltrimethoxysilane (ES) and Tetra-Ethoxysilane (TEOS) as inorganic precursors, Polyvinyl alcohol (PVA) of a polymerisation degree (PD) 20 as a polymeric component, and water. The molar ratio of the components was calculated from the weight ratio used during synthesis of the real hybrid coatings [11] with PD (and proportionally all the other components) scaled down compared to the real formulation. An acid and crosslinker components present in the real systems have been omitted from the models because of their relatively minor weight fractions that, if included, would require computationally unfeasible large size models. The components will however be considered in the future work.

To represent different stages of hydrolysis in the system, three molecular models have been constructed for the MD simulations: original (not hydrolysed);

TABLE I Composition of the model systems representing different stages of hydrolysis

	Weight fraction of components (%)		
Components	Model 1 not hydrolysed*	Model 2 partly hydrolysed	Model 3 fully hydrolysed
PVA	6.1 (6.0)	6.1	6.6
ES	6.1 (6.0)	–	–
ES with hydrolysed epoxy group	–	6.6	–
Fully hydrolysed ES	–	–	5.9
TEOS	12.9 (12.0)	12.9	–
Hydrolysed TEOS	–	–	6.5
WATER	74.9 (76)	74.4	81.0

* Experimental values shown in brackets.

partly hydrolysed (epoxy group in ES hydrolysed); and fully hydrolysed (epoxy, methoxy- and ethoxy- groups in ES and TEOS hydrolysed) [11]. Although we recognise that in reality a fully hydrolysed system will never be formed from the precursors without any condensation reaction between silanols happening at the same time, we decided to model this "hypothetical" stage in order to better understand effects of hydrolysis and associated change in hydrophobicity of the precursors on formation mechanisms. In the future work we will address this by constructing "intermediate" particles composed of several bonded silanes as determined by NMR to model a more realistic partly hydrolysed and partly condensed state. Compositions of the molecular models adopted in this work are presented in Table I.

Average density of the model molecular systems was set to 1.0 g/cm^3 based on the density of the components (0.934 (TEOS), 1.0 (water), 1.07 (ES) and 1.1 (PVA) g/cm^3). Total number of atoms in the unit cell of the model systems varied around 3000 depending on composition. The three dimensional (3D) periodic boundary conditions were applied to the unit cells during all subsequent simulations to mimic infinite systems.

SIMULATION PROTOCOL

To prepare initial model configurations, molecular components of each system specified in Table I were packed into a 3D periodic unit cell using the Theodorou-Suter algorithm [12] to ensure realistic chain statistics for the polymeric component are achieved. Ten starting configurations were generated for each system at the specified density. The subsequent relaxation of the systems was achieved by initial potential energy minimisation followed by molecular dynamics simulation with the periodic boundary conditions.

The COMPASS forcefield has been employed to model the interatomic potentials within the studied systems represented explicitly by all atoms [13]. The Ewald summation algorithm was used for calculation of non-bonded van der Waals and electrostatic interactions.

To achieve a faster relaxation of the starting system configurations molecular dynamics simulations were performed at elevated temperature with subsequent cooling of the systems down to the room temperature. In particular, the MD simulation (NVT ensemble) started at 400 K and then the temperature was reduced down to 300 K in 10 K steps, with 10 ps (10,000 time steps of 1 fs) simulations performed at each temperature. The room temperature equilibration run was then performed for another 200 ps (200,000 time steps) to ensure the system reached equilibrium. The equilibrium was checked by monitoring

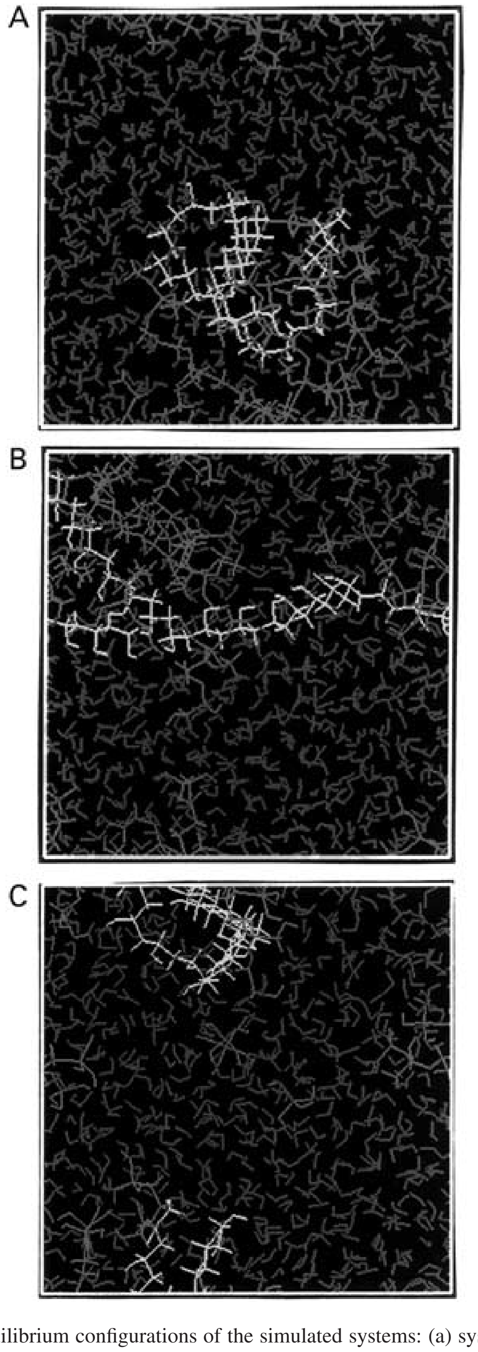

FIGURE 1 Final equilibrium configurations of the simulated systems: (a) system 1, (b) system 2, (c) system 3.

system's temperature and energy which only exhibited fluctuations around a mean value after the equilibrium has been reached. Direct velocity scaling was used to control temperature during the equilibration stage.

After achieving equilibrium the systems were subject to production MD simulations at the room temperature for 300 ps (300,000 time steps). At this stage the temperature was controlled by Andersen's algorithm of a weak coupling of the system to a thermal bath [14]. Atomic coordinates were stored on disk every 200 steps (0.2 ps) producing 15,000 equilibrium configurations for subsequent analysis of each system. All simulations were performed using the Amorphous Cell and Discover software from Accelrys, Inc. on a 4-processor Origin 2000 Silicon Graphics supercomputer.

RESULTS AND DISCUSSION

It was found that for each model system, all 10 different initial configurations followed the same trends as a result of the MD simulation. Therefore, for each model composition an equilibrium configuration of only one of the initial systems is graphically presented in Fig. 1. The figure shows that there are significant differences in structural organisation of the equilibrium configurations of the molecular models depending on the represented stage of the hydrolysis reaction.

In the original, non-hydrolysed model 1, a strong trend towards association of the organofunctionalised silane components of the system (ES and TEOS) was observed as can be seen from Fig. 1a. Both TEOS and ES components tend to agglomerate into a cluster as simulation progresses while the PVA chain attaches itself to the cluster. This mode of behaviour can be explained by the presence of hydrophobic residues on both ES and TEOS (methoxy and ethoxy groups) that tend to avoid interactions with water and, therefore, minimise water/CH_3 and water/CH_2 contacts via self-association. The PVA is capable of hydrogen bonding with water via its hydroxyl groups and therefore is interacting with both water and the silanes.

It can be suggested that the observed kind of agglomeration of the organofunctionalised components represents the first step towards formation of a silica particle. This step is then followed by a progressive hydrolysis of the precursors and condensation reaction between the newly formed –(Si–OH) groups. It can also be suggested that the agglomeration of organically modified components, driven by the hydrophobic effect, occurs *prior* to any significant hydrolysis. Modelling showed that during this aggregation process, the non-hydrolysed organic groups were available on the surface of the clusters resulting in their increased stability in the aqueous solution which is in agreement with the mechanism proposed from experiments [15].

By attaching itself to the precursor particles and thus resulting in being trapped between the inorganic clusters in the solid state, the polymeric component may provide the additional flexibility to the resultant coating observed experimentally [3]. The association with the inorganic cluster can also explain another suggested role of the polymeric component in preparation of the hybrid organic/inorganic materials, that is to prevent unlimited growth of the silica particles which could lead to their precipitation from solution or gelation [15].

Similar effects were observed in the model system 2, representing a partly hydrolysed system (where the epoxy group of ES is hydrolysed) as can be seen from Fig. 1b. In this system, the hydrophobic residues of the precursors are still available and this leads to a similar mode of behaviour, i.e. clustering, governed by the hydrophobic effect as in the system 1.

It could be noted though, that stronger interactions between the hydrolysed ES components and water due to possible H-bonding between the hydroxyl groups of the hydrolysed epoxy and water molecules can explain a slightly lower density of the organofunctionalised clusters formed during the simulation. However, the overall trend towards the aggregation of the organically modified silane components in water is still obvious. The PVA component is again holding itself on the organic/inorganic cluster surface, as in the system 1.

A dramatically different development was observed for the model system 3 representing fully hydrolysed precursors, as can be seen from Fig. 1c. The analyses of this system's time development suggest that hydrolysed TEOS and ES molecules do not form aggregates but are instead dissolved in water due to the favourable hydrogen bonding interactions that occur between the –(Si–OH) groups and water. This suggests that after the hydrolysis reaction had fully progressed, aggregation of the precursors leading to formation of a three-dimensional –(Si–O–Si)– network via condensation reaction is becoming less favourable. Therefore, our hypothesis that the hydrophobic aggregation is the first step and hydrolysis is consequent to the aggregation in the sol-gel processing is further supported.

Overall, the simulation suggests that the hydrophobic effect plays an important role in the mechanism of formation of silica particles from organofunctionalised silane precursors in aqueous solution. A balance between the hydrophobic and hydrophilic interactions of the components (that is governed by the relative amounts of hydrophilic and hydrophobic groups in solution) can be expected to influence the stability of the resultant hydrogel. This is because the hydrophobic/hydrophilic balance controls the size of the silica particles formed during the sol formation [16]. Such a dependence explains an experimentally demonstrated ability to manipulate the materials properties via balancing the hydrophobicity/hydrophilicity of the components by varying the size of the organic chains attached to the silane [16].

To quantitatively confirm the hypotheses made through the visual observations of the system's evolution, the equilibrium configurations were analysed in terms of specific interactions that occur in the systems. To achieve this the intermolecular radial distribution functions (rdf) have been calculated for the

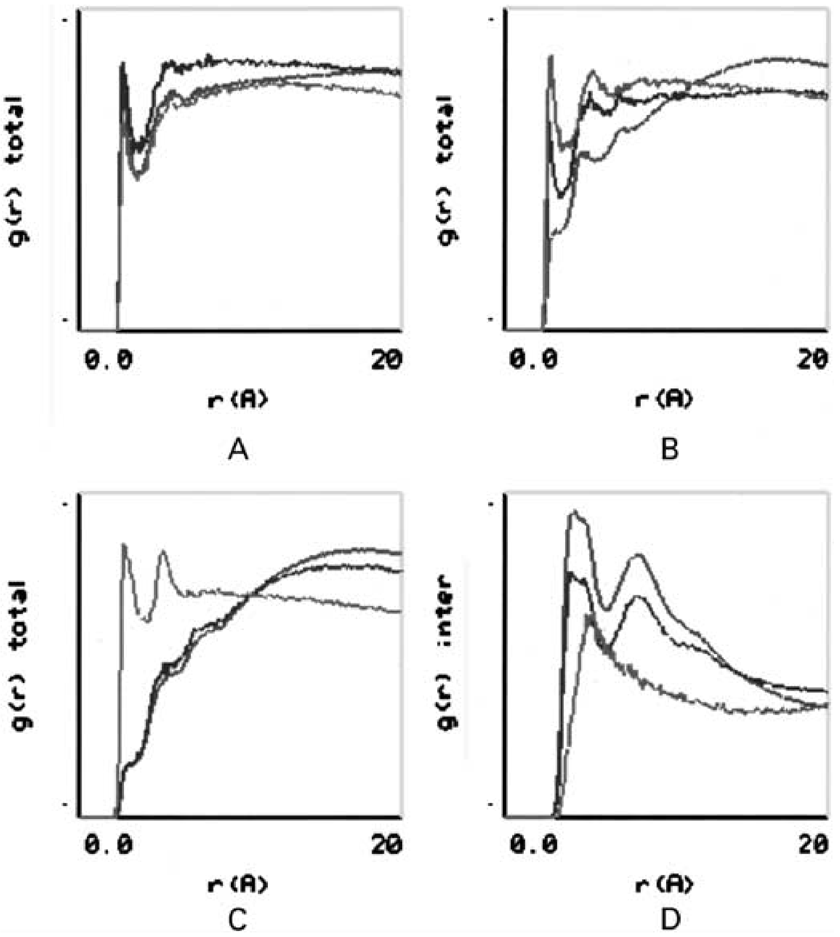

FIGURE 2 Radial distribution functions at different stages of the hydrolysis reaction: (a) between water oxygen atoms and PVA oxygen atoms; (b) between water oxygen atoms and ES oxygen atoms; (c) between water oxygen atoms and TEOS oxygen atoms; (d) between carbon atoms in different components.

following atom pairs (Fig. 2): (a) Water oxygen–PVA oxygen; (b) Water oxygen–ES oxygen;(c) Water oxygen–TEOS oxygen; (d) Carbon–Carbon.

It can be seen from (Fig. 2b,c) that the ES's and TEOS's oxygen exposure to water progressively increased as the hydrolysis reaction proceeded. This is demonstrated by the increased height of the first peak at 2.75 Å in the Oxygen–Oxygen rdfs and is in line with the observed clustering of the TEOS and ES components at the early stages of the hydrolysis reaction and the dissolution of the hydrolysed ES and TEOS in water after the reaction. The first peak indicates hydrogen bonding between water molecules and the silanol –(Si–OH) groups of hydrolysed ES and TEOS molecules suggesting a formation of the first hydration shell around these components. The second peak appearing at 5.25 Å for the hydrolysed systems is indicative of the formation of a second hydration shell around the ES and TEOS components. This demonstrates dissolution of the hydrolysed silanes in water as suggested from visualisation of the equilibrium model systems.

The PVA exposure to water was quite similar for the systems 1 and 2 where the clustering of the organofunctionalised components occurred and the polymer attached itself to the cluster. Hydrogen bonds were formed in both systems between the OH-groups of the polymer and water, as demonstrated by the first peak at 2.75 Å of the rdf (Fig. 2a). For the system 3, the polymer molecule collapsed on itself forming a globular structure. As a result, the PVA molecule was not capable of forming the same amount of hydrogen bonds with the surrounding water molecules due to its more globular structure. Hence, the pronouncedly diminished first peak in the polymer–water rdf for the system 3 (Fig. 2a).

Figure 2d shows the intermolecular radial distribution functions for carbon atoms in all components. The presence of two peaks at 4.15 and 8.05 Å suggests that there is a short to mid range structuring, i.e. clustering, of the organic components in the systems at the early stages of the reaction (systems 1,2). However, it can be noted that the structuring diminishes as the hydrolysis progresses, i.e. in system 2 there is less clustering than in system 1, as demonstrated by the decreased height of the peaks in rdfs. Furthermore, the single peak of lower height at a larger separation distance (5.45 Å) for the system 3 demonstrates a further decrease in clustering which is in line with the visual observations.

To compare dynamic properties of the systems, in particular, mobility of water and other components, diffusion constants have been calculated from the mean-square displacements of the molecule centre of mass using the Einstein relation [17]. The diffusion constants were calculated using the ensemble averages from the equilibrium part of the Molecular Dynamics trajectory and are presented in

TABLE II Diffusion coefficients ($\times 10^5\,\mathrm{cm^2/s}$) of components of organic/inorganic polymer hybrid water solutions

	Water	ES	TEOS
System 1	1.50	0.29	0.20
System 2	1.48	0.25	0.17
System 3	1.70	0.44	1.09

Table II. It should be noted that in the systems 1 and 2 where the component aggregation was observed, it happened during the equilibration stage which resulted a truly linear region in the mean squared displacement during the production stage of the MD simulations. The calculated water diffusion constants are 30–40% lower than those experimentally observed for pure water at 298 K (2.11–$2.66 \times 10^{-5}\,\mathrm{cm^2/s}$ [18]) which is in agreement with other simulations of hydrogels [19] and bio-organic aqueous solutions such as those of polypeptides and proteins [20].

It can be seen that the overall mobility of the components was significantly higher in the fully hydrolysed system 3. This can be explained by the observed formation of a molecular solution in this system, where the components do not form aggregates but rather move freely within the solution. The most dramatic increase in mobility was observed for the hydrolysed TEOS components in the system 3: the molecule is of a significantly lower molecular weight than the original TEOS and it also became highly soluble in water due to the newly formed four hydroxyl groups (silanols).

It is interesting to observe a slight decrease in mobility for the components of the system 2 compared to system 1. This observation can be explained by the fact that hydrogen bonds form between the partly hydrolysed ES component and water. This additional structuring decreased the mobility of both the cluster components and water molecules involved in the hydrogen bonds.

It can be concluded that the observed increase in mobility of the components of the fully hydrolysed system 3 further confirms the hypothesis on the initial agglomeration (and hence demobilisation) of the organically modified silanes due to the hydrophobic effect in the process of sol formation.

CONCLUSION

As a result of the Molecular Dynamics simulations of the model organofunctionalised silanes and PVA polymer in aqueous solution at various realistic and hypothetical stages of hydrolysis reactions it can be suggested that molecular mechanism of initial stages of the sol-gel processing, i.e. formation of a sol, involves hydrophobic association of the organofunctionalised silanes followed by their progressive hydrolysis. The polymeric component associates with the cluster surface due to its relatively good affinity to both organofunctionalised and aqueous parts of the system.

It should be noted that the effects of the component concentration on the sol formation during synthesis of organic/inorganic hybrid materials have also been recently investigated and reported separately [21].

Acknowledgements

Numerous discussions with Prof. Ian Snook (RMIT University) were very helpful. Financial support by BHP is greatly appreciated.

References

[1] Laine, R.M., Sanchez, C., Brinker, C.J. and Ciannelis, E., eds. (1998) Organic/Inorganic Hybrid Materials, Materials Research Society Proceedings (Materials Research Society, PA, USA) **Vol. 519**.

[2] Klein, L.C., Francis, L.F., De Guire, M.R. and Mark, J.E., eds. (1999) Organic/Inorganic Hybrid Materials II, Materials Research Society Proceedings (Materials Research Society, PA, USA) **Vol. 576**.

[3] Klein, L.C., Van Wert, J. and Beaudry, C.L. (1999) “Mechanical properties of soluble polymer/silica gel hybrids”, In: Klein, L.C., Francis, L.F., De Guire, M.R. and Mark, J.E., eds, MRS Proceedings (Materials Research Society, PA, USA) **Vol. 576**, pp 337–342.

[4] Tamai, Y. and Tanaka, H. (1999) “Structure and dynamics of poly(viny1 alcohol) hydrogel”, *Mol. Simul.* **21**, 283.

[5] Yarovsky, I., Hearn, M.T.W. and Aguilar, M.I. (1997) “Molecular simulation of peptide interactions with an RP-HPLC sorbent”, *J. Phys. Chem. B* **101**, 10962.

[6] Netz, P.A. and Dorfmuller, T. (1998) “Computer simulation studies on the polymer-induced modification of water properties in polyacrylamide hydrogels”, *J. Phys. Chem. B* **102**, 4875.

[7] Muller-Plathe, F. (1998) “Microscopic dynamics in water-swollen poly(vinyl alcohol)”, *J. Chem. Phys.* **108**, 8252.

[8] Muller-Plathe, F. and van Gunsteren, W.F. (1997) “Solvation of poly(vinyl alcohol) in water, ethanol and an equimolar water–ethanol mixture: structure and dynamics studied by molecular dynamics simulation”, *Polymer* **38**, 2259.

[9] Tamai, Y., Tanaka, H. and Nakanishi, K. (1996) “Molecular dynamics study of water in hydrogels”, *Mol. Simul.* **16**, 359.

[10] Burgar, I., and Evans, E., Unpublished data, BHP Steel Pty. Ltd., Port Kembla, Australia.

[11] Evans, E., Unpublished data, BHP Steel Pty. Ltd., Port Kembla, Australia.

[12] Theodorou, D.N. and Suter, U.W. (1986) “Atomistic Modeling of mechanical-properties of polymeric glasses”, *Macromolecules* **19**, 139.

[13] Sun, H. (1998) “COMPASS: an *ab initio* force-field optimized for condensed-phase applications—overview with details on alkane and benzene compounds”, *J. Phys. Chem. B* **102**, 7338.

[14] Andersen, H.C. (1980) “Molecular-dynamics simulations at constant pressure and-or temperature”, *J. Chem. Phys.* **72**, 2384.

[15] Schmidt, H.K., Arpac, E., Schirra, H., Sepeur, S. and Jonschker, G. (1998) "Aqueous sol-gel derived nanocomposite coating materials", In: Laine, R.M., Sanchez, C., Brinker, C.J. and Ciannelis, E., eds, MRS Proceedings (Materials Research Society, PA, USA) **Vol. 519**, pp 297–308.
[16] Hench, L.L. and West, J.K. (1990) "The Sol-gel process", *Chem. Rev.* **90**, 33.
[17] Haile, J.M. (1992) *Molecular Dynamics Simulation* (Wiley, New York), pp 297–298.
[18] Eisenberg, D. and Kauzmann, W. (1969) *The Structure and Properties of Water* (Oxford University Press, London, UK).
[19] Tamai, Y., Tanaka, H. and Nakanishi, K. (1996) "Molecular dynamics study of polymer–water interaction in hydrogels. 2. Hydrogen-bond dynamics", *Macromolecules* **29**, 6761.
[20] Kitao, A., Hirata, F. and Go, N. (1993) "Effects of solvent on the conformation and the collective motions of a protein. 2. Structure of hydration in Melittin", *J. Phys. Chem.* **97**, 10223.
[21] Lay, H.C. and Yarovsky, I. (2001) "Effect of water concentration on sol formation in synthesis of organic/inorganic hybrid materials", *Mol. Sim.* in press.