

ESF Exploratory Workshop on

**Hyperbranched polymers as novel
materials for nanoscale
applications: insight from experiment,
theory and simulations
(HYPER-NANO)**

SCIENTIFIC REPORT

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Convened by:

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Executive Summary

At the ESF exploratory workshop entitled “*Hyperbranched polymers as novel materials for nanoscale applications: insight from experiment, theory and simulations*” apart from the two convenors, 24 researchers participated, affiliated in 12 countries (Denmark, France, Germany, Greece, Ireland, Italy, Netherlands, Poland, Russia, Spain, Switzerland, United Kingdom). One researcher (Dr. Sabrina Pricl, Italy) unfortunately could not participate due to last-minute unforeseen personal reasons. Two of the participants (Prof A. Darinskii and Dr. S. V. Lyulin) were invited from a non-ESF associated country, Russia, because it was considered that their international reputation and their expertise in the field of molecular simulations of systems involving hyperbranched polymers, would significantly increase the scientific level of the workshop

The area of expertise of the participants covered theory, experiment and simulations in the field of hyperbranched polymers and polymeric supramolecular compounds, in order to allow a spherical view of the forefront of the research performed in this topic, and to promote contacts between scientists of diverse backgrounds that are active in the field.

The workshop program was organized in such a manner, that each session (composed by 4 talks) would cover a specific thematic area. The first day (26th of May) the topics covered included synthesis, characterization and the structure-properties relation of hyperbranched systems. Synthetic procedures of novel dendritic polymers and supramolecular polymeric structures were presented, assessing also the role of the synthesized materials in a number of actual or potential nanoscale applications (Prof. Anne-Marie Caminade, Dr. Tamis Darbre, Dr. Erwan Nicol). The chemistry protocols which may result to the functional modification of already synthesized hyperbranched polymers, as well as the very important issue regarding their separation in terms of their size and topology were discussed as well (Dr. Albena Lederer, Dr. Wolfgang Radke). As a natural follow-up, experimental techniques (i.e. rheology, dielectric spectroscopy, light, neutron and x-ray scattering, phase-equilibria) which can provide detailed information for their structure, their conformational characteristics, their transport and viscoelastic behavior and their physicochemical properties were presented (prof. Dimitrios Vlassopoulos, Dr. Silke Rathgeber, Dr. Anatoli Serghei, Dr. Christopher Plummer, Dr. Tijs Vlucht, Prof. Rob Richardson, Dr. Nicola Tirelli). On the second day (27th of May), the talks were devoted to the theoretical description of the complex behavior of the hyperbranched systems by means of statistical mechanical methods and computer simulation techniques, under different thermodynamic environments (Prof. Christos Likos), their potential to self-organize and to respond to different stimuli (Prof. Anatoli Darinskii, Dr. Martin Buzza), their ability to form complexes with polymers bearing different topologies (Dr. Andrey Gurtovenko, Dr. S. V. Lyulin) or smaller substances (Dr. Igor Neelov), and finally to the description of possible ways to control their conformational properties (Prof. Juan Freire and Dr. Edward Timoschenko). At the last day (28th of May), the particularly important issue of the utilization of hyperbranched systems for therapeutic purposes was discussed (Dr. Barbara Klajnert, Dr. Zili Sideratou, Dr. Ulrik Boas).

After each individual presentation, a lively discussion followed, giving the possibility to scientists not expert in the presented field, to reach a better level of understanding and to offer ideas originating from their own field of expertise to the discussed subject. At the end of each day, a round-table discussion was organized, focused on the subjects previously presented but also at relevant subjects in the field. The friendly and informal atmosphere of these discussions proved particularly beneficial allowing a closer interaction between the participants. The results of the established contacts are already visible, since during these discussions the basis for several collaborations between participants was set (a consortium between several of the participants has already been formed for a common submission of an ESF COST proposal).

The two organizers, Dr K. Karatasos and Dr. A. V. Lyulin, would also like to thank the ESF delegate prof. M. Waroquier for his lively participation and the support he offered through his useful comments, as well as for his strong encouragement towards participation to other ESF actions.

Scientific content of the event

The first session of the workshop entitled “*Novel hyperbranched systems – Synthesis and some applications*” aimed at familiarizing the audience to the synthetic procedures of novel hyperbranched and supramolecular polymer systems as well as to demonstrate their potential to be utilized in a number of modern “cutting-edge” applications.

In the first talk professor Anne-Marie Caminade made a general introduction to a category of hyperbranched polymers with symmetric topology, the so-called dendrimers, and then she discussed the class of dendrimer molecules which were based on phosphorus chemistry. She elaborated on the synthesis procedure^{1, 2} as well as on the chemistry protocols that can be followed for their functionalization and the modification of their surface groups^{3, 4}, and their usage as building blocks for more complex polymeric architectures⁵. She demonstrated the favorable behavior of the so-produced structures in terms of their physical properties like the thermal stability⁶, their ability to be solubilized and to form hydrogels⁷ or to self-assemble and form supramolecular structures⁸. Next, she showed several of the possible uses of these systems like the production of dendrimer-based nanotubes⁹ and their use in biosensors¹⁰, the build-up of DNA chips (“Dendri-chips”) by the mediation of dendrimers as multifunctional binding sites¹¹⁻¹³, their usage in biosensor applications¹⁴ or as sites assisting the multiplication of human natural-killer cells^{15,16}. In conclusion she emphasized the importance of the structural and chemical characteristics of dendrimers, like the type and the surface density of the functional groups, their generation, the composition of their core, the chemical nature of the branches and the internal architectural details, to the manifestation of their physical properties and consequently to their capability of being used in a wide range of nanoscale applications.

Next, Dr. Tamis Darbre discussed a class of hyperbranched systems of particular biological interest, the peptide dendrimers. The dendritic architecture when applied to peptides, provides a practical entry into globular macromolecules resembling proteins. Dr. Darbre described the synthesis procedure¹⁷ which can produce single molecules of 3-5KDa molecular weight¹⁸ and provide control regarding the number and the kind of residues between the branching units and the final number of generations. Such a high level of control of these characteristics proved essential when it came to the efficiency of their biological action. As Dr. Darbre showed, their ability to catalyze ester hydrolysis reactions sensitively depends on these characteristics^{17, 19}. In a more detailed description, it was also demonstrated how by modifying the sequence of the amino acids within the peptide dendrimer branches, one may significantly affect their catalytic activity¹⁷. In order to explore large libraries of peptide dendrimers, Dr. Darbre explained a combinatorial approach specifically developed for this purpose²⁰. Following this procedure, peptide dendrimers with a single catalytic site was possible to be synthesized²⁰. Moreover, it was described how the specificity of their action (e.g. when binding to specific biological molecules is required) can be “imprinted” in their structure by including specific residues at the appropriate sites within the structure²¹, and how their multifunctionality arising from the dendritic structure can be exploited in order to enhance the biological action against bacteria like the *Pseudomonas Aeruginosa*²²

In the last talk of this session, Dr. Erwan Nicol, discussed synthetic strategies for the production of the so-called polymeric “hyperstructures”. These term describes macromolecular structures formed by elementary macromolecular units which are already characterized by a complex architecture. Dr. Nicol, provided several examples of such molecules, like pom-pom structures comprised by connected dendrimers, flower and garland-like structures which may aggregate to produce gels, or structures comprised by self-assembled micelles which can form nanotubes. He elaborated on a step-like, hierarchical synthetic strategy based on diblock and triblock copolymers as elementary building blocks, through which such supramolecular structures can be produced²³. Then, he focused on their self-assembly properties and the possible routes to obtain control of the structural characteristics of the resulting aggregates. Another approach which he described for the production of these “hyperstructures”, was based on a controlled chemical crosslinking method (e.g. by utilizing photo-sensitive crosslinking agents). To a second level of organization, the produced structures could form a physical network resulting to a gel material. Concluding his talk, Dr. Nicol emphasized the application potential of these materials, while also pointing out the need for a more basic understanding of the mechanisms involved in the manifestation of some transient structural states which may affect their physical properties.

The next session “*Functional modification and characterizations of hyperbranched systems*” focused on the state of the art and the current problems regarding the characterization and the separation techniques of non-regular-in-structure hyperbranched systems (HBP), which, due to their low cost of production, are expected to play a significant role in large-scale industrial applications.

In the first talk of this session, Dr. Christopher Plummer presented a number of industrially important applications, based on irregular in structure hyperbranched polymers. As an introduction Dr. Plummer stressed the main advantages of this class of polymers, namely their potential for tailoring their functionality by modifying their terminal groups and controlling thus properties like their solubility and miscibility with other compounds, their low viscosity compared to same-molecular-weight linear polymers, and their multifunctionality due to the large number of terminal groups at a relatively small volume. Specific applications related to industrially interesting formulations were described, like the control of solubility in an epoxy-resin matrix upon addition of HBP, and the possibility of controlling the phase separation process during cure which enables an optimized second phase toughening with HBP acting as a low viscosity additive²⁴.

Another category of industrially important materials that were described, was the HBP-based polymer-clay nanocomposites^{25, 26}. These materials may exhibit better mechanical and thermoset processing behavior compared to conventional polymeric systems used so far. Dr. Plummer presented results showing that such composites consisted of hyperbranched polyurethanes may significantly improve the performance in applications where conventional rubber is utilized²⁶. It is now conjectured that use of such materials e.g. in the car tyre industry, will lead to a new generation of products which will improve fuel efficiency and increase the tyre life. A different group of applications involving HBPs relies upon the possibility to modify their functionality by appropriate substituting their surface groups. By performing such modification, Dr. Plummer demonstrated the possibility of producing HBP-based multiarm star block copolymers^{27, 28} which may find several applications, like to act as stabilization agents in aqueous dispersions of hydrophobic species e.g. olfactory molecules or pharmaceutical substances²⁹. He also discussed cases where functionalized HBPs were used as major components in a UV curable resin for precision micromoulding³⁰ where control of shrinkage is an important issue^{31, 32}. Summarizing Dr. Plummer argued that HBPs can be used in a wide range of industrial applications based on functionally modified commercial materials, pointing out the cost effectiveness when utilizing these materials instead of the more expensive regular branched analogues, even if their characterization appears to be more tedious.

Dr. Lederer who followed, focused exactly on this point, that is, on methods of characterization and separation of HBPs. The problems related to their characterization arise from the statistical type of the polycondensation reaction in the one-pot procedure followed in their synthesis, which results in broad mass and branching distributions. Their separation in fractions of narrow polydispersity in terms of branching pattern and size is a rather tedious task³³ as Dr. Lederer commented. She noted though that recently a significant progress has been made in this area, by a method based on their degree of branching.³⁴ She described a procedure based on the modification of a hyperbranched polyester, in order to obtain molecules bearing different polarity of the terminal and the linear units so that they could be chromatographically discerned. Apart from that modification, narrow distributed samples of different molar masses were required as standard materials for calibrations of the chromatographic system.³⁵ Dr. Lederer described the techniques for characterization of the produced molecules, which included NMR, SEC coupled to MALLS, RI and viscosity detector (triple SEC). In order to obtain samples with low polydispersity and different molar masses out of the broadly distributed polyesters, she and her colleagues performed elution fractionation. The results from the analysis techniques, showed that the solubility of the samples depended on the type of the end-groups. It was demonstrated that the molecules of polar terminated polyester exhibited a more compact structure, whereas the samples bearing non-polar end-groups assumed a more open structure with higher affinity of the solvent. In this way it became possible for Dr. Lederer to accomplish a better characterization of the HBP polyester, rendering the adopted procedure a promising route towards separation of other HBP molecular species as well.

The last talk of this session by Dr. Wolfgang Radke was also devoted to the description of chromatographic techniques for the separation of HBP samples. After discussing the problems that might be encountered in the characterization of branched polymers using conventional

separation techniques like Size Exclusion Chromatography (SEC), he proposed a new route towards this objective, by utilization of interaction chromatography techniques to separate linear from branched species prior to detection³⁶. He demonstrated a method which involved a 2-dimensional separation of a mixture of linear polymers (polystyrene) with star-shaped analogues. Following this procedure he showed that the elution regions for the linear and branched species could be clearly distinguished, allowing thus the quantification of the amount of star-shaped material from a matrix of linear polymers.³⁷ He also remarked that gradient chromatography methods are suitable for such separations since hyperbranched molecules elute before the linear samples. Summarizing, he stressed that 2D-separation techniques are a promising route for the characterizations of samples involving highly branched polymers.

In the next two sessions, the structure-properties relationship was explored by a detailed description of the physical behavior of hyperbranched systems as detected by a wide range of experimental techniques for hyperbranched systems bearing different topological characteristics.

The first speaker, Prof. Vlassopoulos, focused on the rheological behavior of polymers with different branched topologies and examined the possibility to tune their behavior from polymeric to colloidal response. After a brief introduction on the principles of polymer rheology and the fundamental models associated with their viscoelastic behavior, Prof. Vlassopoulos adopted a hierarchical approach on the examination of the impact of the different polymer topologies on the pertinent rheological behavior. Starting from linear polymers, he then described the behavior of comb-like and star-shaped molecules^{38, 39}. Later he moved to dendritically branched molecules^{40, 41} and symmetric Cayley-tree structures⁴² examining the effect of topology on their dynamic response. He also discussed the behavior of end-functionalized (telechelic) dendritic polymers and their potential to self-assembly forming supramolecular structures. Moreover, Prof. Vlassopoulos demonstrated the possibility to describe the rheological behavior of multiarm stars by adopting an effective soft-potential⁴³ which maybe appropriately tuned to describe systems bearing either polymeric or colloidal features. He concluded that by controlling polymer architecture at molecular level, one can tune the rheological behavior of branched systems to vary anywhere between linear polymer to ideal soft-colloidal particles, or in other words that the chemistry-physics interplay is the key for understanding the rheology of this important class of soft-materials.

Dr. Silke Rathgeber who followed, presented results in her studies of shape-persistent macromolecules combining experimental techniques, theory and simulations. She first described some dynamic aspects of star-like (loose and polymer-like structure) and star-burst (colloidal, sphere-like) dendrimer molecules in relation to their structural properties, obtained through Neutron Spin Echo (NSE) experiments. Structural details like shape, local density within the dendritic structure and location of the terminal groups were examined^{44, 45}, while relaxation dynamics as probed by NSE, was compared to theoretical predictions⁴⁶. Dr. Rathgeber showed that a generalization of the well-known from linear polymers Rouse-Zimm theory which involves a coupled-oscillator with excluded volume interactions model, can be adapted in order to provide a reasonable description of the dendrimer dynamics. She also pointed out that the main contribution to relaxation originated from the collective breathing motions of the (sub)dendrons relative to each other. She then reported results from her recent studies related to the ordering and non-equilibrium phenomena in concentrated bottlebrush polymer solutions. She demonstrated that the structural characteristics of these molecules could be reproduced by considering an ultra-soft interaction potential⁴⁷. To this type of interaction it was attributed the observed shear-thinning behavior of these molecules⁴⁸ at high strain rates, which under certain conditions could trigger a shear-induced transition to ordered phases as was monitored by in-situ combined SAXS-rheology experiments.

The third topic that Dr. Rathgeber discussed was the potential of diblock-copolymer formed micelles to self-assemble and be used for surface templating purposes. She demonstrated that certain features of such systems, like their inherent nano-sized dimensions and the possibility to control their relative spacing combined with their low cost, render them good candidates for pattern-templating applications. She also noted that by changing the diblock-copolymer architecture one can effectively control the formed template properties. Dr Rathgeber described as an example, the possibility of self-organization of gold-loaded micelles on silica and titanium-oxide surfaces discussing also the role of the strength of the polymer-surface interactions in the final template characteristics.

The next talk by Dr. Anatoly Serghei referred to the study of the dynamic response of

hyperbranched polymers under nanoscopic confinement, by means of Dielectric Relaxation Spectroscopy (DRS), Calorimetry and Dilatometry. As he described, in the case of hyperbranched polymers, local dynamics are significantly affected by the confinement⁴⁹ as is the case in linear polymers, but the confinement effect is even stronger, in the sense that changes in local dynamic behavior occur at much larger thicknesses compared to that necessary for linear polymers. Commenting on the mechanism which underlies the apparent increase of the local relaxation rate in confined geometries, he proposed an interpretation based on the suppression of the slow relaxation modes⁵⁰. He therefore suggested a common mechanism to which both, the shift of the average time and the broadening of the pertinent relaxation spectra can be attributed to: the change of the associated distribution of relaxation times. He then attempted to compare results regarding the determination of the glass transition temperature as follows by different macroscopic experimental techniques, like Calorimetry and Dilatometry, and as can be determined from dynamic measurements by means of Dielectric Spectroscopy which probes molecular (microscopic) motions. He reached the interesting result that when it comes to T_g measurements in confined geometries, different techniques do not necessarily yield similar results⁵¹. He then described a novel method for dynamic measurements in ultrathin polymer films by means of Dielectric Spectroscopy⁵² which appears very promising towards probing interfacial dynamics^{52, 53}. By using a similar method, Dr. Serghei demonstrated how by such a technique, dynamics of a single polymer molecule can be probed, pointing out that even a single molecule may exhibit a glass-like transition.

Continuing the second session on structure-properties relationship, Dr. Thijs Vlugt reported on his studies of thermodynamic properties of hyperbranched polymers. Particularly, he focused on 3 topics i) the phenomenology of the phase behavior of systems of hyperbranched polymers and solvents ii) the hyperbranched polymers as process solvents of CO₂ removal from gas streams from the experimental and the theoretical point of view and iii) the prediction of the Henry coefficients of CO₂ in hyperbranched polymers using molecular simulation. The hyperbranched system that Dr. Vlugt and his groups utilized to examine the phase equilibria, was a commercial polyester (Boltorn H3200). They investigated the systems CO₂+H3200, propane+H3200 and butane +H3200 and they were able to construct the relevant phase diagrams. Above a characteristic temperature, they were able to identify two separate two-phase fluid-fluid regions with different critical solution pressure behaviors. For the second task, Dr. Vlugt and his colleagues examined a system of hyperbranched polyglycerol-Methanol-CO₂. They have also appropriately modified the PC-SAFT equation of state to account for the specific branching of the hyperbranched polyglycerol. By comparing experimental results with the theoretical calculations, they were able to demonstrate the good agreement of the modified theory with the experiment. They have also demonstrated the ability of the theory to extrapolate to different solute and solvent concentrations as well as towards different molecular masses of the branched polymer. For the last task Dr. Vlugt and his associates performed Molecular Dynamics simulations, in combination with the Widom test particle insertion method, in order to compute the activity coefficient of CO₂ and N₂ at infinite dilution and for various types of hyperbranched polymers. Comparison to available experimental results proved the validity of their method towards predicting such thermodynamic properties for systems involving hyperbranched polymers.

In the following presentation, Prof. Rob Richardson introduced the audience to yet another class of hyperbranched molecules, namely that of dendrimers bearing liquid-crystalline groups at their surface. The aim of his studies was to determine the structural properties of this class of recently synthesized molecules. The experimental techniques utilized for this purpose were X-ray diffraction and Small Angle Neutron Scattering (SANS). Specific objectives of Prof. Richardson's X-ray studies in these materials were i) to determine whether the mesogenic units assemble into Liquid-Crystalline (LC) phases and ii) to examine the influence of the dendritic structure to the molecular packing. As he demonstrated, it was found that increasing the generation number, changes the molecular packing, driving the phase structure from lamellar to columnar⁵⁴. The low generation dendritic molecules (generations 1 to 4) arrange themselves in simple smectic structures, whereas at higher generations due to packing constraints, in-plane columnar phases are favored. Temperature also affected the dendrimer arrangement, since at low temperatures the mesogenic units were found to orient in a parallel fashion, while as the temperature increased a trend towards a circular disc shape was observed. In the SANS studies, Prof. Richardson explained in brief the preparation of the samples, where a mixture of Hydrogen and Deuterium labeled

molecules was used in order to create sufficient contrast for the technique. In these studies, large in dimensions objects were detected. After excluding possible reasons for creation of such objects (e.g. possibility of crosslinking between different molecules), it was determined that supramolecular aggregates were formed⁵⁵. The tendency for the formation of dendrimer aggregates was enhanced upon increasing of temperature and it was found that this effect was reversible. Concluding, Prof. Richardson noted that after these initial steps towards understanding the ordering phenomena in liquid-crystalline dendrimers, further studies involving interactions of such dendritic species with linear polymers, nanoparticles or smaller solutes might be of particular interest, even more so in the presence of surfaces.

In the next talk, Dr. Nicola Tirelli, elaborated on the potential to use branched macromolecules for bio-related applications⁵⁶. He demonstrated several cases, where the utilization of highly branched molecules with a well defined structure, may prove much more efficient compared to the use of linear analogues, due to the possibility to increase the bioactivity by attaching many bio-functional groups at specific sites. On top of the enhanced bioactivity of such systems, the ability to tailor their structure offers an increased level of control in quantitative terms over their bioactivity as Dr. Tirelli pointed out. He further demonstrated the potential use of hyperbranched molecules tethered from one end either to surfaces or to other polymeric blocks capable of self-association for bio-related applications. In such systems, because of their topological constraints, it is possible to manipulate more easily the asymmetry in their shape, e.g. leading to systems of a controlled curvature. Concluding his presentation, Dr. Tirelli also pointed out several open problems associated with the controlled synthesis of such systems.

After the last talk, an open discussion followed, focusing on the current level of control on the synthesis of hyperbranched polymers as well as our current capabilities/problems for their characterization. It became clear that although a certain level of control is possible, particularly for the regular-branched dendritic systems, the desired level of control has not as yet been accomplished for non-regular in topology (and much cheaper) hyperbranched systems. However it was noted that the prospects towards this direction are much more encouraging compared to the situation only few years ago.

The second day of the workshop was mainly devoted to the examination of the behavior of systems comprised by hyperbranched polymers, from the theoretical and the computer modeling point of view. The first session entitled “*Self organization of hyperbranched polymers: insight from simulations*” started with the talk by Prof. Christos Likos, on the theoretical description of cluster formation in concentrated solutions of amphiphilic dendrimers. As Prof. Likos described, in the case of athermal dendrimers, the effective interaction between them can be well described by potentials of the Gaussian type. On the other hand, in dendrimer models which bear a solvophobic core and solvophilic end-groups the behavior changes dramatically. There is a clear tendency for cluster formation comprised by several molecules, which may arrange in crystal lattices. On a brief report of the state of the art regarding the theoretical description of such systems, he noted that formation of such stable clusters can be encountered for purely repulsive, bounded effective potentials⁵⁷; at sufficiently high densities and at all temperatures these clusters may crystallize into cubic lattices with concentration-independent lattice constants⁵⁸. Prof. Likos showed that an appropriate modeling of the monomer-monomer interactions (defining e.g. separate excluded volume parameters for the core and the shell region of the dendrimer models) sufficed to account for the observed clustering phenomena even in the absence of an explicit attraction term in the original interaction potential. His theoretical results were in good agreement with pertinent simulation findings.⁵⁹ Concluding, Prof. Likos noted that neither electrostatic repulsions nor stiff bonds are necessary for cluster formation, as long as amphiphilicity is present. He also pointed out that the crystals formed by these clusters exhibit unusual features, like the diffusive behavior on the single-particle level, allowing thus mass transport, whereas at the collective level may appear rigid as a conventional solid., rendering them promising systems when such attributes are required.

The next contribution was by Prof. Darinskii, reporting on computer simulations for the “*Self-organization of star diblock copolymers in the presence of linear polyelectrolytes*”. Dr. Darinskii in the beginning of his presentation referred to the factors that can act as external stimuli to polyelectrolyte solutions, like concentration, pH and ionic strength, as well as to the type of possible responses, like the onset of aggregation, the aggregation number, the size and the

morphology of the aggregations. After presenting some experimental results in star block-copolymers, he described the computer model utilized in his study, which included diblock stars of different number of arms with a number of inner hydrophobic and outer hydrophobic beads per arm, in solutions of implicit solvent but with the explicit presence of counterions. The simulation method was Brownian dynamics. He showed that in such systems at neutral pH conditions spherical aggregates (micelles) were formed, while at low pH conditions, formation of a large cylindrical aggregate was favored⁶⁰. Addition of salt seemed to dissolve only to a minor degree the cylindrical shape of the aggregate formed by the low-functionality stars where in the case of the high-functionality stars the cylindrical aggregate was practically disrupted. Next, Prof. Darinskii described results from simulations of diblock stars in the presence of linear chains. He examined 3 different cases, namely when the chain of the linear polymer was less hydrophilic, similar and more hydrophilic compared to the arms of the stars, while he also considered linear chains with varying length. By changing these parameters, Prof. Darinskii demonstrated the possibility to control the morphology of the formed micelles. The morphology of the star-formed micelles proved particularly sensitive to the length of the linear polymer as well as to the relative quality of the solvent with respect to the linear-chain. From his systematic study, Prof. Darinskii showed how the micellar morphology of the final aggregate can be manipulated in order to accomplish desired shape, size and compactness, features that are very important for a number of pertinent applications (mimicry of biological systems, nanoreactors, encapsulation of guest molecules etc). The next session included talks relevant to the complexation properties and the responsiveness of hyperbranched systems to external stimuli. In the first contribution, Dr. Martin Buzza explored the level of responsiveness in terms of their size, of charged dendrimers in solution using Molecular Dynamics simulations. Before embarking in the results of the simulations he and his colleagues performed, he pointed out that although past simulations of charged dendrimers predicted a rather sensitive response of their size in stimuli like the pH of the solution⁶¹, such a level of response has not been experimentally observed⁶². As possible reasons for this discrepancy he noted that in those simulation models the counterions had only been implicitly considered, disregarding thus important phenomena like correlations between counterions or other non-linear phenomena like counterion condensation. To remedy this problems Dr. Buzza considered counterions explicitly and he employed a more detailed forcefield compared to past simulational efforts. He examined dendrimer models of different generations and with different number of spacer bonds between the branching points, while examining solutions of varying ionic strengths as well. The results of his study showed that due to the strong correlation between the charged dendrimer beads and the counterions, local charge neutrality was attained, resulting in much weaker changes of the size of the dendrimers compared to the predictions of the previous simulational efforts where counterions were treated in an implicit manner. The effects of salt addition, were found to be appreciable, only in the case where the bulk concentration in salt was much larger than the internal counterion concentration. The results of the simulations were compared to the prediction of Flory's theory in the osmotic regime, and found to be in a close agreement. Concluding, Dr. Buzza stressed the importance of explicitly including the counterions in simulations of charged dendrimers, since this is the main reason for the accomplishment of local charge neutrality and thus for the weak response of the dendrimer size to the change of the ionic strength of the solution.

In the next talk, Dr. Andrey Gurtovenko presented molecular dynamics simulation results on "*Charged dendrimers and their complexes with linear polyelectrolytes: insight from coarse-grained molecular dynamics simulations*". Dr. Gurtovenko and his collaborators employed a model of a coarse grained representation of a generation 4 dendrimer, where the solvent and the counterions were explicitly considered. Their main goal was to examine the effects related to the presence of counterions, the nature of the linear polyelectrolyte (PE) and role of the dielectric properties of the solvent. To cover a wide range in the relevant parameter space, different cases regarding the valency of the PE charges and the strength of electrostatic interactions were considered. Dr. Gurtovenko showed that complexation of a charged dendrimer with a polyelectrolyte chain had a twofold effect: the compaction of the chain and its dehydration⁶³. In addition, he demonstrated that the presence of the counterions had a pronounced effect on the structure of the formed dendrimer chain complex, which became stronger upon increasing of the strength of the electrostatic interactions (by means of changing of the dielectric permittivity of the solvent)⁶⁴. Concluding, Dr. Gurtovenko emphasized that their study demonstrated the ability for

compaction of guest chains and the possibility for effective screening of the chains from the surrounding medium, which are the two key-attributes for vehicle-mediated delivery of drug and genes into the cells.

Continuing on the properties of complexes comprised by hyperbranched polymers with linear chains, the next talk by Dr. Sergey Lyulin, focused on the “*Anisotropy effects in overcharged hyperbranched polymers*”. The hyperbranched models considered by Dr. Lyulin, were of non-regular branching pattern (HBP) with a degree of branching of 0.5, bearing different architectural details which covered the regime from dendritic-like compact structures, to more open star-like topologies. His main goal was to examine by means of theory and simulations, the effect of the topology and the overcharging phenomena in complexes formed by terminally charged HBPs and oppositely charged linear polyelectrolytes (PE). Apart from the variation of the HBP structure, the chain length of the PE was varied as well. The simulation method adopted was Brownian Dynamics, and the forcefield used included excluded volume, hydrodynamic and electrostatic interactions. The results from the simulations were compared with the results from a specially developed extension of the correlation theory⁶⁵ which took into account the possibility of variation of the size of the macroion (here the HBP)⁶⁶. He was able to identify a tail-release mechanism, depending on the length of the PE and the degree of the overcharging of the HBP, and to describe the significantly different response of the complexes bearing the two different topologies of HBPs. The discrepancies observed between complexes of the two extreme HBP structures were attributed (by comparison to the theoretical results as well) to the distinctly different degree of shape anisotropy assumed by each model. Summarizing, Dr. Lyulin noted that the sensitive response of the models comprised by the more-open in structure HBPs, could potentially be exploited in applications where the control of size and effective charge are crucial, while systems involving more compact dendrimer-like HBPs can be regarded as cost-effective alternatives for applications in which regular dendrimers are so far being used.

In the first afternoon session, the speakers reported on the exploration of the conformational characteristics of hyperbranched systems in different thermodynamic environments and their importance for prospective applications. The first presentation by Prof. Juan Freire referred to the description of conformational properties of dendrimers by means of Monte Carlo computer simulations. Specifically, Prof. Freire described models that were constructed in order to mimic the properties of polyamidoamine dendrimers with an ethylenediamine core and polypropyleneamide with diaminobutane core. He has also tried to reproduce experimental data of mono-dendrons and tri-dendrons of polybenzylether in tetrahydrofurane. The method followed combined short molecular dynamics runs from which some parameters related to the average distance between the dendrimer beads and the distributions of bending angles were extracted, and then ported to the coarse-grained models which were simulated with Monte Carlo. For the calculations related to the viscosity, the Fixman’s variational method was applied, corrected by the inclusion of a term associated with the individual bead friction. The viscosity results obtained by this procedure⁶⁷, were found to be in favorable agreement with available experimental data for the different categories of dendrimers simulated. Furthermore, Prof. Freire showed results for structural properties like the density profiles, the asphericity in shape and the molecular scattering factor. He also reported findings concerning dynamic properties like the overall dendrimer motion in terms of the Rouse-Zimm model and rheological properties like the shear modulus.⁶⁸ In conclusion, he was able to demonstrate that the coarse-graining procedure that he had developed was able to reproduce some key-properties of dendrimers of different structure and flexibility, in a much more computationally efficient way compared to more detailed models that have been employed in previous similar studies.

In the next presentation, Dr. Edward Timoshenko reported on “*Computer simulations of conformations for dendrimers with hydrophobic, hydrophilic and charged units*”. In this contribution, Dr. Timoshenko discussed results from Monte Carlo computer simulations and the Gaussian self-consistent method (GSC)^{69, 70}, on the geometric⁷¹ and the statistical-mechanical characteristics of isolated dendrimers of different structure in selected solvents^{72, 73}. His main focus was on the influence of the hydrophobic/hydrophilic composition and the presence of charged units on the geometrical characteristics and the physical properties of the dendrimers. In addition, he also showed results in the conformational properties of amphiphilic diblock star copolymers in the dilute limit⁷⁴. For the studied systems, properties like the degree of bond stretching and steric congestion, the radial density profiles, static structure factors, asphericity and

scaling laws for the size were obtained. For the amphiphilic co-Dendrimer systems having hydrophobic blocks at the core or polar blocks attached to the core, they were found to be capable of forming micellar-type structures. Dr. Timoshenko also showed that at high generation co-dendrimers adopted elongated cigar-like conformations for the single core case and dumbbell-like conformations for the binary core case. This phenomenon appeared to involve the dendron segregation which occurs at the core of these large co-dendrimers.

In general, the results presented by Dr. Timoshenko, helped to reconcile some of the disparate predictions from previous theoretical and simulational studies. The systems he discussed are of general interest for drug delivery purposes while they may also find use as building blocks for supramolecular chemistry. Therefore the new insight offered by his studies is considered essential for designing systems with optimized performance for such applications.

In the last talk of this session, Prof. Igor Neelov, presented fully atomistic molecular dynamics simulations of systems comprised by a dendrimer/anti-cancer drug complex. Recent experimental findings have shown that such systems are very promising in targeted delivery of drugs.^{75, 76} Dr. Neelov has studied such complexes in aqueous environment with the drug compound (cisplatin) either covalently attached to a polyamidoamine (PAMAM) dendrimer, or physically adsorbed on its surface. He also examined the case in which the dendrimer-drug complex was placed near a water-lipid interface. The analysis of the trajectories focused on the examination of the statics and dynamics of the dendrimer, the distribution of the drug within the dendritic structure, the influence of the presence of the drug in the dendrimer's conformation, the changes in shape of the dendrimer induced by the proximity of the complex near the lipid surface, the distribution of cisplatin molecules with respect to the surface and the concomitant change of the lipid's structure due to the contact with the dendrimer. As it was found, the size and the anisotropy of the dendrimer increased due to the presence of the drug, resulting to a less compact dendritic structure. As a result the water molecules penetrated deeper within the dendrimer interior. In addition the degree of backfolding of the peripheral dendrimer groups increased and their mobility was reduced. In the presence of the lipid bilayer the dendrimer undergone changes in its shape while the close to the contact area, the lipid surface became more curved. The dendrimer surface groups did not penetrate into the lipid and the drug molecules approached the lipid surface. Summarizing Dr. Neelov noted that cisplatin molecules do penetrate in the dendrimer interior in both cases, but to a larger extent when they are chemically attached. The complexation of dendrimer with the drug incurs an increase in the average size of the dendrimer, mainly due to the increase in the anisotropy of its shape. Such shape changes are also observed when the dendrimer approaches the lipid surface which is also affected by the presence of the dendrimer. Such details at molecular level may prove very useful for a better understanding of the mechanisms responsible for an efficient drug-delivery procedure.

After the end of the presentations of the evening session, the discussion which followed focused on the degree of interaction between experiment and simulation and to which extent the knowledge acquired in molecular level from the computer models, can effectively be transferred to the design of actual systems. In general, it was noted by many of the participants, that somehow the two communities (chemists/experimentalists and theorists/simulators) in principle do not interact at a desirable level. This was partly attributed to the fact that there is a lack of a "common language" between the two sides so that information can be exchanged in an efficient manner. It was proposed that this deficiency can be remedied to a certain degree, when people with different backgrounds work in a multidisciplinary environment where contacts between them are realized in a more frequent basis so that familiarization with each others work and exchange of ideas becomes easier.

In the third day of the workshop, the morning session was devoted to the use of hyperbranched systems in pharmaceutical applications.

The first presentation was by Dr. Barbara Klajnert on "*Dendrimers as therapeutic agents in Alzheimer's and prion diseases*". Dr. Klajnert commenced her presentation by noting that recent studies have proved that dendrimers are able to interact with molecules of biological interest providing new routes for controlling their behavior⁷⁷. She then discussed the dendrimer specific action against the formation of protein fibrils⁷⁸ which are responsible for the prion disease or other neurodegenerative disorders including Alzheimer's disease which is also associated with the formation of amyloid aggregates⁷⁹⁻⁸¹. She described how by the use of truncated prion and Alzheimer's peptides the formation of fibrils can be formed mimicking thus the actual disease

conditions⁸¹, but also how by exposing them to the presence of dendrimers the fibril formation could be inhibited⁸⁰. It was found that the larger the dendrimer generation, the lower the concentration needed in order to accomplish the disaggregation effect^{80, 81}. The concentration of the dendrimers was also found to be correlated with the rate of elongation of the aggregates⁸⁰. Next, Dr. Klajnert discussed the mechanisms through which the presence of dendrimers promotes the inhibition of the fibril formation. She showed that dendrimers may prevent the further growth of small-length fibrils by end-blocking or even disrupt already formed fibrils by fibril breakage. She then referred to a specific class of dendritic molecules, namely phosphorus dendrimers demonstrating their action in blocking the undesirable conversion of PrP 185-208 from an α -helical structure to the disease-associated β -sheet conformation. Concluding, she remarked that dendrimers appear as important destabilizing agents of fibrils related to these diseases, emphasizing that although several elementary mechanisms related to the dendrimers' interactions with fibrils have been verified, their action could be further optimized if we better understand the underlying specific interactions; with such knowledge it might be possible to control these interactions in order to trigger a synergistic action that will enhance the probabilities of the disease inhibition.

In the next presentation, Dr. Sideratou discussed the design of functional hyperbranched polymers for drug delivery applications. Dr. Sideratou described a procedure for the appropriate functionalization of well-characterized basic hyperbranched dendritic polymers in order to simultaneously address issues such as stability in the biological milieu, targeting and possibly transport through cell membranes^{82, 83}. She noted that accomplishment of this task would require attachment of targeting ligands, transporting agents and protective coating on the same molecule. She described such functionalization procedures for multi-functional dendritic polyether polyols⁸² with polyethylene glycol (PEG) as protective agents and folate targeting ligands at their end. These systems were found to be non-toxic and more efficiently internalized by cells bearing folate receptors. She also demonstrated (by studying the encapsulation release properties of tamoxifen) that PEGylated hyperbranched polymers apart from their protective action, they enhance the encapsulation efficiency and control of the release of the drug compound. She then showed encouraging results from the use of a surface-functionalized hyperbranched aliphatic polyester as prospective drug delivery vehicle for another drug, paclitaxel. Namely, she reported results from fluorescence experiments which showed enhancement of solubilization of the drug molecule and an effective localization of the drug-loaded system in human lung carcinoma cells. In conclusion, Dr. Sideratou expressed her opinion that selective functionalization of hyperbranched molecules aiming at specific biological activity, is a promising route for manufacturing cost-effective molecularly designed vectors.

In the last talk, Dr. Ulrik Boas introduced the audience in the use of dendrimers⁸⁴ as scaffolds for stimulating motifs, which constitutes a new approach to molecular adjuvants. In general as Dr. Boas explained, an adjuvant is a substance which upon injection activates the host immune system. If injected together with an antigen, the adjuvant-antigen mixture may lead to an immunological memory against that particular antigen, i.e. it can act as a vaccine. After a brief introduction on the action of the commonly used adjuvants, he referred to the "Pathogen associated molecular patterns (PAMP)" which act as molecular motifs presented on microbial surfaces that interact with pattern recognition receptors. Such receptors are found at the surface or inside the immune cells. Desirable attributes for such PAMPs are that they should possess low molecular weight with a well defined molecular motif, and that they could be tailored to direct the immune system towards a particular response. In this context, Dr. Boas argued that dendritic polymers are good candidates to be used as adjuvant agents for a number of reasons: they possess well-defined macromolecular structures with immunogenic dimensions, they can be modified in a well controlled manner, they are multivalent molecules which may enhance immunological effects, they can be considered as high-solubility adjuvants which could minimize biological side-effect (e.g. granuloma formation or tissue necrosis). He then reported on recent attempts to utilize PAMAM dendrimers in adjuvant motifs and to mix PAMP adjuvants based on peptide-dendrimers with antigens. He also discussed results on the biological activity of polysaccharide-dendrimer conjugates. One of his key-conclusions was that dendrimer adjuvants appear as promising candidates for targeting delivery of antigens (i.e. vaccine delivery agents).

After the end of all presentations a round table discussion was set, focusing on the possibilities of future collaborations between the participants in the context of common projects, or in the

framework of a consortia formed by institutes of the participants. Several of the participants expressed their strong interest towards establishing a long-term collaborative relationship between their labs aiming at a multidisciplinary approach of current problems in the field of hyperbranched polymers. Early indications for the onset of this kind of collaborations are already visible, since some of the workshop participants belonging to different disciplines (chemists, biologists, theorist/simulators) are now involved in a broadly based ESF COST proposal (currently under preparation). Several other researchers have agreed to come ASAP to close collaboration in projects of common interest.

Assessment of results

One of major targets of the workshop was to bring in contact scientist active in the general field of hyperbranched polymers and supramolecular polymeric structures, setting the basis for a multidisciplinary collaborative network. The outcome of this effort has already started to be visible as it was described in the previous paragraph.

In addition, it became possible for each one of the participants to form a more spherical picture of the ongoing research in this field, mainly on the European but also on a wider international scale. Some of the general issues related to the current level of research on this class of materials that have emerged during the workshop can be summarized as follows

- The research on the regularly branched polymers (dendrimers) has advanced remarkably within the last few years and have accented these molecules to be of great potential in a continuously expanding range of applications. The main drawback in their wider use lies in the still relatively high cost. However, in view of the potential of some of the related applications (e.g. in biomedicine) investment in manpower and financial resources can be justified
- The non-regular in structure cost-effective hyperbranched polymers appear as promising materials for a wide range of nanoscale applications. Significant steps have been made in the effective characterization and the separation of such polymers, but still further steps must be taken towards this direction.
- Many of the most important applications related to hyperbranched materials are still being developed following the trial-and-error procedure. A deeper understanding of the microscopic mechanisms related to their response in different thermodynamic environments of both, regular and irregular in geometry hyperbranched polymers could decisively improve their action and pave the ground for their optimal performance.
- The availability of more computational resources and the introduction of new models in the description of hyperbranched systems has advanced our ability to simulate them in a much more efficient manner. It appears that we are now able to study problems that were considered intractable only few years ago. If this descriptive capability of analytical/computational methods is directed towards resolving important experimental issues we can expect an even greater advancement on the field of hyperbranched polymers.

Final Program

Sunday, May 26 2008 : arrival of the participants

Monday, May 26

- 8:30-9:00** **Meeting introduction by the convenors**
Presentation of the European Science Foundation (ESF)
- 9:00-10:40** **Session 1 : Novel Hyperbranched Systems – Synthesis and some applications**
Chair : U. Boas
- 9:00-9:40 Anne-Marie Caminade *Phosphorous dendrimers as tools for the elaboration of nano-materials*
- 9:40-10:20 Tamis Darbre *Peptide dendrimers: Synthesis and Applications*
- 10:20-10:40 Erwan Nicol *"Hyper-architectures" obtained from photo-crosslinked self-assembled amphiphilic block copolymers*
- 10:40-11:10** **Coffee Break**
- 11:10-12:50** **Session 2 : Functional modification and characterization of hyperbranched systems**
Chair : D. Vlassopoulos
- 11:10-11:50 Christopher Plummer *Functional modification of Hyperbranched polyesters for technical applications*
- 11:50-12:30 Alben Lederer *Selectively modified aliphatic hyperbranched polyesters and their analysis by different separation methods*
- 12:30-12:50 Wolfgang Radke *Chromatographic Separations of Branched Polymers by Interaction Chromatography*
- 12:50-15:00** **Lunch**
- 15:00-16:40** **Session 3 : Structure-Properties Relationship - I**
Chair : T. Vlught
- 15:00-15:40 Dimitris Vlassopoulos *From dendritically branched polymers to colloidal self-assemblies: tuning the rheology*
- 15:40-16:20 Silke Rathgeber *Fundamental and applications of shape persistent macromolecules – insight from theory, simulation and experiment*
- 16:20-16:40 Anatoli Serghei *Molecular dynamics of polymeric systems with special macromolecular architectures under geometrical nano-confinement*
- 16:40-17:10** **Coffee Break**
- 17:10-18:50** **Session 4 : Structure-Properties Relationship - II**
Chair : C. Plummer
- 17:10-17:50 Thijs J.H. Vlught *High pressure phase behavior of systems with hyperbranched polymers*
- 17:50-18:30 Rob Richardson *Structure of Liquid Crystalline Dendrimers*
- 18:30-18:50 Nicola Tirelli *Branched tethered macromolecules*
- 18:50-20:30** **Discussion**
- 20:30** **Conference Dinner**

Tuesday, May 27

9:00-10:40 **Session 1 : Self-Organization of hyperbranched polymers : insight from simulations**
Chair : K. Karatasos

9:00-9:40 Christos N. Likos *Cluster formation in concentrated solutions of amphiphilic dendrimers*

9:40-10:20 Anatolij A. Darinskii *Self-organization of star diblock copolymers in the presence of linear polyelectrolytes*

10:20-11:10 **Coffee Break**

11:10-12:50 **Session 2 : Complexation and responsiveness of hyperbranched systems**
Chair : C. Likos

11:10-11:50 Martin A. Buzza *Are polyelectrolyte dendrimers stimuli responsive?*

11:50-12:30 Andrey Gurtovenko *Charged dendrimers and their complexes with linear polyelectrolytes: Insight from coarse-grained molecular dynamics simulations*

12:30-12:50 Sergey V. Lyulin *Anisotropy effects in overcharged hyperbranched polymers*

12:50-15:00 **Lunch**

15:00-16:40 **Session 3 : Conformational characteristics of hyperbranched polymers: importance for prospective applications**
Chair : A. Lyulin

15:00-15:40 Juan J. Freire *Conformational properties of dendrimers studied through Monte Carlo simulations*

15:40-16:20 Edward G. Timoshenko *Computer simulations of conformations for dendrimers with hydrophobic, hydrophilic and charged units*

16:20-16:40 Igor Neelov *Molecular dynamics simulation of dendrimer-cisplatin anticancer conjugate and its interaction with lipid bilayers*

16:40-17:00 **Coffee Break**

17:00-19:00 **Discussion**
Free time

Wednesday, May 28

9:00-11:00 **Session 1 : Hyperbranched systems in pharmaceutical applications**
Chair : A.-M. Caminade

9:00-9:40 Barbara Klajnert *Dendrimers as therapeutic agents in Alzheimer's and prion diseases*

9:40-10:20 Ulrik Boas *Dendrimers as scaffolds for immune stimulating motifs, a new approach to molecular adjuvants*

10:20-11:00 Zili Sideratou *Functional Hyperbrached Dendritic Polymers as Drug Delivery Systems*

11:00-11:30 **Coffee Break**

11:30-13:30 **Session 2: Round table discussion, perspectives for future collaborations**
Chair: K. Karatasos, Alexey Lyulin

13:30 **End of Workshop**

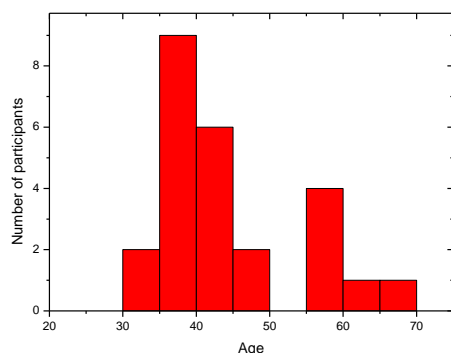
Statistical information on participants

Gender repartition: male: 19 female: 6

Countries of affiliation:

Denmark	1
France	2
Germany	5
Greece	3
Ireland	1
Netherlands	2
Poland	1
Russia	2
Spain	1
Switzerland	2
United Kingdom	5
Total	25

Age distribution



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